Dimeric Tungsten(V) Compounds containing $[(S)W(\mu\text{-}S)_2W(S)]^{2+}$. Syntheses and Structures of Di-μ-sulphido-bis[(diethyl dithiophosphato-*SS'*)sulphidotungsten(V)] and Di-μ-sulphido-bis[(*N,N*-diethyldithiocarbamato-*SS'*)-sulphidotungsten(V)] *

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The compound $[W_2S_4\{S_2P(OEt)_2\}_2]$ has been isolated by two alternative routes: (*a*) treatment of $[WS_4]^{2-}$ with $HS_2P(OEt)_2$ and (*b*) reaction of WS_2Cl_2 with $[NH_4][S_2P(OEt)_2]$. The oxidation product of both reactions is $[(EtO)_2P(S)S-]_2$. The two routes led to two different crystal forms, (**1a**) and (**1b**), of the product $[W_2S_4\{S_2P(OEt)_2\}_2]$. Treating $[W_2S_4\{S_2P(OEt)_2\}_2]$, either form, with $Na(S_2CNEt_2)$ gave $[W_2S_4(S_2CNEt_2)_2]$ (**2**). The crystal structures of (**1a**), (**1b**), and (**2**) have been determined. (**1a**) is monoclinic, space group $P2_1/n$, with a = 18.230(11), b = 12.905(11), c = 10.153(12) Å, β = 90.5(1)° and Z = 4; (**1b**) is monoclinic, space group $P2_1/a$, with a = 13.844(12), b = 10.280(9), c = 17.907(13) Å, β = 113.2(1)°, and Z = 4; (**2**) is orthorhombic, space group $P2_12_12_1$, with a = 13.80(1), b = 10.49(1), c = 14.59(1) Å, and Z = 4. Diffractometer data were collected for all three compounds [independent reflections above background, 5 787 (**1a**), 3 658 (**1b**), and 2 134 (**2**)], the structures determined by the heavy-atom method and refined to give R = 0.061, 0.084, and 0.066 for (**1a**), (**1b**), and (**2**) respectively. All three compounds contain the *syn* form of $[(S)W(\mu\text{-}S)_2W(S)]^{2+}$ {bond length ranges 2.054(12)—2.116(5) [W–S(terminal)], 2.279(8)—2.325(9) [W–S(bridging)], and 2.795(2)—2.819(1) Å (W–W)}. In addition to the bonds in the $[W_2S_4]^{2+}$ moiety, each tungsten atom is co-ordinated to a bidentate ligand with W–S bond lengths in the range 2.429(9)—2.498(6) Å. Apart from the W–W bond each metal atom is five-co-ordinate and has a distorted square-pyramidal structure.

In contrast to the plethora of routes that are known for making species containing $[Mo_2Y_4]^{2+}$ (Y = O or S), few methods for the production of compounds containing the analogous tungsten moieties have been reported.[1–6] Of these the two most attractive for the production of $[W_2S_4]^{2+}$ appeared to us to be the oxidation of $[W(CO)_6]$ by an appropriate disulphide, which had been used previously to prepare a dialkyldithiophosphinate complex,[6] $[W_2S_4(S_2PR_2)]$ (R = Et or Pr^i), and the reduction of $[WS_4]^{2-}$ by the acid form of the ligand, which led[5] to the isolation of $[W_2S_4(edt)_2]^{2-}$ (H_2edt = ethane-1,2-dithiol). We felt that this latter route was the most generally applicable. Unfortunately, using published methods, $[WS_4]^{2-}$ is harder to obtain free from oxo-species than its molybdenum analogue. Accordingly we have developed an improved preparative method for $[WS_4]^{2-}$ and investigated three routes to the $[W_2S_4]^{2+}$ moiety, the third of which requires the use of WS_2Cl_2. As a result of our studies we report the syntheses and single-crystal *X*-ray structures of two forms of $[W_2S_4\{S_2P(OEt)_2\}_2]$, (**1a**) and (**1b**), and of $[W_2S_4(S_2CNEt_2)_2]$ (**2**).

Experimental

All preparations were carried out either on an all-glass vacuum line or under an atmosphere of dry nitrogen. I.r. spectra of the samples were obtained as Nujol mulls using a P.E. 683 spectrophotometer and ^1H n.m.r. spectra with a Varian T60 or HA100 instrument.

