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Registry No. **1a**, BF_4 salt, 80409-82-1; **1a**, PF_6 salt, 64536-78-3; **1b**, BF_4 salt, 80409-83-2; **2a**, BF_4 salt, 80446-89-5; **2a**, PF_6 salt, CH_2Cl_2 adduct, 69044-44-6; **2b**, BF_4 salt, 80446-31-7; **3**, 80409-85-4; **5**, 80409-87-6; $IrCl(cod)(PCy_3)$, 64536-83-0.

Supplementary Material Available: Table 1 (observed and calculated structure factor amplitudes), Table 2 (bond angles), Table 3 (thermal parameters), Tables 4 and 5 (further intramolecular distances), Table 6 (various unweighted least-squares planes, including dihedral angles and equations of planes), and a figure (unit cell) (31 pages). Ordering information is given on any current masthead page.

Contribution from the Laboratoire de Chimie des Polymères Inorganiques and the Laboratoire de Chimie des Mêtaux de Transition (ERA 608), Université Pierre et Marie Curie, 75230 Paris Cedex 05, France

Synthesis and Structure of the First Tungsten Complex Having the $W_2S_4^{2+}$ Core: $[P(C_6H_5)_4]_2W_4S_{12}$

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Acidification of tetrathiotungstate $(WS_4)^{2-}$ produces doubly bridged polynuclear complexes. The first complex $[(W_2S_4)(WS_4)_2]^{2-}$ having the central $W_2S_4^{2+}$ core is generated from acidification of $(WS_4)^{2-}$ in anhydrous medium by acetic acid. The structure of the syn isomer has been determined by X-ray crystallography. The syn isomer crystallizes in space group $P\bar{1}$, with $a = 19.278$ (6) Å, $b = 21.244$ (2) Å, $c = 14.929$ (6) Å, $\alpha = 89.43$ (6)°, $\beta = 89.73$ (6)°, $\delta = 78.23$ (1)°, and $Z = 2$. Least-squares refinement of the structure led to a value of the conventional R index (on F) of 0.067 for the 3518 reflections. In the central $W_2S_4^{2+}$ core, each tungsten has a tetragonal sulfur environment. The apex of each pyramid is occupied by a sulfido group. The equatorial plane is formed by sulfido bridging groups and by sulfur atoms of the $(WS_4)^{2-}$ ligands. The geometries of the $W_2S_4^{2+}$ or $Mo_2S_4^{2+}$ cores are very similar. Strong W–W interactions exist, resulting in a 2.911 (16) Å short distance. Moreover, the complex is diamagnetic. The tetranuclear species is a mixed W(V)–W(VI) valence compound.

Introduction

In the development of structural and biological redox models, interest has grown in sulfur-containing compounds or molybdenum.[2a] Emphasis has been placed on binuclear di-μ-sulfido-bridged Mo(V) species, especially on complexes having the $Mo_2S_4^{2+}$ core. As recently pointed out,[2b] the thiomolybdate series $(MoO_xS_{4-x})^{2-}$ has been useful in synthesis; however, such complexes were still unknown in the thiotungstate series $(WO_xS_{4-x})^{2-}$. By use of the appropriate medium, the reactions involving tungsten were generally slow enough (in contrast to those of molybdenum) to control the generation of many new complexes. This present work is concerned with one of these new thio compounds having the $M_2S_4^{2+}$ core in the syn conformation.

Experimental Section

Synthesis of $[N(CH_3)_4]_2WS_4$. An excess of hydrogen sulfide was bubbled into an aqueous solution (250 mL) of Na_2WO_4 (25 mmol) up to pH 5.5, yielding a mixture of 80% $(WOS_3)^{2-}$ and 20% $(WS_4)^{2-}$. In this pH range, $(WS_4)^{2-}$ is the stable species, but the kinetics conversion from $(WOS_3)^{2-}$ is slow. Thus the solution was kept at 60 °C under H_2S-saturated atmosphere for about 4 days, leading to the complete interconversion of $(WOS_3)^{2-}$ into $(WS_4)^{2-}$. A solution of tetramethylammonium chloride (2/1 Me/W) was added and the mixture stirred. The solution was cooled to 0 °C for about 2 h. Orange needles were isolated, washed with ethanol, and dried with diethyl ether.

