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Contribution from the Corporate Research-Science Laboratories,
Exxon Research and Engineering Company, Annandale, New Jersey 08801

Dinuclear Tungsten(V) and Molybdenum(V) Compounds Containing $M_2S_2(\mu\text{-}S)_2{}^{2+}$ Cores. Synthesis and Reactivity of $[N(C_2H_5)_4]_2M_2S_{12}$ (M = W or Mo) and the Crystal Structure of $[N(C_2H_5)_4]_2W_2S_2(\mu\text{-}S)_2(S_4)_2$

Steven A. Cohen*† and Edward I. Stiefel*

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Rational syntheses of dimeric tungsten(V) and molybdenum(V) sulfide complexes having high sulfur-to-metal ratios are described. The $M_2S_{12}{}^{2-}$ anions (M = W or Mo) have been isolated in high yields as their tetraethylammonium ($NEt_4{}^+$) salts from the reactions of elemental sulfur with the corresponding $(NH_4)_2MS_4$ in hot *N,N*-dimethylformamide. $(NEt_4)_2W_2S_{12}$ (**1**) was found by single-crystal X-ray diffraction methods to crystallize from CH_3CN in the tetragonal space group *P4/ncc* with *a* = 21.185 (4) Å, *c* = 15.320 (3) Å, and *Z* = 8. The structure of the $W_2S_{12}{}^{2-}$ anion consists of a *syn*-$W_2S_2(\mu\text{-}S)_2{}^{2+}$ core coordinated by two bidentate tetrasulfido ($S_4{}^{2-}$) ligands. An analogous structure (i.e., $Mo_2S_4(S_4)_2{}^{2-}$) is indicated for $(NEt_4)_2Mo_2S_{12}$ (**2**). Both **1** and **2** have been found to be convenient precursors for synthesizing other dimeric compounds. The bis(dithiocarbamate) derivatives, $W_2S_4(S_2CNR_2)_2$, where R = *i*-C_4H_9 (**3**) or R = C_2H_5 (**5**), have been prepared in good yields from **1**, while $(NEt_4)_2Mo_2S_4(S_2)_2$ and $Mo_2S_4[S_2CN(i\text{-}C_4H_9)_2]_2$ have been synthesized from **2**. The tungsten and molybdenum dimers have been characterized by a variety of spectroscopic techniques; for the tungsten species **1**, **3**, and $W_2OS(\mu\text{-}S)_2[S_2CN(i\text{-}C_4H_9)_2]_2$ (**4**), these methods include ^{183}W NMR spectroscopy. The relationship between the formation of the $M_2S_{12}{}^{2-}$ anions from $MS_4{}^{2-}$ and elemental sulfur and the externally induced, internal electron-transfer reaction between $MoS_4{}^{2-}$ and organic disulfides is discussed.

Introduction

The importance of molybdenum–sulfur (Mo–S) species in metalloenzymatic and industrial catalytic systems has provoked extensive study of the chemistry of molybdenum in sulfur coordination environments.[1,2] The binary Mo–S anions, $MoS_4{}^{2-}$,[3] $MoS_9{}^{2-}$,[4] $Mo_2S_8{}^{2-}$,[5] $Mo_2S_{10}{}^{2-}$,[6] $Mo_2S_{10.56}{}^{2-}$,[4b] $Mo_2S_{12}{}^{2-}$,[7] $Mo_3S_9{}^{2-}$,[8] and $Mo_3S_{13}{}^{2-}$,[9] are a particularly interesting class of Mo–S complexes, encompassing an unusually wide range of stoichiometries, oxidation states, coordination geometries, and bonding modes. In addition, these anions have been important in the investigation of the chemical reactivity and redox properties of molybdenum–sulfur complexes and have served as convenient precursors for synthesizing other Mo–S species, particularly those containing the *syn*-$Mo_2S_4{}^{2+}$ core structure.[10]

The chemistry of sulfur-coordinated tungsten complexes has received far less attention than that afforded Mo–S compounds, despite the activity of tungsten sulfide hydrotreating catalysts[2] and the recently uncovered role of tungsten in biology.[11] For example, only three binary W–S anions have been reported and of these, only the tetrathiotungstate dianion has shown general synthetic utility.[3,8,12,13] Similarly, complexes containing the $W_2S_4{}^{2+}$ core structure remain rare.[8,13-15] Guided by the concept of metal sulfide reactions via externally induced, internal electron-transfer processes,[5] we have prepared and structurally characterized $(NEt_4)_2W_2S_{12}$, a compound containing the *syn*-$W_2S_4{}^{2+}$ core structure. The synthesis of the analogous compound $(NEt_4)_2Mo_2S_{12}$[16] and the use of $(NEt_4)_2W_2S_{12}$ and $(NEt_4)_2Mo_2S_{12}$ as precursors to other $W_2S_4{}^{2+}$ and $Mo_2S_4{}^{2+}$ core complexes also are described.

Experimental Section

General Considerations. All manipulations were performed by using Schlenk techniques unless noted otherwise. Argon was purified by passage over BASF (Ridox) catalyst and $CaSO_4$ (Drierite). Acetonitrile was distilled from CaH_2. Acetone, methanol, and *N,N*-dimethylformamide (DMF) were vacuum-distilled from $CaSO_4$, $Mg(OCH_3)_2$, and CaH_2, respectively, immediately prior to use. Dichloromethane-d_2 (Stohler), D_2O (Aldrich), and DMF-d_7 (Aldrich) were used as received.

Ammonium tetrathiotungstate (Spex) was washed with methanol and dried in vacuo; $(NH_4)_2MoS_4$ (Spex) was used as received. Sodium diisobutyldithiocarbamate was prepared on the basis of literature procedures for the di-*n*-butyl compound.[17] Tetraethylammonium bromide (Aldrich) and ammonium hexafluorophosphate (Ozark-Mahoning) were dried under vacuum at 110 and 60 °C, respectively. All other reagents and solvents were used as received.

Physical Measurements. Infrared and UV–vis spectra were recorded on Perkin-Elmer 683 and 303 spectrophotometers, respectively. Infrared spectra of samples were measured as KBr pressed pellets and referenced to polystyrene bands. Fast atom bombardment (FAB) and field desorption (FD) mass spectroscopic data were obtained in the Mass

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† Present address: Amoco Research Center, P.O. Box 400, Naperville, IL 60566.

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Spectrometry Laboratory, School of Chemical Sciences, University of Illinois—Urbana on VG Instruments ZAB-HF and Finnigan MAT 731 spectrometers, respectively. High-field ^{183}W NMR spectra (16.64 Hz = 1 ppm) were obtained on a JEOL GX400 using 10-mm sample tubes and externally referenced to 1.00 M Na_2WO_4 in H_2O/D_2O (3:1, pH 9.5). High-performance liquid chromatography was performed on a Beckman chromatograph using an Altex 4.6 × 150-mm Ultrasphere ODS column. Elemental analyses were performed by the Analytical and Information Division of Exxon Research and Engineering Co. and Galbraith Laboratories Inc., Knoxville, TN. The crystal structure determination was carried out by Dr. Cynthia Day of Crystalytics Co., Lincoln, NE.