The sulphidohalide WS_2Cl_2 was prepared as previously reported.[7,8]

Preparation.—$[NH_4]_2[WS_4]$ *and* $[NMe_4]_2[WS_4]$. Sodium tungstate dihydrate, $Na_2[WO_4]\cdot 2H_2O$ (19.0 g), was dissolved in the minimum of distilled water (20 cm^3) and dilute HCl added until a creamy white precipitate of 'hydrated WO_3' was deposited. The precipitate was isolated, washed with distilled water, and air-dried overnight. The solid was placed in a round-bottomed flask and ammonia added (50 cm^3, s.g. 0.880). The resulting mixture was stirred for 1.5 h after which H_2S was bubbled through the flask until all the solid completely dissolved to give a yellowish green solution. The mixture was allowed to stand for 4 d during which time pure $[NH_4]_2[WS_4]$ precipitated as orange crystals. Yield: 80%.

A solution of NMe_4Cl (0.5 g in 20 cm^3 of water) was added to an aqueous solution of $[NH_4]_2[WS_4]$ (1.0 g in 20 cm^3), whence $[NMe_4]_2[WS_4]$ precipitated quantitatively.

$[W_2S_4\{S_2P(OEt)_2\}_2]$ (**1**). (*a*) *From* $[NMe_4]_2[WS_4]$. The compound $[NMe_4]_2[WS_4]$ (1.0 g) was dissolved in MeCN (5 cm^3) and an excess of $HS_2P(OEt)_2$ added (7 cm^3). The resulting mixture was allowed to stand under an atmosphere of nitrogen for 3 d. Red crystals were deposited during this period. Yield: 75% (Found: C, 11.2; H, 2.3. $C_8H_{20}O_4P_2S_8W_2$ requires C, 11.0; H, 2.3%).

The crystals obtained directly from the preparation were suitable for single-crystal *X*-ray work and are denoted (**1a**) in the *X*-ray section.

(*b*) *From* WS_2Cl_2. Dichlorodisulphidotungsten(VI) (1.74 g) and $[NH_4][S_2P(OEt)_2]$ (2.06 g) were added under a flow of dry nitrogen to a glass ampoule containing a magnetic follower. The vessel was quickly evacuated, cooled in liquid nitrogen, and into it was distilled dry CH_2Cl_2 (50 cm^3). The ampoule was sealed under vacuum and the mixture allowed to warm to room temperature. A brown solution and a grey precipitate were formed. The mixture was stirred for 30 d after which the ampoule was opened under dry nitrogen and the contents

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* *Supplementary data available*: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. Atomic co-ordinates (× 10^4) for (**1a**) with estimated standard deviations in parentheses

Atom	x	y	z
W(1)	2 521.1(4)	1 602(1)	1 160(1)
W(2)	4 065.8(4)	1 712(1)	1 186(1)
S(3)	3 299(3)	1 571(4)	−634(5)
S(4)	3 272(3)	2 274(4)	2 802(6)
S(11)	1 633(3)	1 997(5)	−622(6)
S(12)	1 636(3)	2 732(5)	2 328(6)
S(1)	2 269(3)	66(4)	1 698(7)
S(2)	4 420(3)	193(5)	1 676(7)
S(21)	4 906(3)	2 864(6)	2 477(7)
S(22)	4 904(3)	2 330(5)	−557(6)
P(13)	1 009(3)	2 772(4)	688(6)
P(23)	5 513(3)	3 016(5)	867(7)
O(24)	6 303(6)	2 581(13)	919(20)
O(27)	5 640(9)	4 234(15)	681(22)
C(25)	6 441(12)	1 531(20)	1 186(26)
C(26)	7 197(17)	1 389(26)	1 355(35)
C(28)	6 176(17)	4 607(24)	−319(38)
C(29)	6 650(18)	5 306(34)	290(38)
O(14)	234(6)	2 337(12)	842(18)
O(17)	790(8)	3 882(12)	209(20)
C(15)	98(11)	1 303(19)	1 145(30)
C(16)	−717(14)	1 092(22)	1 121(46)
C(18)	1 385(13)	4 660(17)	29(30)
C(19)	1 037(15)	5 563(20)	−718(37)

Table 2. Atomic co-ordinates (× 10^4) for (**1b**) with estimated standard deviations in parentheses