Synthesis of $[P(C_6H_5)_4]_2WS_4$. The tetraphenylphosphonium salt was prepared by cation exchange from a solution of tetramethylammonium tetrathiotungstate. A solution of $P(C_6H_5)_4Cl$ (2 mmol) in ethanol (10 mL) was added with stirring in an aqueous solution of $[N(CH_3)_4]_2WS_4$, resulting in the precipitation of the orange $WS_4[P(C_6H_5)_4]_2$. The mixture was filtered off, washed with ethanol and ether, and vacuum-dried.

Synthesis of $[P(C_6H_5)_4]_2W_4S_{12}$. The tungsten(VI) tetrathiotungstate $[P(C_6H_5)_4]_2WS_4$ was reacted with an excess of acetic acid in dichloromethane. The acidification by acetic acid was dependent on tungsten and acid concentrations.

Dilute Tungsten Medium. A 0.35-mol quantity of acetic acid was added with stirring to a solution of 0.5 mmol of $[P(C_6H_5)_4]_2WS_4$ in 100 mL of dichloromethane. An orange to red color change was observed immediately upon addition of acid. At the same time, the $(WS_4)^{2-}$ spectrum changed to a new characteristic spectrum. A steady absorbance was reached within 2 h. After about 4 h a red crystalline product was isolated. Powder-diffraction photographs, indexed by the use of cell parameters determined from a monocrystal study, proved that the red crystalline powder contained only one species. The crystal formula determined from chemical analysis data[3] was $[(WS_3)_2P(C_6H_5)_4]_n$. Anal. Calcd for $[P(C_6H_5)_4(WS_3)_2]_n$: W, 40.9; S, 21.35; C, 32.03. Found: W, 40.8; S, 20.90; C, 32.10. The n value was determined by ultracentrifuge methods ($n = 2$) and was confirmed by X-ray data. The filtrate did not contain any other species, since the crystal electronic spectra (in DMF solution) (Figure 1) were identical with the spectra of the filtrate and of the mother solution.

Keeping a dilute tungsten medium, we then added variable amounts of acid to 0.5 mmol of $[P(C_6H_5)_4]_2WS_4$ in 100 mL of dichloromethane. With the addition of more than 0.35 mol of acid, only $(W_4S_{12})^{2-}$ was present in solution as revealed by absorbance recording in the 500–200-nm range. With lower acid concentration $(WS_4)^{2-}$ was present in solution with the tetranuclear complex.

Concentrated Tungsten Medium. In concentrated tungsten medium, the formation of another compound was observed. In high acidic medium, 0.35 mol of acetic acid was added to a solution of 0.5 mmol of $[P(C_6H_5)_4]_2WS_4$ in 10 mL of dichloromethane, producing a red precipitate. The solid was washed with ethanol and dried with diethyl ether. The solid was identified as $[P(C_6H_5)_4]_2W_3S_9$ by the chemical analysis (Anal. Calcd: W, 36.8; S, 19.2; C, 38.4. Found: W, 36.10; S, 18.7; C, 37.7.), electronic spectrum, and IR absorption. These results were confirmed by indexing powder-diffraction photographs using the $[P(C_6H_5)_4]_2W_3S_9$ cell parameters previously reported.[4] In the filtrate, a transient species was observed owing to its characteristic

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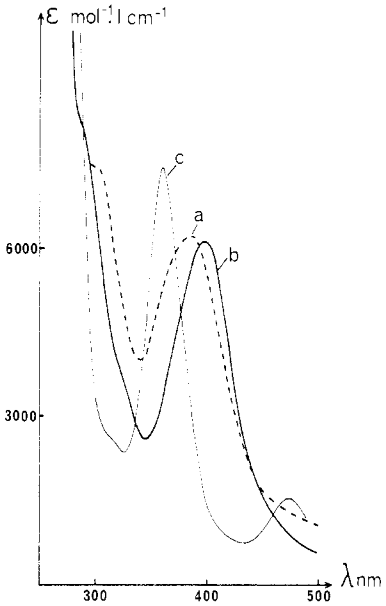

