Synthesis and Crystal Structure of Tetramethylammonium μ-Pentachlorothiophenolato-bis[pentacarbonyltungstate(0)]

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The reaction of $[NEt_4][W(CO)_5Cl]$ with $Tl[SC_6Cl_5]$ and $Ag[BF_4]$ yields the title complex $[NEt_4][(CO)_5W-SC_6Cl_5-W(CO)_5]$. The i.r. spectrum of this complex in tetrahydrofuran has distinct carbonyl-stretching bands at 2 073w, 2 062m, 1 977m (sh), 1 941vs, 1 916s, and 1 876s cm^{-1} which are consistent with a bent W–S–W bridge. *X*-Ray analysis using 2 770 diffractometer data (Mo-K_α radiation) shows that the W–S–W angle is 132.1°. Crystals are triclinic, space group $P\bar{1}$, with a = 13.682(3), b = 11.699(2), c = 10.597(2) Å, α = 91.71(2), β = 100.31(2), γ = 92.20(2)°, and Z = 2.

IN earlier papers we have described various mononuclear complexes containing anionic sulphur ligands bonded to metals in low oxidation states.[1,2] We report here the preparation, characterisation, and *X*-ray analysis of the binuclear species $[NEt_4][W_2(CO)_{10}(\mu-SC_6Cl_5)]$. The i.r.-active stretching frequencies in the carbonyl region are discussed in relation to the possible stereochemistry of the complex in solution.

EXPERIMENTAL

Preparations.—All experiments were carried out under a nitrogen atmosphere. Tetraethylammonium pentacarbonylchlorotungstate(0) (0.92 g, 2.0 mmol) was added to a suspension of thallium(I) pentachlorothiophenolate (0.49 g, 1.0 mmol) in tetrahydrofuran (thf) (50 cm^3). The reaction mixture was stirred at room temperature for 1 h when all the thallium derivative appeared to have reacted. On addition of silver tetrafluoroborate (0.20 g, 1.0 mmol) a heavy precipitate formed immediately. However, the solution was stirred for another 2 h to ensure complete reaction. The reaction mixture was then filtered through microcrystalline cellulose. Light petroleum (50 cm^3) was added to the filtrate which was then allowed to stand for several hours during which time orange crystals formed, m.p. 132—134 °C (Found: C, 27.15; H, 1.95; Cl, 17.1; N, 1.40. Calc. for $C_{24}H_{20}Cl_5NO_{10}SW_2$: C, 27.2; H, 1.90; Cl, 16.7; N, 1.30%). This method also gave a high yield of the thiophenolate analogue for which a different method of preparation has been reported.

Apparatus and Techniques.—Infrared spectra of the complexes were recorded as thf solutions on a Perkin-Elmer 457 grating spectrophotometer calibrated against CO_2 and polystyrene film and are believed to be accurate to ± 2 cm^{-1}. Melting points were recorded in air on a Reichert hot-stage apparatus with a microscope and are corrected. Microanalyses were performed by the Australian Microanalytical Service, Division of Applied Chemistry, CSIRO, University of Melbourne.

Crystal Data.—$C_{24}H_{20}Cl_5NO_{10}SW_2$, M = 1 059.5, Triclinic, a = 13.682(3), b = 11.699(2), c = 10.597(2) Å, α = 91.71(2), β = 100.31(2), γ = 92.20(2)°, U = 1 666.5 Å^3, D_c = 2.11 g cm^{-3}, Z = 2, $F(000)$ = 1 000, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 78.02 cm^{-1}, space group $P\bar{1}$ assumed and confirmed by satisfactory refinement.

Intensity Measurements.—Intensity measurements, in the range θ 3—25°, were made on a Philips PW1100 four-circle diffractometer using a θ—2θ scan technique and Mo-K_α radiation from a graphite-crystal monochromator. Weak reflections which gave $I_t - 2(I_t)^{\frac{1}{2}} < I_b$ on the first scan were omitted; I_t is the count rate at the maximum of the reflection peak and I_b is the mean count of two preliminary 5-s background measurements at the extremities of the scan. The background measuring time for each reflection was proportional to I_b/I_i, where I_i is the total count recorded in the first scan. Reflections for which I_i was