Atom	x	y	z
W(1)	8 178(1)	1 078(1)	3 544(1)
W(2)	8 257(1)	1 248(1)	2 000(1)
S(4)	8 314(8)	−609(8)	2 725(6)
S(1)	9 673(8)	1 558(9)	4 382(6)
S(3)	7 573(8)	2 741(7)	2 598(6)
S(2)	9 768(9)	1 800(10)	2 213(6)
S(11)	7 015(9)	2 159(8)	4 068(6)
S(12)	7 608(9)	−743(8)	4 143(6)
S(22)	7 157(9)	2 530(10)	793(6)
S(21)	7 787(12)	−393(9)	898(6)
P(13)	6 934(8)	507(8)	4 647(6)
P(23)	7 116(12)	1 024(12)	76(7)
O(14)	7 423(19)	608(24)	5 565(14)
O(17)	5 809(22)	141(22)	4 556(18)
O(24)	5 936(31)	945(47)	−472(23)
O(27)	7 673(33)	1 189(28)	−481(24)
C(15A)	8 528(45)	471(116)	6 117(35)
C(15B)	8 517(33)	978(67)	6 043(21)
C(16)	8 723(31)	1 050(35)	6 946(18)
C(18A)	4 872(48)	207(45)	3 728(28)
C(18B)	5 353(101)	−261(153)	3 692(46)
C(19)	4 428(40)	−1 102(36)	3 566(33)
C(25)	5 689(57)	64(63)	−1 131(44)
C(26)	4 668(58)	278(70)	−1 781(49)
C(28)	8 818(38)	1 470(52)	−231(32)
C(29A)	8 346(230)	1 648(226)	−1 118(46)
C(29B)	9 068(63)	1 275(49)	−968(33)

filtered. The insoluble solid proved to be NH_4Cl. Removal of the solvent from the solution yielded a reddish brown oil, the i.r. spectrum of which indicated the presence of disulphide $[(EtO)_2P(S)S-]_2$. Extraction of the oil with light petroleum (b.p. 80—100 °C) left a reddish brown crystalline solid. Yield: 70% (Found: C, 11.1; H, 2.6%). Recrystallisation of the compound from $CHCl_3$ gave crystals that were suitable for a single-crystal *X*-ray study and are denoted (**1b**) in the *X*-ray section.

Table 3. Atomic co-ordinates (× 10^4) for (**2**) with estimated standard deviations in parentheses

Atom	x	y	z
W(1)	−2 397(1)	−2 384(1)	−4 168(1)
W(2)	−2 664(1)	−285(1)	−5 321(1)
S(3)	−2 431(7)	−255(7)	−3 758(5)
S(4)	−3 190(7)	−2 336(8)	−5 568(5)
S(11)	−2 673(8)	−2 729(8)	−2 543(6)
S(1)	−964(8)	−2 934(10)	−4 379(8)
S(12)	−3 346(8)	−4 335(9)	−3 981(6)
S(21)	−3 892(6)	207(8)	−6 473(6)
S(22)	−3 325(7)	1 839(8)	−5 021(6)
S(2)	−1 344(7)	−28(11)	−5 996(7)
C(13)	−3 212(27)	−4 176(33)	−2 813(20)
N(14)	−3 459(25)	−4 963(33)	−2 208(20)
C(23)	−4 077(28)	1 596(33)	−5 928(24)
N(24)	−4 675(18)	2 469(25)	−6 208(16)
C(25)	−4 921(32)	3 630(29)	−5 636(27)
C(26)	−4 534(29)	4 805(38)	−6 172(38)
C(27)	−5 357(28)	2 207(27)	−7 067(21)
C(28)	−6 315(31)	1 626(64)	−6 841(33)
C(15)	−3 427(40)	−4 728(39)	−1 203(26)
C(16)	−4 215(42)	−3 932(43)	−796(34)
C(17)	−4 035(64)	−6 173(55)	−2 455(52)
C(18A)	−3 891(77)	−7 357(94)	−2 219(73)
C(18B)	−4 720(63)	−6 793(78)	−1 921(58)

$[W_2S_4(S_2CNEt_2)_2]$ (**2**). (*a*) *From* $[W(CO)_6]$ *and* $[Et_2NC(S)S-]_2$. Hexacarbonyltungsten (3 g) and $[Et_2NC(S)S-]_2$ (6.4 g) were heated under reflux in 1,2,5-trimethylbenzene (60 cm^3) until the solution became green. On cooling a red solid was deposited. Yield: 70% (Found: C, 15.9; H, 2.6; N, 3.4. $C_{10}H_{20}N_2S_8W_2$ requires C, 15.2; H, 2.5; N, 3.5%).

On allowing the filtrate to stand a green compound was deposited which we were unable to identify, even though identical analytical results were obtained from a number of reactions (*viz.* C, 20.1; H, 3.9; N, 4.8%).

(*b*) *From* $[W_2S_4\{S_2P(OEt)_2\}_2]$ *and* $Na(S_2CNEt_2)$. The compound $Na(S_2CNEt_2)$, dissolved in methanol (0.36 g in 5 cm^3), was added to a tetrahydrofuran solution of $[W_2S_4\{S_2P(OEt)_2\}_2]$ (0.7 g in 10 cm^3). A reddish orange solid was deposited. Yield: 75% (Found: C, 15.3; H, 2.6; N, 3.3%).

Crystals of $[W_2S_4(S_2CNEt_2)_2]$ (**2**) suitable for *X*-ray study were obtained by vapour diffusion of 2-methylbutane into an MeCN solution of the complex.