Procedures. $(NEt_4)_2W_2S_{12}$ (1). Sulfur (1.18 g, 4.60 mmol) was added to a stirred solution of $(NH_4)_2WS_4$ (3.20 g, 9.20 mmol) in 50 mL of DMF, and the mixture was heated for 2 h at 110 °C while being purged slowly with Ar. The resulting orange-red solution was allowed to cool, excess NEt_4Br (2.55 g, 12.1 mmol) was added, and the mixture was heated at 110 °C for an additional 60 min. Volatiles were removed at 60 °C under vacuum, leaving an oily orange-red solid. Repeated recrystallization of the product from acetonitrile with intermittent washings with toluene, methanol, and diethyl ether yielded 3.85 g (83%) of red crystalline **1**. Excess sulfur (0.39 g) was recovered separately. Anal. Calcd for $C_{16}H_{40}N_2S_{12}W_2$: C, 18.97; H, 3.98; N, 2.77; S, 37.98; W, 36.30. Found: C, 19.00; H, 3.86; N, 2.68; S, 37.44; W, 36.25. IR: 3000 (w), 2980 (w), 1474 (s), 1445 (m), 1432 (m), 1417 (w), 1390 (m), 1385 (m), 1312 (m), 1184 (w), 1168 (s), 1065 (w), 1049 (w), 996 (s), 777 (s), 506 (vs), 495 (sh), 460 (w), 423 (m), 414 (m), 356 (w), 330 (m), 321 (w), 294 (m) cm^{-1}. FAB-MS (in tetramethylene sulfone) *m/e* for parent negative ion $[(NEt_4)W_2S_{12}]^-$ (rel abundance calcd, exptl): 878 (19, 25); 879 (23, 28); 880 (62, 62); 881 (45, 51); 882 (100, 100); 883 (55, 61); 884 (96, 98); 885 (32, 42); 886 (60, 62); 887 (14, 19); 888 (21, 25). Fragments corresponding to $[(NEt_4)W_2S_{12-n}]^-$, where $n = 1, 2, 3, 4$, and 5, also were observed. ^{183}W NMR (3937 scans, pulse width 10 μs, 1.11 g of **1** in 2.2 mL of DMF and 0.7 mL of DMF-d_7): δ 2131.9. The ^{183}W NMR resonance for 0.25 M $(NH_4)_2WS_4$ in DMF/DMF-d_7 (3:1) was observed at δ 3649.0.

The preparation of **1** is quite water-sensitive. Samples hydrolyzed during the synthesis and workup procedures display an intense W═O stretch at 949 cm^{-1} in the infrared spectrum. Once recrystallized, however, analytically pure samples of **1** suffer no measurable decomposition or hydrolysis after weeks in air at ambient temperatures.

$(NEt_4)_2Mo_2S_{12}$ (2). The preparation of **2** was carried out by using a procedure similar to that used for **1**. Sulfur (11.0 g, 43.0 mmol of S_8) was added to a stirred solution of $(NH_4)_2MoS_4$ (11.25 g, 43.2 mmol) in 140 mL of DMF, and the mixture was heated for 3.5 h at 95 °C while being purged with Ar. Tetraethylammonium bromide (9.29 g, 44.2 mmol) was added to the resulting red-black solution. The volatiles were removed under vacuum at 65 °C, leaving a hard brown-black solid. (*Caution!* Dimethylammonium bromide, a skin and mucous membrane irritant, is present as a byproduct in the solid.) The solid was crushed and extracted with 8 × 100 mL of MeCN; filtration yielded a red-black solution and a brown residue. The filtrate was evaporated to a dark solid, which was washed in air with methanol, toluene, water, and diethyl ether. Recrystallization from acetonitrile (four crops) afforded 11.2 g (62%) of black crystalline **2**. Anal. Calcd for $C_{16}H_{40}N_2Mo_2S_{12}$: C, 22.96; H, 4.82; N, 3.35; Mo, 22.92; S, 45.96. Found: C, 23.14; H, 4.78; N, 3.31; Mo, 23.29; S, 45.59. IR: 3000 (w), 2975 (w), 1470 (s), 1442 (m), 1429 (m), 1414 (w), 1385 (m), 1358 (m), 1180 (m), 1167 (s), 1066 (w), 1050 (m), 996 (s), 779 (s), 523 (vs), 496 (w), 439 (m), 416 (w), 348 (w), 325 (w), 315 (w), 298 (m) cm^{-1}.

$W_2S_4[S_2CN(i\text{-}Bu)_2]_2$ (3). An acetonitrile solution (40 mL) containing PPh_3 (1.65 g, 6.29 mmol), NH_4PF_6 (1.01 g, 6.20 mmol), $NaS_2CN(i\text{-}Bu)_2 \cdot 3H_2O$ (1.00 g, 3.55 mmol), and **1** (1.01 g, 0.997 mmol) was heated at 85 °C for 3.5 h, producing an orange-brown slurry. Volatiles were removed in vacuo, and the resulting orange solid was extracted with 5 × 25 mL of toluene. The orange solution was filtered, concentrated to ca. 20 mL, and chromatographed (in air) on a 5 cm × 35 cm silica-gel column (Baker, 60–200 mesh, toluene eluent). Fractions containing the first orange band yielded 400 mg (45%) of red-orange crystalline **3**. Anal. Calcd for $C_{18}H_{36}N_2S_8W_2$: C, 23.90; H, 4.01; N, 3.10; S, 28.35; W, 40.64. Found: C, 24.12; H, 3.82; N, 3.01; S, 28.34; W, 40.62. IR: 2960 (m), 2925 (w), 2870 (w), 1516 (vs), 1460 (m), 1435 (s), 1388 (w), 1357 (w), 1338 (m), 1272 (w), 1254 (s), 1191 (w), 1154 (s), 1089 (m), 979 (vw), 922 (vw), 915 (w), 880 (vw), 847 (vw), 804 (vw), 606 (vw), 532 (s), 520 (m), 447 (m), 374 (w), 330 (m), 308 (m) cm^{-1}. Field desorption MS *m/e* for parent $W_2S_8C_{18}H_{36}N_2$ (rel abundance calcd, exptl): 900 (20, 26); 901 (27, 27); 902 (65, 64); 903 (50, 53); 904 (100, 88); 905 (59, 64); 906 (90, 100); 907 (33, 41); 908 (51, 58); 909 (14, 16); 910 (13, 17); 911 (3, 7); 912 (2, 3). ^1H NMR (399.65 MHz, in C_7D_8): δ 3.27 (dd), 3.20 (dd), 1.84 (nonet), 0.70 (d), 0.57 (d) for $CH^aH^bCH^c(CH^d{}_3)(CH^e{}_3)$, respectively; $J_{ab} = 13.7$ Hz, $J_{ac} = J_{bc} = 7.8$ Hz, $J_{cd} = J_{ce} = 6.8$ Hz. $^{13}C\{^1H\}$ NMR (22.4 MHz, in CD_2Cl_2): δ 20.21 (CH_3), 27.87 (CH), 59.22 (CH_2), 213.56 (NCS_2). ^{183}W NMR (28 040 scans, 0.13 M in CD_2Cl_2): δ 2270.5.