Figure 1. Electronic spectra in DMF solutions: (a) $W_4S_{12}^{2-}$; (b) $W_3S_9^{2-}$; (c) filtrate.

electronic spectrum (Figure 1). This new product transformed into $(W_4S_{12})^{2-}$. It has been possible, by other methods, to isolate this new compound as a solid.[5]

With the maintenance of concentrated tungsten, but with a decrease in the acid concentration, addition of 0.0525 mol of acetic acid to 0.5 mmol of $[P(C_6H_5)_4]_2WS_4$ in 10 mL of CH_2Cl_2 produced within 2 min the red precipitate of $[P(C_6H_5)_4]_2W_3S_9$. After a few minutes dark red crystals deposited, leading to a mixture of $[P(C_6H_5)_4]_2W_3S_9$ and $[P(C_6H_5)_4]_4W_4S_{12}$. The electronic spectrum of the filtered solution revealed the presence of the transient species previously observed in high acidic and concentrated tungsten medium (see above). Less acidic medium always led to a mixture of $(W_3S_9)^{2-}$ and $(W_4S_{12})^{2-}$. In order to obtain pure $(W_4S_{12})^{2-}$, we carried out the acidification of $(WS_4)^{2-}$ using the preparation described for dilute medium: 0.5 mmol of $[P(C_6H_5)_4]_2WS_4$ was reacted with 0.35 mol of acetic acid in 100 mL of CH_2Cl_2 at 20 °C. When a steady absorbance was reached within 2 h, the red solution was cooled to ca. 0 °C. Crystals appeared after about 24 h. They were washed with ethanol and dried with diethyl ether.

Molecular Weight Determination. Molecular weight measurements were carried out by using a Beckman Model E ultracentrifuge equipped with UV optics and a photoelectric scanner. The molecular weight was determined by the equilibrium sedimentation method in a six-channel cell at 30 000 rpm. Equilibrium was reached within 6 h at 20 °C for concentrations of 0.5, 1.0, and 1.5 mg mL^{-1} (crystals were dissolved in acetonitrile). Calculations were carried out from absorbance values recorded at 500 nm. The resulting molecular weight is shown in Table I.

Electronic Spectra. Spectra were recorded at 20 °C with a Beckman Acta V or Beckman Acta MIV; crystals were dissolved in DMF.

Infrared Spectra. IR spectra were recorded on a Perkin-Elmer 457 spectrophotometer. $P(C_6H_5)_4Cl$ and the title complex were sampled as KBr pellets.

Magnetic Measurements. Magnetic susceptibilities of solids were measured by the Faraday method at room temperature. $[P(C_6H_5)_4]_2W_4S_{12}$ was diamagnetic: $X = -498 \times 10^{-6}$ cm^3 mol^{-1}.

X-ray Diffraction Study. The selected crystal was trapezoidal. All pertinent crystallographic data are shown in Table I. Of the two possible triclinic space groups, $P1$ and $P\bar{1}$, suggested by preliminary precession and Laue photographs, the $P\bar{1}$ group was selected and confirmed from the centrosymmetric tests of the MULTAN 77 program.[6] The successful refinement of the structure indicated that this choice was correct. Unit cell parameters were determined from diffractometer alignments by a least-squares procedure using 9 reflections. A total of 11 187 independent reflections with $2\theta \leq 40°$ were recorded on an automatic three-circle diffractometer at room temperature. Two standards ($\bar{6}00$ and $10,\bar{6},0$) were monitored every 100 reflections. No significant intensity decay was observed during data collection. Computations were performed by using standard programs[6] on a CII IRIS 80 computer. Each structure factor was assigned a standard deviation $\sigma = F_o(\Delta I)/(2I)$ where ΔI was the statistical error on integrated intensity. Atomic factors were taken from Cromer and Mann[7] including $\Delta f'$ and $\Delta f''$. A least-squares procedure was used in refinement. The minimized quantity was $\sum w^2(|F_o| - |F_c|)^2$. The weighting scheme based on counting statistics was $w = 2F/\Delta I$. The agreement indices were defined as