Crystal-structure Determinations.—Crystal data for $[W_2S_4\{S_2P(OEt)_2\}_2]$ (**1a**). $C_8H_{20}O_4P_2S_8W_2$, $M = 866.4$, monoclinic, $a = 18.230(11)$, $b = 12.905(11)$, $c = 10.153(12)$ Å, $\beta = 90.5(1)°$, $U = 2\,388.5$ Å^3, $D_m = 2.37(5)$, $D_c = 2.41$ g cm^{-3}, $Z = 4$, $F(000) = 1\,624$, Mo-K_α radiation, $\lambda = 0.710\,7$ Å, $\mu = 109.9$ cm^{-1}, and space group $P2_1/n$.

Crystal data for $[W_2S_4\{S_2P(OEt)_2\}_2]$ (**1b**). $C_8H_{20}O_4P_2S_8W_2$, $M = 866.4$, monoclinic, $a = 13.844(12)$, $b = 10.280(9)$, $c = 17.907(13)$ Å, $\beta = 113.2(1)°$, $U = 2\,342.4$ Å^3, $D_m = 2.37(5)$, $D_c = 2.45$ g cm^{-3}, $Z = 4$, $F(000) = 1\,624$, Mo-K_α radiation, $\lambda = 0.7107$ Å, $\mu = 112.0$ cm^{-1}, and space group $P2_1/a$.

Crystal data for $[W_2S_4(S_2CNEt_2)_2]$ (**2**). $C_{10}H_{20}N_2S_8W_2$, $M = 792.5$, orthorhombic, $a = 13.80(1)$, $b = 10.49(1)$, $c = 14.59(1)$ Å, $U = 2\,112.1$ Å^3, $D_c = 2.49$ g cm^{-3}, $Z = 4$, $F(000) = 1\,480$, Mo-K_α radiation, $\lambda = 0.7107$ Å, $\mu = 122.6$ cm^{-1}, and space group $P2_12_12_1$.

Precession photographs established the preliminary cell constants and space groups. Crystals were mounted to rotate around the *a* axes on a Stoe Stadi2 diffractometer and data collected *via* variable-width ω scans. Background counts were 20

Table 4. Molecular dimensions in the metal co-ordination spheres of (**1a**), (**1b**), and (**2**); distances in Å, angles in degrees

	(**1a**)	(**1b**)	(**2**)
W(1)–W(2)	2.819(1)	2.813(2)	2.795(2)
W(1)–S(1)	2.111(5)	2.081(10)	2.083(12)
W(2)–S(2)	2.116(5)	2.054(12)	2.088(9)
W(1)–S(3)	2.318(5)	2.318(9)	2.312(7)
W(1)–S(4)	2.315(5)	2.325(9)	2.318(8)
W(1)–S(11)	2.473(5)	2.430(9)	2.429(9)
W(1)–S(12)	2.483(5)	2.438(8)	2.445(10)
W(2)–S(3)	2.312(5)	2.279(8)	2.303(8)
W(2)–S(4)	2.312(5)	2.292(8)	2.299(9)
W(2)–S(21)	2.498(6)	2.480(10)	2.442(8)
W(2)–S(22)	2.473(5)	2.477(10)	2.448(9)
S(3)–W(1)–S(4)	102.04(16)	100.7(3)	101.40(29)
S(3)–W(1)–S(11)	80.26(17)	80.8(3)	83.57(28)
S(4)–W(1)–S(11)	146.02(19)	144.6(4)	142.13(33)
S(3)–W(1)–S(1)	108.87(20)	108.8(3)	108.99(37)
S(4)–W(1)–S(1)	107.22(22)	109.1(4)	108.92(40)
S(11)–W(1)–S(1)	103.85(21)	103.6(4)	104.57(41)
S(3)–W(1)–S(12)	142.05(19)	143.2(4)	140.23(36)
S(4)–W(1)–S(12)	79.51(16)	80.0(3)	82.17(32)
S(11)–W(1)–S(12)	78.73(18)	78.6(3)	71.46(29)
S(12)–W(1)–S(1)	106.66(20)	105.5(4)	107.01(39)
S(3)–W(2)–S(4)	102.04(16)	102.9(3)	102.27(27)
S(3)–W(2)–S(21)	145.95(21)	144.0(4)	140.84(32)
S(4)–W(2)–S(21)	80.00(18)	79.8(3)	82.57(29)
S(3)–W(2)–S(22)	79.97(17)	80.0(3)	82.10(27)
S(4)–W(2)–S(22)	142.74(19)	144.0(4)	139.66(34)
S(21)–W(2)–S(22)	78.63(19)	77.8(4)	70.82(29)
S(3)–W(2)–S(2)	107.25(21)	108.0(4)	110.08(38)
S(4)–W(2)–S(2)	108.33(21)	108.6(4)	108.80(38)
S(21)–W(2)–S(2)	106.26(20)	105.3(4)	104.68(37)
S(22)–W(2)–S(2)	104.00(22)	104.2(4)	106.98(38)
W(1)–S(3)–W(2)	75.00(15)	75.4(2)	74.52(22)
W(1)–S(4)–W(2)	75.05(16)	75.1(2)	74.50(26)

s and a scan rate of 0.0333° s^{-1} was applied to a width of $(2.0 + 0.5\sin\mu/\tan\theta)$.