TABLE 1

Fractional atomic co-ordinates

Atom	*x*	*y*	*z*
W(1)	0.272 43(5)	0.262 06(5)	0.480 46(6)
W(2)	0.152 96(4)	0.252 95(5)	0.033 06(6)
S	0.195 8(3)	0.169 3(3)	0.258 4(4)
Cl(1)	0.081 2(3)	−0.059 3(4)	0.305 7(4)
Cl(2)	0.167 6(4)	−0.294 4(3)	0.276 0(5)
Cl(3)	0.381 6(4)	−0.311 6(4)	0.214 7(5)
Cl(4)	0.496 9(3)	−0.093 8(4)	0.153 4(5)
Cl(5)	0.412 1(3)	0.143 0(3)	0.187 8(4)
C(1)	0.197 4(10)	−0.064 8(11)	0.264 2(13)
C(2)	0.236 7(12)	−0.171 6(14)	0.252 7(16)
C(3)	0.328 5(10)	−0.180 5(12)	0.219 9(14)
C(4)	0.383 9(11)	−0.082 4(13)	0.198 8(15)
C(5)	0.344 1(10)	0.023 4(11)	0.215 6(13)
C(6)	0.248 7(10)	0.035 0(11)	0.244 6(13)
C(11)	0.185 2(13)	0.151 1(15)	0.558 7(18)
C(12)	0.168 0(13)	0.377 5(15)	0.463 5(18)
C(13)	0.360 4(15)	0.370 6(17)	0.409 1(20)
C(14)	0.384 9(15)	0.158 0(17)	0.508 1(20)
C(15)	0.323 6(14)	0.323 1(16)	0.650 7(19)
O(11)	0.137 3(10)	0.092 4(12)	0.606 3(14)
O(12)	0.108 6(10)	0.445 6(11)	0.460 6(13)
O(13)	0.416 1(11)	0.433 8(13)	0.368 5(15)
O(14)	0.453 4(11)	0.100 3(12)	0.532 4(14)
O(15)	0.356 0(10)	0.358 8(12)	0.759 8(14)
C(21)	0.023 0(12)	0.163 4(12)	0.016 1(15)
C(22)	0.096 8(12)	0.388 3(14)	0.114 3(16)
C(23)	0.280 5(12)	0.348 4(13)	0.051 8(15)
C(24)	0.213 7(12)	0.124 2(15)	−0.050 4(17)
C(25)	0.114 4(11)	0.311 9(13)	−0.137 9(16)
O(21)	−0.054 0(9)	0.117 7(10)	0.011 1(12)
O(22)	0.066 0(9)	0.466 8(11)	0.156 1(13)
O(23)	0.350 8(10)	0.409 5(11)	0.059 7(13)
O(24)	0.250 7(10)	0.052 4(11)	−0.099 4(13)
O(25)	0.087 6(9)	0.346 0(10)	−0.239 3(12)
N	0.750 8(10)	0.287 8(10)	0.254 6(13)
C(31a)	0.803 7(21)	0.398 5(24)	0.208 7(29)
C(32)	0.829 4(14)	0.378 5(16)	0.076 3(19)
C(33a)	0.657 0(26)	0.254 3(30)	0.144 7(35)
C(34a)	0.579 2(28)	0.338 9(32)	0.115 2(39)
C(35a)	0.819 1(26)	0.195 9(30)	0.274 8(35)
C(36)	0.918 5(16)	0.214 0(18)	0.359 4(21)
C(37a)	0.714 2(27)	0.338 5(31)	0.376 8(37)
C(38a)	0.644 6(26)	0.244 0(31)	0.418 1(35)
C(37b)	0.697 1(29)	0.167 4(33)	0.285 0(40)
C(31b)	0.776 0(34)	0.264 4(39)	0.123 3(47)
C(33b)	0.683 3(34)	0.388 3(38)	0.279 8(47)
C(34b)	0.596 9(38)	0.379 0(42)	0.178 1(53)
C(35b)	0.841 6(34)	0.307 8(39)	0.370 2(46)
C(38b)	0.674 1(35)	0.169 7(41)	0.417 2(48)

TABLE 2

Bond lengths and angles with standard deviations in parentheses

(*a*) Lengths (Å)