Continued elution of the chromatography column with toluene yielded 100 mg (12%) of a second orange compound, $W_2OS_3[S_2CN(i\text{-}Bu)_2]_2$ (**4**). Anal. Calcd for $C_{18}H_{36}N_2OS_7W_2$: C, 24.33; H, 4.08; N, 3.15; S, 25.25; W, 41.38. Found: C, 24.44; H, 3.98; N, 2.97; S, 25.12; W, 40.45. IR: 2981 (s), 2930 (w), 2875 (w), 1520 (vs), 1461 (s), 1440 (s), 1392 (m), 1375 (w), 1358 (w), 1340 (m), 1257 (s), 1190 (w), 1156 (s), 1123 (vw), 1090 (m), 969 (s), 930 (vw), 883 (vw), 858 (vw), 826 (vw), 532 (s), 453 (m), 376 (w), 328 (w), 313 (m) cm^{-1}. Field desorption MS *m/e* for parent $W_2S_7OC_{18}H_{36}N_2$ (rel abundance calcd, exptl): 884 (21, 24); 885 (28, 31); 886 (66, 68); 887 (50, 52); 888 (100, 100); 889 (58, 61); 890 (88, 99); 891 (30, 36); 892 (48, 48); 893 (13, 11); 894 (12, 12); 895 (3, 4). $^{13}C\{^1H\}$ NMR (22.4 MHz, in CD_2Cl_2): δ 20.21 (CH_3), 27.87 (CH), 59.26 (CH_2), 212.95 (NCS_2WO), 213.30 (NCS_2WS). ^{183}W NMR (113 494 scans, 0.17 M in CD_2Cl_2): δ 881.8 (W═O), 2239.7 (W═S).

$W_2S_4(S_2CNEt_2)_2$ (5). An acetonitrile solution (50 mL) containing PPh_3 (0.8 g, 3 mmol), NH_4PF_6 (0.48 g, 2.9 mmol), $Na(S_2CNEt_2) \cdot 3H_2O$ (0.35 g, 1.6 mmol), and **1** (0.508 g, 0.502 mmol) was heated at 75 °C for 45 min, resulting in the formation of an orange slurry. Volatiles were removed in vacuo, leaving a mixture of orange and white solids. The mixture was cooled to 0 °C and washed with 2 × 15 mL of CH_3OH, 2 × 20 mL of acetone, and 3 × 20 mL of ether. The resulting orange powder was dried under vacuum. Yield of **5**: 300 mg (75%). Air-stable **5** is very slightly soluble in DMF and hot acetonitrile. Anal. Calcd for $C_{10}H_{20}N_2S_8W_2$: C, 15.16; H, 2.54; N, 3.53; S, 32.36. Found: C, 14.94; H, 2.30; N, 3.57; S, 32.34. IR: 2980 (w), 2935 (w), 1530 (s), 1456 (m), 1440 (m), 1382 (w), 1358 (m), 1297 (w), 1281 (s), 1201 (m), 1152 (m), 1098 (w), 1077 (m), 1006 (w), 996 (w), 908 (w), 847 (w), 779 (w), 527 (s), 519 (s), 445 (m), 371 (m), 323 (m) cm^{-1}. (The oxo impurity exhibits ν(W═O) at 971 cm^{-1}.) Field desorption MS *m/e* for parent $W_2S_8C_{10}H_{20}N_2$ (rel abundance calcd, exptl): 788 (21, 21); 789 (26, 24); 790 (66, 68); 791 (46, 43); 792 (100, 100); 793 (52, 60); 794 (89, 79); 795 (26, 32); 796 (50, 41).

$(NEt_4)_2Mo_2S_8$. Triphenylphosphine (1.06 g, 4.04 mmol) was added to an aluminum-foil-covered flask containing a stirred solution of $(NEt_4)_2Mo_2S_{12}$ (845 mg, 1.01 mmol) in 30 mL of CH_3CN. The slurry was heated for 3.5 h at 60 °C, allowed to cool, and then stirred at ambient temperature for 2 days. Solvent was removed under vacuum, and the oily purple product was washed with 40 mL of toluene, followed by 30 mL of diethyl ether. Infrared and UV–vis spectra of the resulting solid matched those from authentic samples of $(NEt_4)_2Mo_2S_8$.[5] Yield of $(NEt_4)_2Mo_2S_8$: 600 mg (85%). Evaporation of the toluene and ether washings afforded 1.14 g (96%) of white crystalline Ph_3PS (identified by IR).

$Mo_2S_4[S_2CN(i\text{-}Bu)_2]_2$. An acetonitrile solution (60 mL) containing **2** (855 mg, 1.02 mmol), Ph_3P (1.64 g, 6.25 mmol), NH_4PF_6 (745 mg, 4.57 mmol), and $NaS_2CN(i\text{-}Bu)_2 \cdot 3H_2O$ (1.83 g, 6.50 mmol) was heated for 90 min at 73 °C and allowed to cool. Volatiles were removed in vacuo, and the resulting orange solid was extracted with 3 × 50 mL of toluene. The orange solutions were combined, concentrated to ca. 20 mL, and chromatographed in air on silica gel (toluene eluent), yielding 275 mg (37%) of red-orange crystalline $Mo_2S_4[S_2CN(i\text{-}Bu)_2]_2$.[10c]

$(NEt_4)_2W_2S_{12} + 4Ph_3P$. Triphenylphosphine (1.10 g, 4.20 mmol) was added to a solution of **1** (1.04 g, 1.03 mmol) in 35 mL of CH_3CN. After being stirred for 21 h at ambient temperature, the deep orange-red solution was filtered to remove solid Ph_3PS. The filtrate was concentrated in vacuo, and the remaining orange-red residue was washed with 50 mL of toluene and 5 × 20 mL of diethyl ether, enabling the isolation of 825 mg of orange powder (91% based on $(NEt_4)_2W_2S_8$). IR: 3000 (w), 2980 (w), 2940 (w), 1480 (s), 1474 (s), 1456 (m), 1435 (m), 1391 (m), 1365 (w), 1305 (w), 1183 (m), 1170 (m), 998 (m), 783 (m), 516 (m), 502 (sh), 490 (s), 450 (m), 400 (w), 333 (w) cm^{-1}. The total yield of Ph_3PS, characterized by comparisons of HPLC and IR data with those from authentic samples of PPh_3 and Ph_3PS, was 1.13 g (92%).