For (**1a**), 5 787 independent reflections with $2\theta < 60°$ were measured of which 3 444 with $I > 3\sigma(I)$ were used subsequently. For (**1b**), 3 658 independent reflections were measured with $2\theta < 40°$. The crystal decomposed by *ca.* 50% during the intensity collection. A linear correction was made within each layer to account for the decomposition and a scale factor for each layer was refined subsequently. 2 350 Reflections with $I > 2\sigma(I)$ were used in further refinement. For (**2**), 2 134 independent reflections with $2\theta < 50°$ were measured of which 1 969 having $I > 3\sigma(I)$ were used in subsequent refinement.

Data for all three crystals were corrected for absorption using an empirical method.[9] All three structures were solved from the Patterson function and subsequent Fourier syntheses.

In (**1b**), three carbon atoms were disordered over two positions. They were given an equivalent thermal parameter (which was refined) and occupancies that added up to 2.0. In (**2**), two positions were refined for C(18), one of the methyl carbon atoms. They were given an equivalent thermal parameter and occupancies of x and $1 - x$; x was refined.

In all three structures, the non-hydrogen atoms were refined anisotropically except for the disordered carbons which were refined isotropically. Hydrogen atoms were included in calculated positions. Hydrogen atoms in the same methyl or methylene group were given a common thermal parameter which was then refined.

In (**1a**), two of the methyl groups did not refine satisfactorily and these hydrogen atoms were removed from the final refinement. In (**2**), two of the methyl groups were treated similarly. However in (**1b**) no hydrogen atoms were included because of the disorder. Final R values were 0.061 (R' 0.062) for (**1a**), 0.084 (R' 0.086) for (**1b**), and 0.066 (R' 0.073) for (**2**). Calculations were carried out using SHELX 76[10] and some of our own programs on the Amdahl V7 computer at the University of Reading. Positional parameters for (**1a**), (**1b**), and (**2**) are given in Tables 1—3 respectively. Dimensions in the co-ordination spheres for (**1a**), (**1b**), and (**2**) are compared in Table 4.

Results and Discussion

Preparative Methods.—$[W_2S_4\{S_2P(OEt)_2\}_2]$ (**1**). Two routes to $[W_2S_4\{S_2P(OEt)_2\}_2]$ have been investigated, the first involves the use of $[WS_4]^{2-}$ and the second WS_2Cl_2.[7,8] The more convenient of the two routes is to (**1a**) in which $[WS_4]^{2-}$ was used. This is a compound that has proved difficult to obtain free from impurities such as $[WOS_3]^{2-}$. However the new route reported here (see Experimental section) readily yields pure $[WS_4]^{2-}$. Treatment of MeCN solutions of $[WS_4]^{2-}$ with an excess of $HS_2P(OEt)_2$ gave $[W_2S_4\{S_2P(OEt)_2\}_2]$ in high yield together with $[(EtO)_2P(S)S\text{–}]_2$. The reaction takes place at room temperature in contrast to the formation of $[W_2S_4L_2]^{2-}$ [L = edt or *o*-aminobenzenethiol] where *NN*-dimethylformamide solutions of $[WS_4]^{2-}$–L mixtures[5] required heating under argon to *ca.* 135 °C.

The redox process leading to the formation of the $[W_2S_4]^{2+}$ fragment from $[WS_4]^{2-}$ is given by reaction (1a).

$$2[WS_4]^{2-} + 8H^+ + 2e^- \longrightarrow [W_2S_4]^{2+} + 4H_2S$$
$$2[S_2P(OEt)_2]^- \longrightarrow [(EtO)_2P(S)S\text{–}]_2 + 2e^- \quad (1a)$$

The formation of $[(EtO)_2P(S)S\text{–}]_2$ as one of the products of the reaction proves that the ligand $[S_2P(OEt)_2]^-$ is the reducing agent rather than S^{2-}. It had previously been suggested that S^{2-} was the reducing agent in the type of system under discussion[5] and also in the formation of the mixed Mo^{VI}–Mo^{IV} compound[11] $[(S_2)(S)Mo(\mu\text{-}S)_2Mo(S)(S_2)]^{2-}$.