$$R_w = [\sum w^2(|F_o| - |F_c|)^2/\sum w^2|F_o|^2]^{1/2}$$

$$R = \sum(|F_o| - |F_c|)/\sum|F_o|$$

Table I. Crystal Data

dimens, mm	0.275 × 0.125 × 0.040
a, Å	19.278 (1)
b, Å	21.244 (2)
c, Å	14.929 (6)
α, deg	89.43 (6)
β, deg	89.73 (6)
γ, deg	78.23 (1)
V, Å^3	5985
space group	$P\bar{1}$
Z	2
d(obsd)	1.996
d(calcd)	2.000
λ, Å	0.710 69
μ, cm^{-1}	86.2
scan type	θ-2θ
scan width, deg	$1 + 0.345 \tan\theta$
scan rate, deg min^{-1}	1.5
no. of independent data	11 187
no. of refinement data	3518
no. of variable parameters	297
final R	0.0672
final R_w	0.0704
goodness of fit	1.837
mol wt	1798

The values of the intensities were corrected from Lorentz and polarization factors. The linear absorption coefficient with Mo Kα radiation was 86.2 cm^{-1}. An absorption correction was made, and transmission coefficients ranged from 0.163 to 0.71. For the minimization of calculation time, refinements were performed with 3518 reflections ($F_o \geq 15.0$ on the scale of F_o). Also the number of variable parameters was reduced by considering the 16 phenyl rings as rigid groups.

The position of the 8 W atoms of the asymmetric unit was determined with the help of the MULTAN 77 program.[6] Refinement of the overall scale factor and positional parameters of the tungstens gave the agreement index $R = 0.26$. Subsequent Fourier syntheses revealed the positions of the 24 sulfur and the phosphorus atoms ($R = 0.16$). Introducing the phenyl rings as rigid groups dropped the R value to 0.097. Absorption correction and anisotropic refinements of the tungsten atom parameters gave the final values of $R = 0.067$ and $R_w = 0.070$. The final positional and parameters of nongroup atoms are collected in Table II. A list of observed and calculated structure factors (on the scale of F_c) and the rigid-group parameters are available as supplementary material.

Description of the Structure

The asymmetric unit consists of two discrete $(W_4S_{12})^{2-}$ anions and four discrete $[P(C_6H_5)_4]^+$ cations. The inner coordination geometry with the labeling scheme is shown in Figure 2, and a stereodrawing of the molecular packing is proposed in Figure 3. The bond distances and angles with their standard deviations are given in Tables III and IV.

The anion geometry is well described as two tetragonal pyramids sharing a basal edge respectively with two WS_4 tetrahedra. A sulfido group lies on the apex of each pyramid;

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(5) Secheresse, F.; Lefebvre, J., to be submitted for publication.

(6) Programs utilized were Germain, Main, and Woolfson's MULTAN, Zalkin's FORDAP, Ibers' NUCLS, Busing and Levy's ORFLS, and Johnson's ORTEP.

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Table II. Positional Parameters for the Nongroup Atoms of $[P(C_6H_5)_4]_2W_4S_{12}$