Attempts to recrystallize the product from CH_3CN, CH_3CN/Et_2O, and $(CH_3)_2CO/Et_2O$ yielded mixtures of yellow crystals with red microcrystalline solids. The yellow crystals were found by IR and UV–vis spectroscopy to be ca. 90:10 mixtures of $(NEt_4)_2WS_4$ and $(NEt_4)_2WOS_3$.[3] The red material exhibits infrared absorbances at 952 (s), 944 (sh), 509 (m), 440 (m), 327 (m), and 315 (m) cm^{-1} and has been tentatively identified as $(NEt_4)_2W_2O_2(\mu\text{-}S)_2(S_2)_2$.[18]

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Table I. Crystal and Space Group Data

$C_{16}H_{40}N_2S_{12}W_2$ — tetragonal space group $P4/ncc$
$a = 21.185$ (4) Å — $\rho_{calcd} = 1.96$ g cm^{-3}
$c = 15.320$ (3) Å — $\rho_{exptl} = 1.97 \pm 0.02$ g cm^{-3}[a]
$V = 6876$ (3) Å^3 — λ(Mo Kα) = 0.71073 Å
$Z = 8$ — $\mu = 75.5$ cm^{-1}

[a] Flotation in $C_2H_5I/BrCH_2CH_2CH_2Br$.

Crystal Structure Determination. Data Collection. Well-formed crystals of $(NEt_4)_2W_2S_{12}$ were obtained by slow diffusion of diethyl ether into an acetonitrile solution of 1. A crystal 0.50 × 0.52 × 0.57 mm was glued to the inside of a glass capillary and mounted with its longest edge nearly parallel with the ϕ axis of a Four-Circle Nicolet Autodiffractometer. Photographic and diffractometer data indicated that the crystal possessed $4/mmm$ Laue symmetry with the following restrictions: $hk0$, $h + k = 2n$; hhl, $l = 2n$; $0kl$, $l = 2n$. Thus the data established the space group as $P4/ncc$ (No. 130).[19] Cell dimensions were determined by least-squares refinement using 15 reflections having $2\theta > 20°$. Crystal data are given in Table I.

Intensities of all $(+h,+k,+l)$ reflections were measured at 20 ± 1 °C with graphite-monochromated Mo Kα radiation using ω scans. The scan rate for reflections with 2θ values between 3 and 43° was 6.00°/min; for $43 \leq 2\theta \leq 55°$, 4.00°/min. A scan width of 0.90° was employed with a background count time of half the net scan time. A variance $\sigma^2(I)$ was calculated for each reflection on the basis of counting statistics, background counts, and an "ignorance factor" $(p|F_o|)^2$, where $p = 0.01$. The intensities of six check reflections monitored every 300 reflections indicated no degradation during the data collection.

The intensities and variances of the 3949 reflections were corrected empirically for absorption effects ($\mu = 75.5$ cm^{-1}; relative range of transmission factors 0.36–1.00), by using ψ scans for 15 reflections between 5.9 and 21.4°, and for Lorentz and polarization effects. Reflections for which $F^2 < 3\sigma(F^2)$ were considered unobserved and given weights of zero, yielding 1455 reflections in the working data set.[20]

Solution and Refinement. The structure was solved by heavy-atom Patterson methods. Placement of the single independent W atom gave an R_1 index $(\sum||F_o| - |F_c||/\sum|F_o|)$ of 0.218. Positions for the remaining non-hydrogen atoms were established by conventional Fourier and least-squares techniques.[21] In addition to the crystallographically imposed disordering of the methylene carbon atom in cation II that led to its refinement as C21 and C21x with assigned populations of 0.5, disordering of both tetrasulfide sulfur atoms β to the W atom was indicated. One sulfur position was successfully refined as S5 and S5a with site occupancies of 0.75 (1) and 0.25 (1), respectively. Repeated attempts to refine two partially occupied sites for the second β-sulfur atom failed, however. Since an alternate (though unrefinable) position for S4 is observable in the final difference Fourier (1.4 e/Å^3) at 0.54, 2.09, and 2.18 Å from S4, S3, and S5, respectively, metrical data involving S4 are considered less reliable than those derived from the refined positions of other atoms in the structure. Models based on di-, tri-, and pentasulfide ligands also were considered but were rejected as unreasonable.

The final positional and anisotropic thermal parameters are listed in Table II and in Table VI of the supplementary material, respectively, and give an R_1 index of 0.058, an R_2 index, $[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, 0.049, and a goodness-of-fit index, $[\sum w(|F_o| - |F_c|)^2/(N - P)]^{1/2}$, of 1.77, where $N = 1455$ data and $P = 166$ parameters. In the final cycle of refinement, the maximum shift for all parameters was 0.23σ; the average shift was 0.04σ. Except for the alternate position of S4, the final difference Fourier map contained no residual electron density peaks above the noise level (0.8 e/Å^3).

Table II. Final Atomic Positional Parameters (Fractional Coordinates × 10^4)[a,b]

atom	x	y	z
W	5674 (1)	1613 (1)	2388 (1)
S1	6224 (2)	2446 (3)	2350 (3)
S2	6065 (3)	917 (3)	1348 (3)
S3	4944 (4)	1723 (5)	1203 (5)
S4	4300 (8)	2356 (10)	1641 (10)
S5	3999 (5)	2045 (6)	2552 (8)
S5a	4367 (10)	2527 (14)	2971 (20)
S6	4800 (4)	1775 (5)	3336 (5)
N1	7500	2500	0
C11	8080 (8)	2535 (12)	−606 (11)
C12	8730 (8)	2597 (14)	−136 (14)
N2	2500	2500	4798 (22)
C21	2937 (32)	2130 (33)	5399 (24)
C22	3330 (20)	1613 (21)	4814 (21)
C21x	2923 (29)	2120 (31)	4160 (24)
N3	−4490 (8)	510	7500
C31	−3917 (15)	500 (15)	6883 (33)
C32	−3786 (21)	−154 (21)	6433 (27)
C33	−5106 (16)	464 (18)	7016 (50)
C34	−4971 (25)	975 (21)	6150 (31)

[a] Final scale factor is 0.156. [b] Final extinction parameter is 1.0 × 10^{-4} and is of the form $[1 + 0.002(x)F_c^2 \sin^{-1}(2\theta)]^{-1/4}$.

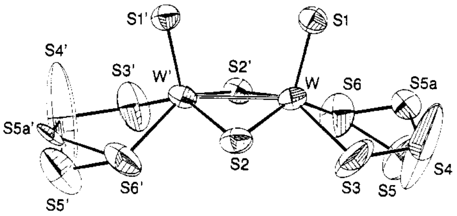

Figure 1. ORTEP view of the $W_2S_4(S_4)_2^{2-}$ anion giving the atom-labeling scheme used.

Results and Discussion

Synthesis and Characterization of $(NEt_4)_2W_2S_{12}$. Heating ammonium tetrathiotungstate and elemental sulfur in dimethylformamide followed by the addition of NEt_4Br and recrystallization from acetonitrile affords red crystalline $(NEt_4)_2W_2S_{12}$ (1) in high yield (70–85%) (eq 1). An important

$$2(NH_4)_2WS_4 + {}^5/_8S_8 \xrightarrow[\text{2. NEt}_4\text{Br}]{\text{1. DMF, 110 °C, Ar}} (NEt_4)_2W_2S_{12} + 2NH_4Br + (NH_4)_2S \quad (1)$$

factor in the synthesis of 1 appears to be the argon or nitrogen purge above the solution during the reaction. Failure to purge the system results in significantly reduced yields of 1 and reisolation of the starting WS_4^{2-} as $(NEt_4)_2WS_4$. Analytical and spectroscopic data are consistent with the formulation of 1 as a dimeric species containing a $W_2S_4^{2+}$ core. The infrared spectrum of 1 exhibits an intense band at 506 cm^{-1} and a shoulder at 495 cm^{-1} that are assigned as the W=S stretches and several weaker bands between 460 and 290 cm^{-1}. Observation of the parent negative ion, $[NEt_4W_2S_{12}]^-$, in the FAB mass spectrum and a single resonance at δ 2131.9 in the ^{183}W NMR spectrum further supports the formulation. The presence of the *syn*-$W_2S_4^{2+}$ core and the complete molecular structure of 1 have been established by single-crystal X-ray diffraction techniques.