(*i*) The anionic complex

W(1)–S	2.586(4)	C(1)–C(2)	1.39(2)
W(1)–C(11)	2.02(2)	C(2)–C(3)	1.37(2)
W(1)–C(12)	1.99(2)	C(3)–C(4)	1.40(2)
W(1)–C(13)	1.97(2)	C(4)–C(5)	1.39(2)
W(1)–C(14)	1.98(2)	C(5)–C(6)	1.40(2)
W(1)–C(15)	1.92(2)	C(1)–C(6)	1.38(2)
W(2)–S	2.586(4)	C(11)–O(11)	1.12(2)
W(2)–C(21)	2.00(2)	C(12)–O(12)	1.16(2)
W(2)–C(22)	2.02(2)	C(13)–O(13)	1.19(3)
W(2)–C(23)	2.01(2)	C(14)–O(14)	1.17(2)
W(2)–C(24)	2.01(2)	C(15)–O(15)	1.22(2)
W(2)–C(25)	1.95(2)		
S–C(6)	1.77(1)	C(21)–O(21)	1.16(2)
Cl(1)–C(1)	1.73(1)	C(22)–O(22)	1.14(2)
Cl(2)–C(2)	1.74(2)	C(23)–O(23)	1.17(2)
Cl(3)–C(3)	1.73(1)	C(24)–O(24)	1.15(2)
Cl(4)–C(4)	1.71(2)	C(25)–O(25)	1.16(2)
Cl(5)–C(5)	1.71(1)		

(*ii*) The disordered tetraethylammonium cation: a = occupancy 0.57, b = occupancy 0.43

N–C(31a)	1.59(3)	N–C(31b)	1.51(5)
N–C(33a)	1.60(3)	N–C(33b)	1.57(5)
N–C(35a)	1.45(4)	N–C(35b)	1.59(4)
N–C(37a)	1.58(4)	N–C(37b)	1.63(4)
C(31a)–C(32)	1.52(4)	C(31b)–C(32)	1.63(5)
C(33a)–C(34a)	1.48(5)	C(33b)–C(34b)	1.44(6)
C(35a)–C(36)	1.49(4)	C(35b)–C(36)	1.57(5)
C(37a)–C(38a)	1.55(5)	C(37b)–C(38b)	1.49(7)

(*b*) Angles (°)

(*i*) The anionic complex

S–W(1)–C(11)	87.9(5)	S–W(2)–C(21)	86.0(4)
S–W(1)–C(12)	91.1(5)	S–W(2)–C(22)	88.5(5)
S–W(1)–C(13)	93.7(6)	S–W(2)–C(23)	94.3(5)
S–W(1)–C(14)	93.8(6)	S–W(2)–C(24)	93.0(5)
S–W(1)–C(15)	175.9(6)	S–W(2)–C(25)	177.2(4)
C(11)–W(1)–C(12)	91.1(8)	C(21)–W(2)–C(22)	91.3(6)
C(11)–W(1)–C(13)	178.2(7)	C(21)–W(2)–C(23)	177.7(6)
C(11)–W(1)–C(14)	91.7(8)	C(21)–W(2)–C(24)	91.4(7)
C(11)–W(1)–C(15)	88.0(8)	C(21)–W(2)–C(25)	91.2(6)
C(12)–W(1)–C(13)	89.7(8)	C(22)–W(2)–C(23)	86.5(7)
C(12)–W(1)–C(14)	174.5(7)	C(22)–W(2)–C(24)	177.1(7)
C(12)–W(1)–C(15)	89.1(8)	C(22)–W(2)–C(25)	91.6(7)
C(13)–W(1)–C(14)	87.5(9)	C(23)–W(2)–C(24)	90.8(7)
C(13)–W(1)–C(15)	90.4(8)	C(23)–W(2)–C(25)	88.4(6)
C(14)–W(1)–C(15)	86.2(8)	C(24)–W(2)–C(25)	87.1(7)
W(1)–C(11)–O(11)	177.3(2)	W(2)–C(21)–O(21)	175.3(1)
W(1)–C(12)–O(12)	176.4(2)	W(2)–C(22)–O(22)	177.4(2)
W(1)–C(13)–O(13)	177.6(2)	W(2)–C(23)–O(23)	175.7(1)
W(1)–C(14)–O(14)	175.4(2)	W(2)–C(24)–O(24)	178.0(2)
W(1)–C(15)–O(15)	178.2(2)	W(2)–C(25)–O(25)	177.3(1)
W(1)–S–W(2)	132.1(1)	C(1)–C(2)–C(3)	120.2(1)
W(1)–S–C(6)	108.1(4)	C(1)–C(6)–C(5)	116.5(12)
W(2)–S–C(6)	109.0(5)	C(2)–C(3)–C(4)	120.4(14)
S–C(6)–C(1)	120.8(10)	C(3)–C(4)–C(5)	118.0(14)
S–C(6)–C(5)	122.8(10)	C(4)–C(5)–C(6)	122.8(13)