atom	*x/a*	*y/b*	*z/c*	*B*, Å^2
W(1)	0.0919 (2)	0.1730 (2)	0.3461 (2)	
W(2)	0.4286 (2)	0.3084 (2)	0.6916 (3)	
W(3)	0.5392 (2)	0.2626 (2)	0.5429 (3)	
W(4)	−0.0256 (2)	0.2294 (2)	0.4803 (2)	
W(5)	0.5900 (2)	0.2132 (1)	0.3687 (2)	
W(6)	−0.0862 (2)	0.2910 (1)	0.6447 (2)	
W(7)	0.5898 (2)	0.1651 (2)	0.1757 (2)	
W(8)	−0.0908 (2)	0.3475 (2)	0.8359 (2)	
S(1)	0.038 (1)	0.2753 (9)	0.358 (1)	4.8 (4)
S(2)	0.060 (1)	0.1265 (9)	0.228 (1)	5.2 (4)
S(3)	0.0588 (9)	0.1278 (9)	0.474 (1)	4.7 (4)
S(4)	0.205 (1)	0.167 (1)	0.342 (1)	5.8 (4)
S(5)	0.490 (1)	0.2085 (9)	0.668 (1)	4.9 (4)
S(6)	0.446 (1)	0.3633 (9)	0.567 (1)	4.9 (4)
S(7)	0.462 (1)	0.352 (1)	0.807 (2)	7.1 (5)
S(8)	0.317 (1)	0.305 (1)	0.703 (1)	5.8 (4)
S(9)	0.5623 (9)	0.1579 (8)	0.494 (1)	4.1 (4)
S(10)	0.631 (1)	0.278 (1)	0.600 (1)	5.2 (4)
S(11)	0.5251 (8)	0.3159 (7)	0.404 (1)	3.3 (3)
S(12)	−0.119 (1)	0.2162 (9)	0.416 (1)	4.5 (4)
S(13)	−0.0377 (9)	0.3372 (8)	0.522 (1)	3.8 (3)
S(14)	−0.0308 (8)	0.1850 (8)	0.625 (1)	3.5 (3)
S(15)	0.5834 (9)	0.1074 (9)	0.304 (1)	3.8 (3)
S(16)	0.5576 (9)	0.2696 (9)	0.221 (1)	4.8 (4)
S(17)	0.6979 (9)	0.2164 (9)	0.380 (1)	4.9 (4)
S(18)	−0.071 (1)	0.394 (1)	0.706 (1)	5.3 (4)
S(19)	−0.0808 (8)	0.2436 (7)	0.801 (1)	3.5 (3)
S(20)	−0.193 (1)	0.3037 (9)	0.615 (1)	5.1 (4)
S(21)	0.513 (1)	0.148 (1)	0.081 (2)	7.4 (6)
S(22)	0.696 (1)	0.140 (1)	0.122 (1)	5.9 (4)
S(23)	−0.196 (1)	0.390 (1)	0.883 (1)	5.5 (4)
S(24)	−0.016 (1)	0.356 (1)	0.938 (2)	6.1 (5)
P(1)	−0.2577 (8)	0.4135 (8)	0.158 (1)	3.2 (3)
P(2)	−0.2512 (9)	0.0825 (8)	−0.193 (1)	3.9 (3)
P(3)	0.2515 (8)	0.4024 (8)	0.345 (1)	3.6 (3)
P(4)	0.2494 (8)	0.0903 (7)	−0.302 (1)	3.4 (3)

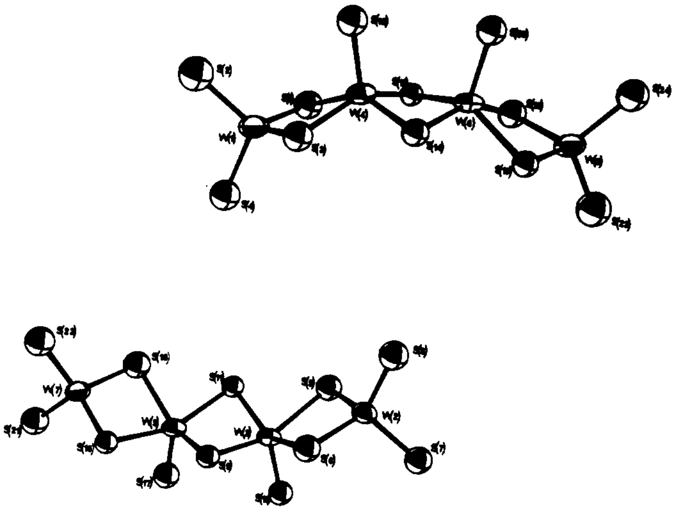

Figure 2. ORTEP drawing of the asymmetric unit with the labeling scheme.