Structure of $(NEt_4)_2W_2S_{12}$. The crystal structure of 1 consists of the dinuclear tungsten sulfide anion, $W_2S_{12}^{2-}$, and tetraethylammonium counterions. A view of the dianion with the atomic labeling scheme is shown in Figure 1. The $W_2S_{12}^{2-}$ anions are located at crystallographic twofold sites, with half of the dimer comprising the asymmetric unit. Two crystallographically independent NEt_4^+ ions (cations I and III) are well-behaved (Figures II and IV of the supplementary material) and occupy crystallographic $\bar{4}$ and 2 sites, respectively, whereas a third, cation II

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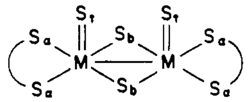
(19) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1969; Vol. I.

(20) (a) For small l values, the $h + k + l$ odd reflections are weaker and more often "unobserved" than are the $h + k + l$ even data. This arises from the tungsten atoms being located near $z = {}^1/_4$ (0.2388 and 0.2612) or $z = {}^3/_4$ (0.7388 and 0.7612), thus *approximating* a body-centered lattice. Since $h + k + l$ odd reflections are systematically absent in body-centered lattices,[20b] the strong scattering of the tungsten atoms contribute little net intensity to these reflections at small l. Inclusion of the $F^2 < 3\sigma(F^2)$ data in the refinement would not be expected to substantially alter the gross features of the structure, however. The authors wish to thank Drs. Richard Marsh and Bernard Santarsiero of Caltech for very enlightening discussions concerning this point. (b) Stout, G. H.; Jensen, L. H. "X-Ray Structure Determination"; Macmillan: New York, 1969; pp 442–444.

(21) The function $\sum w(|F_o| - |F_c|)^2$ was minimized in the least-squares calculations. All calculations were performed on a Data General Eclipse S-200 computer with 64K of 16-bit words, a parallel floating-point processor for 32- and 64-bit arithmetic, and a Data General disk with 10 million 16-bit words using versions of the Nicolet (Syntex) E-XTL or SHELXTL interactive crystallographic software package as modified at Crystalytics Co.

Table III. Structural Data for Selected Anions Containing *syn*-$M_2X_2(\mu\text{-}S)_2^{2+}$ Cores



dianion	M–M, Å	$M–S_t$, Å	$M–S_b$, Å	$M–S_\alpha$, Å	$S_b–M–S_b$, deg	ref
$W_2S_4(S_4)_2^{2-}$	2.836 (2)	2.116 (5)	2.320 (6)	2.387 (11)	100.1 (2)	this work
$W_2O_2S_2Cl_4^{2-}$	2.844 (1)		2.303 (25)		100.6 (5)	18c
$W_2S_4(WS_4)_2^{2-}$	2.912 (9)[a]	2.089 (26)[a]	2.334 (22)[a]	2.487 (35)[a]	98.7 (6)	13b
$W_2S_4(SC_2H_4S)_2^{2-}$	2.862 (1)	2.144 (2)	2.328 (7)	2.404 (12)	100.7 (1)	22
$Mo_2S_4(SC_2H_4S)_2^{2-}$	2.863 (2)	2.100 (16)	2.320 (4)	2.406 (2)	99.8 (2)	23b
$Mo_2S_4(S_4)(S_2)^{2-}$	2.837 (1)	2.112 (2)[b]	2.342 (13)[b]	2.406 (4)[b]	100.7 (1)[b]	6[c]
		2.108 (2)[d]	2.296 (10)[d]	2.394 (2)[d]	103.4 (1)[d]	
$Mo_2S_4(S_2)_2^{2-}$	2.821 (1)	2.118 (14)	2.310 (4)	2.394 (14)	101.2 (2)	5

[a] Data for central $W_2S_2(\mu\text{-}S)_2^{2+}$ core only. [b] Metal bonded to S_4 ligand. [c] Similar results found for major isomer of $(PPh_4)_2Mo_2S_{10.56}$.[4b] [d] Metal bonded to S_2 ligand.

Table IV. Interatomic Distances (Å) in $W_2S_{12}^{2-}$

W–W′	2.836 (2)	S3–S4	2.03 (2)
W–S1	2.116 (5)	S4–S5	1.67 (2)
W–S2	2.324 (6)	S4–S5a	2.07 (3)
W–S2′	2.316 (6)	S6–S5	2.16 (1)
W–S3	2.395 (8)	S6–S5a	1.92 (3)
W–S6	2.379 (8)		
S1–S2	3.60 (1)	S1–S1′	3.69 (1)
S1–S2′	3.60 (1)	S2–S2′	3.56 (1)
S1–S3	3.58 (1)	S2–S3	2.93 (1)
S1–S6	3.66 (1)	S2′–S6	2.85 (1)
		S3–S6	3.29 (2)

Table V. Interatomic Angles (deg) in $W_2S_{12}^{2-}$

S1–W–S2	108.3 (2)	S2–W–S2′	100.1 (2)
S1–W–S2′	108.6 (2)	S2–W–S3	76.9 (3)
S1–W–S3	104.7 (3)	S2′–W–S6	74.6 (3)
S1–W–S6	109.0 (3)	S2–W–S6	142.0 (3)
S1–W–W′	101.6 (1)	S2′–W–S3	145.7 (3)
S3–W–W′	127.8 (2)	S2–W–W′	52.2 (1)
S6–W–W′	125.0 (2)	S2′–W–W′	52.5 (2)
S3–W–S6	87.0 (3)		
		W–S2–W′	75.3 (2)
S3–S4–S5	105.9 (11)		
S3–S4–S5a	113.3 (11)	W–S3–S4	104.3 (6)
S4–S5–S6	105.7 (8)	W–S6–S5	108.1 (5)
S4–S5a–S6	100.1 (14)	W–S6–S5a	108.2 (9)

(Figure III, supplementary material), occupies a fourfold crystallographic site and exhibits apparent C_4 symmetry via a statistical disordering of the methylene carbons (C21 and C21x). Structural data for the NEt_4^+ cations (Table VII, supplementary material) are typical of those found in other NEt_4^+ structures. No unusually short contacts are observed between the tetraethylammonium and the sulfidotungsten ions.

The $W_2S_{12}^{2-}$ anion contains a *syn*-$W_2S_4^{2+}$ core coordinated by two bidentate tetrasulfido (S_4^{2-}) ligands. The skeletal geometry of the anion is similar to those of other tungsten and molybdenum complexes containing *syn*-$M_2X_2(\mu\text{-}S)_2^{2+}$ units, where X = O or S (Table III). The coordination geometry about the tungsten atoms in **1** is best described as that of two square pyramids sharing a common basal edge. Interatomic distances and angles for the $W_2S_{12}^{2-}$ anion are given in Tables IV and V.