Although WS_2Cl_2 has been known for some years[7,8] it is still not clear whether it is a tungsten(VI) species, or a tungsten(V) or tungsten(IV) compound containing S^{2-} and $(S_2)^{2-}$ fragments [*i.e.* $W_2S_2(S_2)Cl_4$ or $W_2(S_2)_2Cl_4$]. The synthesis of $[W_2S_4\{S_2P(OEt)_2\}_2]$ from WS_2Cl_2 and $[NH_4][S_2P(OEt)_2]$ demonstrates that WS_2Cl_2 is a tungsten(VI) compound since $[(EtO)_2P(S)S\text{–}]_2$ is also formed *via* the oxidation of $[(EtO)_2PS_2]^-$ and concomitant reduction of tungsten(VI) to tungsten(V) *via* reaction (1b).

$$2WS_2Cl_2 + 4[S_2P(OEt)_2]^- \longrightarrow [W_2S_4\{S_2P(OEt)_2\}_2] + [(EtO)_2P(S)S\text{–}]_2 \quad (1b)$$

$[W_2S_4(S_2CNEt_2)_2]$ (**2**). Two routes for the preparation of $[W_2S_4(S_2CNEt_2)_2]$ have been developed. In the first a 1,2,5-trimethylbenzene solution of $[Et_2NC(S)S\text{–}]_2$ and $[W(CO)_6]$ (2.5:1 molar ratio) was heated under nitrogen, thus $[Et_2NC(S)S\text{–}]_2$ is used to oxidise tungsten(0) to tungsten(V). We had hoped to obtain $[W_2S_4(S_2CNEt_2)_2]$ from $[WS_4]^{2-}$ using an analogous route to that employed for $[W_2S_4\{S_2P(OEt)_2\}_2]$, but unfortunately all reactions involving $Na(S_2CNEt_2)$–$[WS_4]^{2-}$ mixtures failed to give the desired product. However $[W_2S_4(S_2CNEt_2)_2]$ was obtained by a ligand substitution reaction in which a tetrahydrofuran solution of $[W_2S_4\{S_2P(OEt)_2\}_2]$ was mixed with a methanol solution of $Na(S_2CNEt_2)$.

This study has shown that the new route to the $[W_2S_4]^{2+}$ core reported here, *i.e.* the reaction of $[WS_4]^{2-}$ with $HS_2P(OEt)_2$, is more convenient than those in the literature as it provides a ready source of $[W_2S_4\{S_2P(OEt)_2\}_2]$ from which other species can be obtained by ligand-substitution reactions.

Table 5. I.r. (540—300 cm^{-1}) and ^{1}H n.m.r. data for (**1**), (**2**), and $[NH_4][S_2P(OEt)_2]$

	Compound	ν/cm^{-1}	δ(^{1}H)/p.p.m.
(**1**)	$[W_2S_4\{S_2P(OEt)_2\}_2]$ *	535s, 440m, 427m, 397m, 350m, 300s	1.28 (t), 1.67 (t), 3.89 (d of q), 4.91 (d of q)
(**2**)	$[W_2S_4(S_2CNEt_2)_2]$	532s, 523m, 447m, 392w, 373m, 326ms	
	$[NH_4][S_2P(OEt)_2]$		1.22 (t), 3.94 (d of q)

* Coupling constants/Hz: $^3J_{HH}$ = 7 and $^3J_{PH}$ = 10.

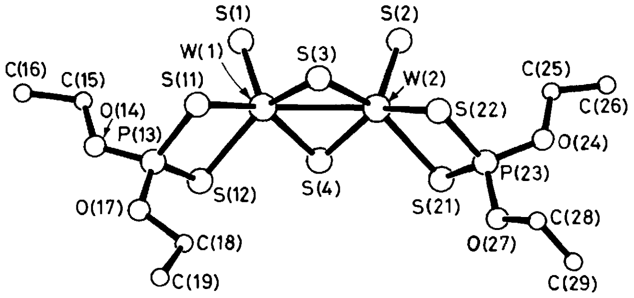

Figure 1. The structure of $[W_2S_4\{S_2P(OEt)_2\}_2]$ (**1a**), prepared from $[WS_4]^{2-}$

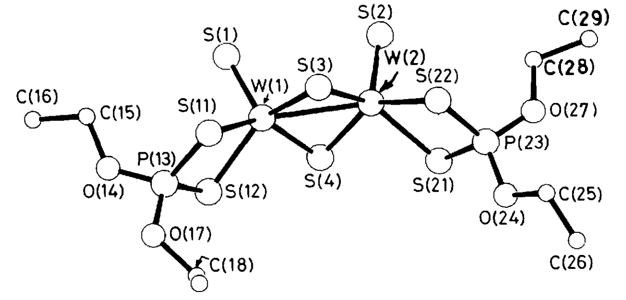

Figure 2. The structure of $[W_2S_4\{S_2P(OEt)_2\}_2]$ (**1b**), prepared from WS_2Cl_2