Table III. Interatomic Distances (Å) for $[P(C_6H_5)_4]_2W_4S_{12}$

Tungsten–Tungsten Distances			
W(1)–W(4)	3.078 (6)	W(2)–W(3)	3.093 (7)
W(4)–W(6)	2.918 (5)	W(3)–W(5)	2.905 (6)
W(6)–W(8)	3.101 (5)	W(5)–W(7)	3.066 (6)
Tungsten–(Bridging Sulfur) Distances			
W(1)–S(1)	2.217 (20)	W(2)–S(5)	2.242 (20)
W(1)–S(3)	2.278 (20)	W(2)–S(6)	2.245 (20)
W(4)–S(13)	2.497 (20)	W(3)–S(5)	2.462 (21)
W(4)–S(3)	2.426 (19)	W(3)–S(6)	2.519 (19)
W(4)–S(1)	2.342 (17)	W(3)–S(9)	2.306 (18)
W(4)–S(14)	2.359 (18)	W(3)–S(11)	2.341 (17)
W(6)–S(13)	2.355 (18)	W(5)–S(9)	2.313 (19)
W(6)–S(14)	2.307 (17)	W(5)–S(11)	2.346 (16)
W(6)–S(18)	2.466 (22)	W(5)–S(15)	2.513 (19)
W(6)–S(19)	2.531 (16)	W(5)–S(16)	2.480 (18)
W(8)–S(18)	2.236 (23)	W(7)–S(15)	2.284 (19)
W(8)–S(19)	2.241 (16)	W(7)–S(16)	2.290 (19)
Tungsten–(Terminal Sulfur) Distances			
W(1)–S(2)	2.182 (19)	W(2)–S(7)	2.127 (24)
W(1)–S(4)	2.154 (19)	W(2)–S(8)	2.174 (19)
W(4)–S(12)	2.116 (17)	W(3)–S(10)	2.057 (19)
W(6)–S(10)	2.081 (18)	W(5)–S(17)	2.102 (18)
W(8)–S(23)	2.164 (20)	W(7)–S(21)	2.133 (24)
W(8)–S(24)	2.140 (20)	W(7)–S(22)	2.170 (21)

Table IV. Bond Angles (Deg) for $[P(C_6H_5)_4]_2W_4S_{12}$

Tetrahedral Tungstens			
S(1)–W(1)–S(2)	113.2 (7)	S(18)–W(8)–S(19)	111.9 (7)
S(1)–W(1)–S(3)	116.9 (5)	S(18)–W(8)–S(23)	109.2 (8)
S(1)–W(1)–S(4)	108.8 (7)	S(18)–W(8)–S(24)	113.3 (8)
S(2)–W(1)–S(3)	111.1 (7)	S(19)–W(8)–S(23)	111.9 (7)
S(2)–W(1)–S(4)	109.2 (8)	S(19)–W(8)–S(24)	109.3 (7)
S(3)–W(1)–S(4)	111.4 (7)	S(23)–W(8)–S(24)	108.9 (9)
S(5)–W(2)–S(6)	104.4 (8)	S(15)–W(7)–S(16)	103.4 (7)
S(5)–W(2)–S(7)	113.5 (8)	S(15)–W(7)–S(21)	110.4 (9)
S(5)–W(2)–S(8)	108.4 (7)	S(15)–W(7)–S(22)	109.2 (7)
S(6)–W(2)–S(7)	110.7 (8)	S(16)–W(7)–S(21)	108.1 (8)
S(6)–W(2)–S(8)	109.6 (7)	S(16)–W(7)–S(22)	114.0 (7)
S(7)–W(2)–S(8)	110.0 (9)	S(21)–W(7)–S(22)	111.4 (10)
Pyramidal Tungstens			
S(1)–W(4)–S(3)	91.3 (6)	S(13)–W(6)–S(14)	99.1 (6)
S(1)–W(4)–S(12)	102.4 (7)	S(13)–W(6)–S(20)	104.2 (7)
S(1)–W(4)–S(13)	77.0 (6)	S(13)–W(6)–S(18)	78.1 (7)
S(1)–W(4)–S(14)	152.0 (6)	S(13)–W(6)–S(19)	153.0 (5)
S(3)–W(4)–S(12)	107.3 (7)	S(14)–W(6)–S(20)	110.4 (7)
S(3)–W(4)–S(13)	142.8 (6)	S(14)–W(6)–S(18)	143.5 (6)
S(3)–W(4)–S(14)	76.0 (6)	S(14)–W(6)–S(19)	76.3 (6)
S(12)–W(4)–S(13)	109.7 (7)	S(20)–W(6)–S(18)	105.5 (7)
S(12)–W(4)–S(14)	105.1 (7)	S(20)–W(6)–S(19)	102.2 (7)
S(13)–W(4)–S(14)	97.9 (6)	S(18)–W(6)–S(19)	90.0 (6)
S(5)–W(3)–S(6)	90.7 (7)	S(9)–W(5)–S(11)	98.8 (6)
S(5)–W(3)–S(10)	100.5 (8)	S(9)–W(5)–S(17)	106.4 (7)
S(5)–W(3)–S(9)	79.2 (7)	S(9)–W(5)–S(15)	78.2 (6)
S(5)–W(3)–S(11)	150.4 (6)	S(9)–W(5)–S(16)	151.5 (6)
S(6)–W(3)–S(10)	106.6 (7)	S(11)–W(5)–S(17)	107.1 (6)
S(6)–W(3)–S(11)	74.3 (6)	S(11)–W(5)–S(15)	144.9 (5)
S(6)–W(3)–S(19)	146.3 (6)	S(11)–W(5)–S(16)	74.1 (6)
S(10)–W(3)–S(9)	106.9 (7)	S(17)–W(5)–S(15)	107.2 (7)
S(10)–W(3)–S(11)	108.1 (7)	S(17)–W(5)–S(16)	102.1 (7)
S(9)–W(3)–S(11)	99.1 (6)	S(15)–W(5)–S(16)	91.9 (6)
Bridging Sulfido Atoms			
W(1)–S(1)–W(4)	81.3 (6)	W(2)–S(5)–W(3)	82.1 (6)
W(1)–S(3)–W(4)	81.7 (6)	W(2)–S(6)–W(3)	80.7 (6)
W(4)–S(13)–W(6)	76.8 (5)	W(3)–S(9)–W(5)	77.9 (6)
W(4)–S(14)–W(6)	77.4 (5)	W(3)–S(11)–W(5)	76.6 (5)
W(6)–S(18)–W(8)	82.4 (7)	W(5)–S(15)–W(7)	80.0 (6)
W(6)–S(19)–W(8)	80.8 (5)	W(5)–S(16)–W(7)	79.2 (6)