The single crystallographically independent tungsten atom in $W_2S_{12}^{2-}$ is bonded to five sulfur ligands in a distorted square-pyramidal arrangement with the metal lying 0.71 Å above the basal plane defined by S2, S2′, S3, and S6. The apical sulfur-tungsten distance observed for **1**, 2.116 (5) Å (W–S1), compares favorably with the values reported for terminal sulfur-metal multiple-bond distances in related compounds ($M{=}S_t$; Table III). The bridging sulfur atoms, S2 and S2′, are symmetrically disposed between the tungsten atoms in the dianion (Tables IV and V). The average $W–S_b$ distance, 2.320 (6) Å, and $S_b–W–S_b$ angle, 100.1 (2)°, agree well with the averaged values of the corresponding parameters found in other $M_2(\mu\text{-}S)_2$ core structures ($M–S_b$, $S_b–M–S_b$; Table III). Similarly, the terminal (S_α) sulfur atoms of the bidentate tetrasulfido group (S3 and S6) are coordinated to the tungsten center in a nearly symmetrical fashion, the average $W–S_\alpha$ distance, 2.387 (11) Å, and the $S_\alpha–W–S_\alpha$ angle, 87.0 (3)°, being within the ranges observed for related tetrasulfido complexes: $(NEt_4)_2W_2S_4(SC_2H_4S)_2$,[22] 2.404 (12) Å and 81.5 (2)°; $(AsPh_4)_2Mo_2S_{10}$,[6] 2.406 (3) Å and 85.1 (1)°; $(PPh_4)_2Mo_2S_{10.56}$,[4b] 2.413 (20) Å and 87.17 (9)°; $(NEt_4)_2MoS_9$,[4b] 2.359 (40) Å and 90.32 (3)°; $(\eta^5\text{-}C_5H_5)_2MoS_4$,[24] 2.453 (3) Å and 88.2 (2)°; $(\eta^5\text{-}C_5H_5)_2WS_4$,[25] 2.419 (3) Å and 89.1 (1)°.

A short W–W separation, 2.836 (2) Å, is observed in $W_2S_{12}^{2-}$. The metal–metal distance, considerably shorter than the nonbonding metal–metal separation in W_2Cl_{10} (W⋯W = 3.814 (2) Å),[26] is comparable to the M–M distances found in other M(V)–M(V) dimers having $M_2X_2(\mu\text{-}S)_2^{2+}$ cores (M–M; Table III). Consistent with arguments put forth previously,[22,27] a metal–metal single bond between the tungsten atoms in **1** is suggested.

Beyond establishing the presence and connectivity of the tetrasulfido ligand in $W_2S_{12}^{2-}$, structural details for the S_4^{2-} groups are limited, owing to the disorder of the internal (β) sulfur atoms (vide supra). The most pronounced effects are the unusually large thermal ellipsoid for S4, a significant residual electron density peak near S4, and the unreasonably short central sulfur–sulfur bond (mean 1.77 Å). The latter is reminiscent of the short $S_\beta–S_\beta$ distance observed in the disordered S_4^{2-} ligand of $(AsPh_4)_2Mo_2S_{10}$[6] as well as the uncorrected C–C distance noted for *syn*-$(NEt_4)_2Mo_2S_4(SC_2H_4S)_2$.[23] The remaining S–S bond lengths appear to be affected by the disorder to a lesser extent: the S–S distances span a wide range, 1.92 (3)–2.16 (1) Å, while exhibiting a not unreasonable mean value of 2.06 Å.[28] Unfortunately, questions concerning bond length alternation in the tetrasulfide ligand and the conformation of the WS_4 ring in $W_2S_{12}^{2-}$ cannot be meaningfully addressed.[25,29]

Interligand sulfur–sulfur separations substantially shorter than the van der Waals contact distance (ca. 3.4–3.7 Å)[30] are observed between the terminal sulfur atoms of the tetrasulfido ligand and

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the bridging sulfur atoms in **1**: S2···S3, 2.93 (1) Å; S2′···S6, 2.85 (1) Å (Table IV). Theoretical calculations[31] suggest that the close contacts observed between the bridging sulfur atoms and the disulfide ligand in the related dianion $Mo_2S_8^{2-}$ may correspond to weak bonding interactions between the sulfur atoms. Thus, an electronic basis for the close $S_b \cdots S_\alpha$ distances in $W_2S_{12}^{2-}$ and perhaps those in other complexes cannot be dismissed.

Synthesis and Characterization of $(NEt_4)_2Mo_2S_{12}$. Similar to the preparation of $(NEt_4)_2W_2S_{12}$ (**1**), heating $(NH_4)_2MoS_4$, elemental sulfur, and tetraethylammonium bromide in dimethylformamide affords $(NEt_4)_2Mo_2S_{12}$ (**2**) in good yield (eq 2).

$$2(NH_4)_2MoS_4 + {}^5/_8S_8 \xrightarrow[\text{2. NEt}_4\text{Br}]{\text{1. DMF, 95 °C, Ar}} (NEt_4)_2Mo_2S_{12} + (NH_4)_2S + 2NH_4Br \quad (2)$$

Analytical and spectroscopic data suggest that the MoS_{12}^{2-} anion in **2** is analogous to the $W_2S_{12}^{2-}$ ion in **1**, consisting of a *syn*-$Mo_2S_4^{2+}$ core coordinated by two tetrasulfide ligands. The infrared spectrum of **2** displays an intense Mo=S stretch at 523 cm^{-1} and series of weaker bands between 496 and 296 cm^{-1}, differing substantially from the infrared spectrum exhibited by another isomer of the $Mo_2S_{12}^{2-}$ anion,[7] $Mo_2(\eta^2\text{-}S_2)_4(\mu_2\text{-}S_2)_2^{2-}$. Least-squares refinement of 25 X-ray diffraction reflections yielded a tetragonal unit cell for **2** with a = 21.035 (5) Å and c = 15.331 (5) Å, values close to those found for **1**.[32] Although confirmation by single-crystal X-ray diffraction experiments is required, it appears that the $Mo_2S_{12}^{2-}$ ion prepared via eq 2 is isostructural with $W_2S_{12}^{2-}$ and identical with the minor anionic component in the crystal structure of $(Ph_4P)_2[(Mo_2S_{10})_{0.72}(Mo_2S_{12})_{0.28}]$ reported by Coucouvanis et al.[4b]