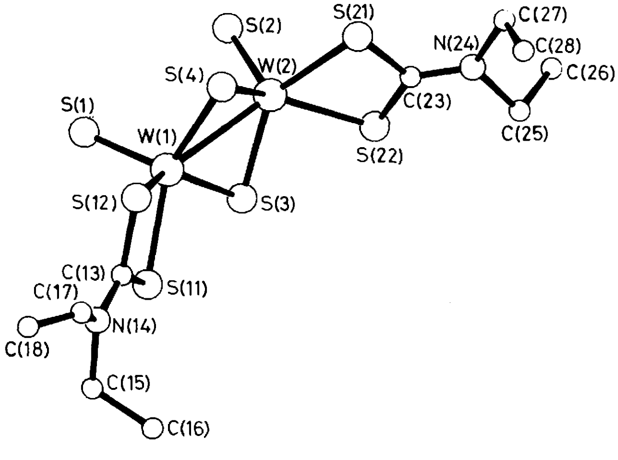

Figure 3. The structure of $[W_2S_4(S_2CNEt_2)_2]$ (**2**)

Spectroscopic Properties.—Selected i.r. and ^{1}H n.m.r. data are recorded in Table 5. The i.r. spectra of the compounds in the region 540—300 cm^{-1} are similar. The highest energy i.r. band is the stretching mode of the terminal W–S group. The W–S–W–S non-planar ring should give rise to four i.r. active modes and these are assigned to the four bands in the region 450—320 cm^{-1}.

Co-ordination to the tungsten atom causes the ^{1}H n.m.r. resonances of $[(EtO)_2PS_2]^-$ to move to higher frequency as would be expected. More significantly, two magnetic environments are revealed for the ethyl groups. Thus $[W_2S_4\{S_2P(OEt)_2\}_2]$ is non-fluxional on the n.m.r. time-scale and in solution must retain the type of structure depicted in Figures 1 and 2 where it can be clearly seen that the two ethyl groups of a given ligand are in different environments.

The structures of (**1a**), (**1b**), and (**2**) are shown in Figures 1—3 respectively together with the atomic numbering schemes. The three structures are very similar, each containing the $[W_2S_4]^{2+}$ moiety. This moiety is rare for tungsten, there being only three previous structure determinations, namely $[W_4S_{12}]^{2-}$,[4] $[W_2S_4(edt)_2]^{2-}$ (**3**),[5] in which the tungsten atoms are five-co-ordinate, and $[W_2S_4Cl_2(py)_2]$ (**4**) (py = pyridine),[7] in which the tungsten atoms are six-co-ordinate. However there are many more examples of the equivalent molybdenum $[Mo_2S_4]^{2+}$moiety. In the three present structures the tungsten atoms can be considered to be five co-ordinate* having an approximate square-pyramidal environment, each being bound to a terminal sulphur atom in the axial position while the equatorial plane contains two sulphur atoms, which form bridges between the two metal centres, and the bidentate chelate ligand.

Least-squares planes calculations show that the metal atoms are out of the plane of the four sulphur atoms by 0.68, 0.68 in (**1a**); 0.84, 0.69 in (**1b**), and 0.72, 0.73 Å in (**2**) [*cf.* 0.72, 0.72 in (**3**) but only 0.32, 0.34 Å in the six-co-ordinate (**4**)]. There is a wide range of terminal W–S bond lengths in the three structures: 2.111(5), 2.116(5) in (**1a**); 2.081(10), 2.054(12) in (**1b**); and 2.083(12), 2.088(9) Å in (**2**). Other values for this terminal bond are 2.144(2) in (**3**), and 2.15(2) Å in (**4**). Clearly the overall values for this bond length in the present compounds are significantly less than in (**3**). Similarly the W(1)–W(2) distance is shorter in (**1a**) [2.819(1)], (**1b**) [2.813(2)], and (**2**) [2.795(2) Å] than in (**3**) [2.862(1) Å]. These differences could reflect the nature of the charge on the species as (**1a**), (**1b**), and (**2**) are neutral while (**3**) is a dianion, but could also be due in part to packing effects.