the equatorial positions are occupied by bridging sulfido groups and by sulfur atoms from WS_4 ligands. Each pyramidal tungsten is bonded to two bridging sulfur atoms S(b), two sulfur donor atoms S(1), and one terminal sulfur atom S(t) (with use of the Spivack and Dori labeling[9]). As previously reported,[8] two isomers are possible for two pyramids sharing a basal edge. The molecule adopts here the syn configuration.

The average W–S(t) bond length of 2.070 (18) Å is shorter than the other tungsten–sulfur distances in the molecule, respectively 2.483 (19) Å for W–S(b) bonds and 2.333 (22) Å for W–S(1) bonds. The central W(3)–W(4) and W(5)–W(6)

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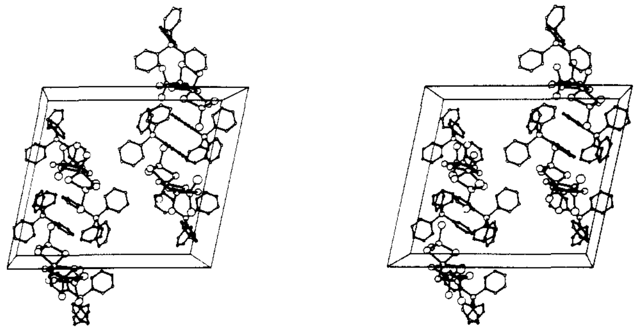

Figure 3. Sterescopic view showing the molecular packing of $W_4S_{12}[P(C_6H_5)_4]_2$.

tungsten atoms are displaced 0.65 Å from the basal sulfur plane toward the apex (Table 3 of supplementary data). The dihedral angle between the WS_2 planes in the four-membered W_2S_2 rings (147.5°) and the bond angles at the bridging sulfido groups (Table 4 of supplementary data) are in the range of the previously reported data for W_2S_2[3] or Mo_2S_2 bridges.[10]