Reactions of $(NEt_4)_2Mo_2S_{12}$ and $(NEt_4)_2W_2S_{12}$. The treatment of $(NEt_4)_2Mo_2S_{12}$ (**2**) with 4 equiv of triphenylphosphine results in the abstraction of four sulfur atoms per dimer, affording $(NEt_4)_2Mo_2S_8$[5] and triphenylphosphine sulfide in high yield (eq 3). The analogous reaction between 4 equiv of triphenylphosphine

$$(NEt_4)_2Mo_2S_{12} + 4Ph_3P \rightarrow (NEt_4)_2Mo_2S_8 + 4Ph_3PS \quad (3)$$

and $(NEt_4)_2W_2S_{12}$ (**1**) yields the expected Ph_3PS and an oily red solid that exhibits infrared absorbances at 516, 502, 490, 450, 400, and 333 cm^{-1} as well as bands characteristic of the tetraethylammonium cation (eq 4). Attempts to further characterize the

$$(NEt_4)_2W_2S_{12} + 4Ph_3P \rightarrow 4Ph_3PS + \text{“}(NEt_4)_2W_2S_8\text{”} \quad (4)$$

product have not succeeded, however, due largely to the increased moisture sensitivity of putative $W_2S_8^{2-}$ vis-à-vis $W_2S_{12}^{2-}$ and $Mo_2S_8^{2-}$. Exposure to even traces of water during the synthesis or purification steps effects the decomposition of “$W_2S_8^{2-}$” to WS_4^{2-}, WOS_3^{2-}, and at least one other species, as observed by UV–vis and IR spectroscopy. Although the hydrolysis and dimer fragmentation reactions appear to be facile, derivatives possessing the $W_2S_2(\mu\text{-}S)_2^{2+}$ core structure can be synthesized by sulfur atom abstraction from **1** if the reactions are carried out in the presence of suitable trapping ligands (eq 5). Thus, triphenylphosphine,

$$(NEt_4)_2W_2S_{12} + Ph_3P \text{ (excess)} + NaS_2CNR_2 \text{ (excess)} \xrightarrow{NH_4^+} W_2S_4(S_2CNR_2)_2 \quad (5)$$

hydrated NaS_2CNR_2 (R = C_2H_5, $i\text{-}C_4H_9$), NH_4PF_6, and **1** react smoothly in acetonitrile, yielding $W_2S_4(S_2CNR_2)_2$ as orange crystalline compounds. Toluene-soluble $W_2S_4[S_2CN(i\text{-}Bu)_2]_2$ (**3**) is isolated from the reaction in moderate yields (ca. 40%) following column chromatography on silica gel. An oxygen-containing byproduct, $W_2OS_3[S_2CN(i\text{-}Bu)_2]_2$ (**4**), also is formed in the reaction and is isolable in low yield as a pure compound via chromatography. The diethyldithiocarbamate derivative, $W_2S_4(S_2CNEt_2)_2$ (**5**), is only slightly soluble in acetonitrile and thus precipitates from the solution as it is formed (eq 5). The use of $(NEt_4)_2Mo_2S_{12}$ (**2**) and $NaS_2CN(i\text{-}Bu)_2$ in reaction 5[10a] produces the analogous complex $Mo_2S_4[S_2CN(i\text{-}Bu)_2]_2$, a compound that has been prepared and characterized independently.[10c] The synthesis of $W_2S_4(S_2CNR_2)_2$ from $W_2S_{12}^{2-}$ offers an alternative to the recently reported[15] preparation of a variety of $W_2S_4(S_2CNR'_2)_2$ compounds by treatment of the corresponding dioxo complexes, $W_2O_2S_2(S_2CNR'_2)_2$,[33] with P_4S_{10}.

The tungsten bis(dithiocarbamate) dimers **3**, **4**, and **5** have been characterized by a variety of spectroscopic and analytical techniques. The field desorption mass spectra exhibit the correct isotope patterns for the parent ions of compounds **3**, **4**, and **5**. The infrared spectrum of **3** (R = i-Bu), displays two W=S stretches at 532 and 520 cm^{-1} while the corresponding bands for **5** (R = Et) are found at 527 and 519 cm^{-1}. The IR spectrum of **4** has a single ν(W=S) band at 532 cm^{-1} and a ν(W=O) band at 969 cm^{-1}. Three additional tungsten–sulfur modes at ca. 450, 375, and 325 cm^{-1} are observed for each of the compounds.[34] The isobutyl derivatives **3** and **4** also have been characterized by ^1H, ^{13}C, and ^{183}W NMR spectroscopy. The metal centers in the symmetrical dimer $W_2S_4[S_2CN(i\text{-}Bu)_2]_2$ (**3**) give rise to a single ^{183}W NMR resonance at δ 2270.5 while the spectrum of $W_2OS_3[S_2CN(i\text{-}Bu)_2]_2$ (**4**) consists of two singlets at δ 2239.7 and 881.8, corresponding to the W=S and W=O resonances, respectively.[35,36] Similarly, the sp^2-hybridized carbon centers of the inequivalent dithiocarbamate ligands in **4** appear at δ 213.30 and 212.95 whereas one singlet at δ 213.56 is found for **3**. The proton and carbon chemical shifts for the isobutyl groups in **3** and **4** do not vary with changes in the apical ligand. Analogous to the structurally characterized *syn*-$Mo_2S_2(\mu\text{-}S)_2(S_2CNEt_2)_2$,[37] the bis(dithiocarbamate) complexes **3**, **4**, and **5** are formulated as W(V)–W(V) dimers having the *syn*-$WS(\mu\text{-}S)_2WX^{2+}$ core structure (X = S, O) capped at each end with a bidentate dithiocarbamate ligand.

Formation of $(NEt_4)_2M_2S_2(\mu\text{-}S)_2(S_4)_2$. The addition of elemental sulfur to the tungsten(VI) and molybdenum(VI) compounds $(NH_4)_2MS_4$ in hot dimethylformamide results in the formation of sulfide ion (as NH_4HS or H_2S) and the dimeric M(V)–M(V) anions $M_2S_2(\mu\text{-}S)_2(S_4)_2^{2-}$ (eq 6). Similar products

$$2MS_4^{2-} + {}^5/_8S_8 \xrightarrow{NH_4^+} M_2S_2(\mu\text{-}S)_2(S_4)_2^{2-} + S^{2-} \quad (6)$$

are observed when MoS_4^{2-} and an organic disulfide, rather than S_8, are used (eq 7).[5] In the latter reaction, the organic disulfide

$$2MoS_4^{2-} + RSSR \xrightarrow{NH_4^+} Mo_2S_2(\mu\text{-}S)_2(S_2)_2^{2-} + 2RS^- \quad (7)$$

undergoes a two-electron reduction to generate 2 equiv of thiolate anion (RS^-) while each metal center in the Mo(V)–Mo(V) dimer is reduced by one electron from the Mo(VI) oxidation state in MoS_4^{2-}. The required four electrons per $Mo_2S_8^{2-}$ are provided by the oxidative coupling of four sulfide anions to the two disulfide ligands observed in the dimer (eq 8). This unusual combination

$$4S^{2-} \rightarrow 2S_2^{2-} + 4e^- \quad (8)$$

of intermolecular and intramolecular redox processes is an example of an externally induced, internal electron-transfer reaction, a class of redox reactions described by Taube.[38] The formation of

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(33) (a) Lozano, R.; Alarcon, E.; Doadrio, A. L.; Doadrio, A. *Polyhedron* **1983**, *2*, 435–441. (b) Lozano, R.; Doadrio, A. L.; Alarcon, E.; Roman, J.; Doadrio, A. *Rev. Chim. Miner.* **1983**, *20*, 109–117.