(*ii*) The disordered tetraethylammonium cation

C(31a)–N–C(33a)	106(2)	C(31b)–N–C(33b)	121(3)
C(31a)–N–C(35a)	111(2)	C(31b)–N–C(35b)	117(3)
C(31a)–N–C(37a)	101(2)	C(31b)–N–C(37b)	103(2)
C(33a)–N–C(35a)	112(2)	C(33b)–N–C(35b)	101(2)
C(33a)–N–C(37a)	110(2)	C(33b)–N–C(37b)	109(2)
C(35a)–N–C(37a)	116(2)	C(35b)–N–C(37b)	104(2)
N–C(31a)–C(32)	111(2)	N–C(31b)–C(32)	110(3)
N–C(33a)–C(34a)	118(3)	N–C(33b)–C(34b)	106(3)
N–C(35a)–C(36)	121(3)	N–C(35b)–C(36)	109(3)
N–C(37a)–C(38a)	106(3)	N–C(37b)–C(38b)	111(3)

less than 500 counts were scanned a second time. A constant scan speed of 0.025° s^{-1} and a scan width of 0.7° were used. Three standard reflections were measured at intervals of 6 h during data collection and showed no significant variation in intensity.

TABLE 3

Intermolecular contact distances of less than 3.5 Å and important intramolecular non-bonded contacts

Contact	Distance (Å)	Contact	Distance (Å)
Cl(5) ··· C(34a^{I})	3.38(4)	O(15) ··· O(23^{IV})	3.23(2)
O(12) ··· O(22^{I})	3.19(2)	O(22) ··· C(32^{V})	3.31(2)
O(13) ··· O(23^{I})	3.24(2)	Cl(2) ··· O(22^{VI})	3.19(1)
O(23) ··· C(34b^{I})	3.41(5)	O(11) ··· O(24^{VII})	3.28(2)
O(23) ··· C(34a^{I})	3.22(5)	O(15) ··· O(23^{VII})	3.23(2)
O(22) ··· C(32a^{II})	3.21(2)	O(12) ··· C(35b^{VIII})	3.33(5)
O(21) ··· C(31b^{II})	3.31(5)	O(15) ··· C(33b^{VIII})	3.05(5)
Cl(2) ··· O(22^{III})	3.19(1)	O(15) ··· C(34b^{VIII})	3.13(5)
O(11) ··· O(24^{IV})	3.28(2)		

Roman numeral superscripts denote the following equivalent positions relative to the first atom at x,y,z:

I x, y, z
II $1 + x, y, z$
III $x, 1 + y, z$
IV $x, y, 1 + z$
V $-1 + x, y, z$
VI $x, -1 + y, z$
VII $x, y, -1 + z$
VIII $1 - x, 1 - y, 1 - z$

Reflection intensities were calculated using a program written for the PW1100 diffractometer.[4] The variance of the intensity I was calculated as the sum of the variance due to counting statistics and $(0.04I)^2$ where the term in I^2 was introduced to allow for other sources of error.[5] Cor-

TABLE 4

Least-squares planes in direct space expressed in the form $Px + Qy + Rz = S$ with deviations (Å) from the plane in square brackets

Plane (1): W(1), C(11), C(12), C(13), C(14)

$P = 2.415, Q = 4.218, R = 9.035, S = 6.149$

[W(1) −0.04, C(11) −0.01, C(12) 0.04, C(13) 0.02, C(14) 0.04]

Plane (2): W(2), C(21), C(22), C(23), C(24)

$P = 2.173, Q = 4.802, R = 9.239, S = -0.589$

[W(2) 0.01, C(21) 0.00, C(22) −0.01, C(23) 0.00, C(24) −0.01]

Plane (3): W(1), W(2), S, C(6)

$P = 13.137, Q = 2.263, R = -3.556, S = 2.360$

[W(1) 0.10, W(2) 0.10, S −0.32, C(6) 0.12]