One surprising feature of the structure of (**3**) was that there were several differences between potentially equivalent angles subtended at the metals which reduced the molecular symmetry from C_{2v} to C_s. In particular the angles S(3)–W–S(12) and S(4)–W–S(11) differ by *ca.* 11° as do S(3)–W–S(21) and S(4)–W–S(22) [the numbering system in (**3**) has been changed to conform to that in (**1**) and (**2**)]. In (**1a**), **1b**), and (**2**) there are only minor variations between these angles of less than 2° in a particular compound. Also in (**3**) the angles involving terminal

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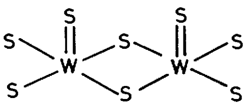
* It is convenient in describing the geometry of the tungsten co-ordination spheres to ignore the metal–metal bond which has only a limited effect on the geometry.

sulphur atoms S_{term} [S(1) and S(2)] and an equatorial sulphur atom vary considerably. The angles to the bridging sulphur atoms S_{br} [S(3), S(4)] are different from those to the bidentate ligand S_{lig} [S(11), S(12), S(21), or S(22)] as expected, but there are also large differences within each group of *ca.* 8°. In (**1a**), (**1b**), and (**2**), S_{term}–W–S_{br} angles are greater (range 107.2—110.1°) than S_{term}–W–S_{lig} (range 103.6–107.0°) but the values within each group are equivalent to within experimental error in each compound. This demonstrates that the structure of (**3**) is anomalous. In a previous discussion of this structure,[7] we concluded that the distortions in (**3**) were inexplicable on the basis of intramolecular effects and this opinion is reinforced by the dimensions of the three structures reported here. It is of course possible that the distortions are due to packing effects though this cannot easily be proved.

It seems clear from the three present structures that the moiety shown below does indeed contain approximate C_{2v} symmetry. There are some variations in (**1b**) but these we ascribe to the low accuracy of the structure caused by the difficulties in data collection. The dithiocarbamate ligand in (**2**) has a considerably smaller bite than the diethyl dithiophosphate ligand in (**1a**) and (**1b**). The W–S_{lig} bond lengths are similarly slightly smaller in (**2**) [2.429(9), 2.445(10), 2.442(8), 2.448(9) Å] than in (**1a**) [2.473(5), 2.483(5), 2.498(6), 2.473(5)] and (**1b**) [2.430(9), 2.438(8), 2.480(10) 2.477(10) Å], but consequentially the S_{lig}–W–S_{lig} angles are much smaller, 71.5(3), 70.8(3) in (**2**) compared to 78.7(2), 78.6(2) in (**1a**) and 78.6(3), 77.8(4)° in (**1b**). However this does not seem to have any significant effect on the co-ordination sphere of the tungsten atoms; the *cis* S_{br}–W–S_{lig} angles are *ca.* 2—3° larger [mean values 82.8 in (**2**) *vs.* 79.9 in (**1a**), 80.1° in (**1b**)] and *trans* S_{br}–W–S_{lig} *ca.* 4—5° smaller [mean values 140.7 *vs.* 144.1 in (**1a**) and 144.0 in (**1b**)] but that is about all. The remaining dimensions are very similar in all three compounds.

The geometry of the bidentate ligands is as expected in all three compounds. Calculation of intermolecular distances showed no distances less than the sum of van der Waals radii.



Indeed there were no significant distances involving the terminal sulphur atoms that could account for the variations in bond length.

Acknowledgements

We thank A. W. Johans for his assistance with the crystallographic investigations and the S.E.R.C. for funds for the diffractometer and for a grant (to N. T.). We also thank the Food and Agriculture Organisation of the United Nations for a grant (to P. P. E. M. M.).

References

1 R. Mattes and K. Mennemann, *Z. Anorg. Allg. Chem.*, 1977, **437**, 175.
2 S. Khalil and B. Sheldrick, *Acta Crystallogr., Sect. B*, 1978, **34**, 3751.
3 M. G. B. Drew, E. M. Page, and D. A. Rice, *Inorg. Chim. Acta*, 1983, **76**, L33.
4 F. Secheresse, J. Lefebvre, J. C. Daran, and Y. Jeannin, *Inorg. Chem.*, 1982, **21**, 1311.
5 W. Pan, T. Chandler, J. H. Enemark, and E. I. Stiefel, *Inorg. Chem.*, 1984, **23**, 4265.
6 H. Keck, W. Kuchen, J. Mathew, B. Meyer, D. Mootz, and W. Wunderlich, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 975.
7 M. G. B. Drew, R. J. Hobson, D. A. Rice, and N. Turp, *J. Chem. Soc., Dalton Trans.*, 1986, 2165.
8 G. W. A. Fowles, R. J. Hobson, D. A. Rice, and K. J. Shanton, *J. Chem. Soc., Chem. Commun.*, 1976, 552.
9 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **35**, 925.
10 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determination, University of Cambridge, 1976.
11 W. Pan, M. A. Harmer, T. R. Halbert, and E. I. Stiefel, *J. Am. Chem. Soc.*, 1984, **106**, 459.

Received 21st July 1986; *Paper* 6/1464