(34) Assignments of the infrared bands for related $W_2S_{4-n}O_n(S_2CNR'_2)_2$ compounds (n = 2, 3, 4) have been reported.[33a]

(35) (a) Sufficient signal-to-noise ratios have not been achieved that allow observation of the W–W coupling between the two inequivalent tungsten atoms in **4**. (b) Chemical shifts observed for W(V) dimers are in accord with trends seen for $WS_{4-n}O_n^{2-}$ anions (n = 0–4).[35c] (c) Gheller, S. F.; Hambley, T. W.; Rodgers, J. R.; Brownlee, R. T. C.; O'Connor, M. J.; Snow, M. R.; Wedd, A. G. *Inorg. Chem.* **1984**, *23*, 2519–2528.

(36) A third species, $W_2O_2(\mu\text{-}S)_2[S_2CN(i\text{-}Bu)_2]_2$,[33b] has been isolated from the reaction of **1** with Ph_3P and $NaS_2CN(i\text{-}Bu)_2$. Strong ν(W=O) bands are found at 978 and 970 cm^{-1}; the compound exhibits a singlet in the ^{183}W NMR spectrum at δ 844.2 and a singlet at δ 212.75 in the ^{13}C NMR spectrum for the S_2CN resonance and has a chromatographic retention time (R_t) on silica gel of 0.05 relative to toluene (R_t = 1.0). The corresponding R_t values for **3** and **4** are 0.56 and 0.18, respectively.

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$[M_2S_2(\mu\text{-}S)_2(S_4)_2]^{2-}$ and S^{2-} in eq 6 also may proceed via an induced internal redox pathway, since elemental sulfur, like the organic disulfides in eq 7, would be expected to act as an electron acceptor. However, complications arising from the sulfur/sulfide/polysulfide equilibria do not readily allow the initial steps of the reaction in eq 6 to be determined. Thus, whether reductions of the W(VI) or Mo(VI) atoms are in fact initiated by the interaction of the MS_4^{2-} ion with elemental sulfur as an external oxidant or whether they are induced by another means[39] will require further study.

Regardless of mechanism, the dramatic reorganizations that occur about the tungsten and molybdenum centers under relatively nonforcing conditions on going from two tetrathiometalate ions to one $M_2S_{12}^{2-}$ or $Mo_2S_8^{2-}$ anion bespeak the facile redox and bond making/breaking processes accessible to tungsten and molybdenum sulfide compounds. The ever-increasing number of molybdenum–sulfur and tungsten–sulfur complexes that is observed as well as the important role metal sulfides play in solid-state catalysis and metalloenzymatic processes undoubtedly derives in part from these diverse redox and bonding capabilities. Reactions that utilize and more fully explore properties of transition-metal–sulfur compounds will be reported in forthcoming publications.

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Note Added in Proof. Single-crystal X-ray diffraction experiments reveal $(NEt_4)_2Mo_2S_{12}$ to be isostructural with **1**.[32]

Registry No. **1**, 98991-17-4; **2**, 98991-19-6; **3**, 92389-51-0; **4**, 98991-20-9; **5**, 97591-84-9; $(NEt_4)_2Mo_2S_8$, 88335-52-8; $Mo_2S_4[S_2CN(i\text{-}Bu)_2]_2$, 36539-30-7; $(NEt_4)_2W_2O_2(\mu\text{-}S)_2(S_2)_2$, 98991-22-1; $(NEt_4)_2W_2S_8$, 98991-24-3; $(NH_4)_2WS_4$, 13862-78-7; $(NH_4)_2MoS_4$, 15060-55-6; PPh_3, 603-35-0; S, 7704-34-9.

Supplementary Material Available: Final anisotropic thermal parameters (Table VI), bond distances and angles for the NEt_4^+ cations (Table VII), ORTEP drawings of the NEt_4^+ cations (Figures II–IV), least-squares plane of basal sulfur atoms (Table VIII), and structure factors (13 pages). Ordering information is given on any current masthead page.

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[38] Taube, H. "Electron Transfer Reactions of Complex Ions in Solution"; Academic Press: New York, 1970; pp 73–98 and references therein.

[39] Dissociation of a S^{2-} ligand from the $[MS_4]^{2-}$ ion could initiate the reaction, as proposed for the formation of $[M_2S_2(\mu\text{-}S)_2(SC_2H_4S)_2]^{2-}$ and $[M_3S_9]^{2-}$.[8]

Contribution No. 7191 from the Arthur Amos Noyes Laboratory,
California Institute of Technology, Pasadena, California 91125

Chemistry and Spectroscopy of Binuclear Platinum Diphosphite Complexes

Chi-Ming Che,[1a] Leslie G. Butler,[1b] Paula J. Grunthaner,[1c] and Harry B. Gray*

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Modifications have been made to the procedure for the preparation of $K_4[Pt_2(pop)_4]\cdot 2H_2O$ (pop = $P_2O_5H_2$) in order to obtain material that is not contaminated by partially oxidized platinum species. Several other pure salts (Na^+, Ba^{2+}, Bu_4N^+, Ph_4As^+) of $Pt_2(pop)_4^{4-}$ also have been obtained. Oxidation of $Pt_2(pop)_4^{4-}$ in the presence of ligands yields $d^7,d^7\text{-}Pt_2(pop)_4X_2^{4-}$ (X = Cl, Br, I, NO_2, SCN) and $\text{-}Pt_2(pop)_4L_2^{2-}$ (L = H_2O, nicotinamide, pyridine). The influence of axial ligands on the electronic structure of the Pt^{III}–Pt^{III} unit has been studied by UV–vis and X-ray photoelectron spectroscopy. It is inferred that the X (or L) perturbation of the Pt–Pt dσ interaction increases according to $H_2O < Cl^- < Br^- < NO_2^- < SCN^- \sim I^-$.

Introduction

The spectroscopic and photochemical properties of the intensely luminescent, binuclear platinum(II) diphosphite complex, $Pt_2(pop)_4^{4-}$ (pop = $P_2O_5H_2$),[2,3] have attracted great interest in recent years.[4-8] It is now well established by spectroscopic experiments that the $^3A_{2u}(d\sigma)^2(d\sigma^*p\sigma)$ excited state of this d^8,d^8 complex ($^1A_{1g}(d\sigma)^2(d\sigma^*)^2$ ground state) possesses a relatively strong Pt–Pt bond, as predicted by theory,[5] and the $d\sigma^*p\sigma$ triplet is versatile in a chemical sense, being at the same time a very powerful reductant[5a] and a strong oxidant.[7b]

The discovery that $Pt_2(pop)_4^{4-}$ is readily oxidized by a variety of reagents to give discrete binuclear Pt^{III} complexes[9,10] as well as oligomeric mixed-valence species[11] prompted the UV–vis and X-ray photoelectron spectroscopic investigation that is reported

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[1] (a) Department of Chemistry, University of Hong Kong, Hong Kong. (b) Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803-1804. (c) Jet Propulsion Laboratory, Pasadena, CA 91109.

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