Infrared Spectra

Two types of terminal bonds exist in the $(W_4S_{12})^{2-}$ anion: the W(4)═S(12) bond type and the W(1)—S(2) bond type. Four W—S bands are expected[15] but only one is observed at 525 cm^{-1}. The bands observed at 495 and 485 cm^{-1} can doubtless be attributed to the W(1)—S(2) bond type vibration.[3,4] Two types of bridging bonds exist in the anion: the W(1)—S(1)—W(4) type and the W(4)—S(13)—W(6) type. The two bands observed at 448 cm^{-1} can be attributed to the W(1)—S(1)—W(4) type,[3,4] so the remaining band at 350 cm^{-1} could be attributed to the W(4)—S(13)—W(6) type.

Discussion of the Structure

Some reports mention the occurrence of Mo(V) complexes containing the $Mo_2S_4^{2+}$ core.[10] This compound is the first report of the $W_4S_{12}^{2-}$ anion. It can be interpreted as $W_2S_4^{2+}$ coordinated by two WS_4^{2-} anions. The unequal W-W distances are consistent with such an interpretation.

The average value of the four W-S bonds in the WS_4 terminal groups (2.204 (20) Å) is in good agreement with the data recently published.[3,11] The characteristic tetrahedral coordination geometry of tungsten(VI) is retained in the WS_4 groups. A +5 formal valence state is attributed to each pyramidal tungsten with respect to the charge of the anion[12] and evidence of two hexavalent tungsten atoms.

There is a strong spin coupling of the two W(V) atoms since the complex is diamagnetic at room temperature in the solid state as well as in DMF or Me_2SO solutions. A direct W-W bond is postulated, explaining the short intermetallic distance and the diamagnetism of the complex. This interpretation is consistent with the recent calculation of Chandler et al.[16] In previously reported data on the $Mo_2S_4^{2+}$ core, MoS_4 groups are bonded to organic ligands through sulfido groups. Despite the fact that the $W_2S_4^{2+}$ core is bonded to two metals through sulfido groups, the geometries in $Mo_2S_4^{2+}$ and $W_2S_4^{2+}$ are very similar (Table 3 of supplementary data). Each pyramid in the W_2S_4 group is distorted as was observed in Mo[8,9,10,12] and in W complexes:[3] (i) The W-S(t) bond is rather shorter than the bridging W-S(b) bonds: thus it shows a strong π character. (ii) This multiple bond brings the tungsten out of the sulfur basal plane. (iii) The ligand trans to the doubly bonded sulfido group is absent.

Another featuring detail in the bonding scheme of $W_2S_4^{2+}$ is the off-center position of the tungsten in each pyramidal environment. In our previous paper about $[WO(WS_4)_2]^{2-}$[3] the pyramidal tungsten had a similar off-center position in the sulfur polyhedra, leading to cis-dissymmetric equatorial bond lengths. In this last example, regarding the symmetric position of the pyramid between the two tetrahedra, the dissymmetry was unclear. Thus, we believed that additional factors could influence the pyramidal distortion. (i) Steric interactions: the average value of S(3)-S(14) type distances of 3.00 Å is very short in regard to the 1.85-Å van der Waals radius of sulfur. (ii) Motion of the central ion toward a basal edge: the W(V) atom is displaced from the center of the sulfur polyhedra owing to its small dimension[13] and would be fixed in that off-center position by the strong π bond.[14]

Registry No. $[P(C_6H_5)_4]_2W_4S_{12}$, 75012-47-4; $[P(C_6H_5)_4]_2WS_4$, 14348-11-9; $[N(CH_3)_4]_2WS_4$, 14348-06-2; $[P(C_6H_5)_4]W_3S_9$, 73871-58-6; Na_2WO_4, 13472-45-2; H_2S, 7783-06-4.

Supplementary Material Available: Listings of rigid-group parameters (Table I), derived parameters for rigid-group atoms (Table 2), least-squares planes and displacement of atoms (Table 3), $W_2S_4^{2+}$ and $Mo_2S_4^{2+}$ geometry comparisons, (Table 4), anisotropic thermal parameters for tungsten atoms (Table 5), and observed and calculated structure factor amplitudes (Table 6) (30 pages). Ordering information is given on any current masthead page.

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