Plane (4): W(1), W(2), S

$P = 13.255, Q = -2.595, R = -3.487, S = 1.256$

Plane (5): the chlorophenyl group

$P = 3.355, Q = 0.203, R = 9.621, S = 3.197$

[Cl(1) 0.00, Cl(2) −0.04, Cl(3) 0.09, Cl(4) −0.07, Cl(5) 0.02, C(1) −0.01, C(2) −0.01, C(3) −0.02, C(4) −0.01, C(5) 0.04, C(6) 0.00]

Angles (°) between planes or lines:

First plane	Second plane or line	Dihedral angles
(1)	(2)	134.6
(4)	(5)	85.8
(4)	W(1)–C(11)	55.7
(4)	W(1)–C(12)	35.4
(4)	W(1)–C(13)	55.0
(4)	W(1)–C(14)	33.0
(4)	W(2)–C(21)	44.5
(4)	W(2)–C(22)	47.0
(4)	W(2)–C(23)	46.8
(4)	W(2)–C(24)	44.5

rections were made for Lorentz and polarisation factors but not for absorption. Equivalent reflections were averaged to give a total of 2 770 unique reflections with $I/\sigma(I) > 3$.

Structure Solution and Refinement.—The two tungsten atoms were located from a Patterson synthesis; the remaining non-hydrogen atom positions were obtained from subsequent difference syntheses. Two orientations of the tetraethylammonium cation are present in the crystal so that all but two of the carbon atoms are disordered. The pairs of disordered atoms were judged to have occupancies of *ca.* 0.6 and 0.4 respectively. The positional and occupancy parameters of these atoms were initially refined with fixed thermal parameters ($U = 0.08$ A^2). The mean of the occupancy values obtained for the two orientations, 0.57 and 0.43, were assigned to the relevant atoms and were not refined further. The tungsten, sulphur, and chlorine atoms were given anisotropic temperature factors and the positional and thermal parameters of the atoms of the anion and the cation were refined in separate cycles with the reflections weighted as $1/\sigma^2(F_o)$. The final R was 0.036, $R' = 0.047$ ($= \Sigma w^{\frac{1}{2}}|F_o - F_c|/\Sigma w^{\frac{1}{2}}|F_o|$). The scattering factors used for all atoms were those of Cromer and Mann [6] and corrections for the real part of the anomalous dispersion were included for tungsten, sulphur, and chlorine. Computer programs were those of the '*X*-Ray '74' crystallographic system.[7]

The final atomic co-ordinates are given in Table 1, bond lengths and angles in Table 2, intermolecular contact distances and important non-bonded intramolecular contacts in Table 3, and least-squares planes in direct space in Table 4. Supplementary Publication No. SUP 22703 (15 pp.) * contains thermal parameters and the observed and calculated structure factors.

RESULTS AND DISCUSSION

The crystal structure consists of alternating cationic and anionic groups; neither has symmetry higher than C_1. The structure and numbering of the complex anion are shown in Figure 1, and the two orientations of the disordered cation in Figure 2.

Both orientations of the tetraethylammonium cation have virtual C_{2v} symmetry and are related to each other approximately by a mirror plane through N, C(36), and C(32). The closest contacts between the anion and cation involve carbonyl oxygen atoms or chlorine atoms of the pentachlorothiophenolate ligand (Table 3).

The anion has two tungsten atoms bridged by the sulphur atom of the pentachlorothiophenolate ligand. An approximately octahedral co-ordination round each tungsten atom is completed by five carbonyl groups. The distortion from octahedral geometry can most readily be seen in the S-W-*cis*-C angles which range from 86.0 to 94.3°. These deviations from the angles of 90° expected for a regular geometry may be attributed to close contacts between the carbonyl groups on the two halves of the bridged anion (Table 3) and to the steric requirements of the pentachlorothiophenolate ligand.

Equivalent bond lengths in the two halves of the complex anion are in good agreement. The tungsten–carbonyl bonds *cis* to the bridging sulphur atom, mean 2.002(6) Å, are longer than the corresponding *trans* bonds, mean 1.935(12) Å. The longer W-C bonds may be attributed to the competition of the mutually *trans* carbonyl ligands for π-electron density from the tungsten atoms which would reduce the W-C bond order.

The structure of the complex anion may be envisaged to a first approximation as having C_{2v} symmetry with the four equatorial carbonyl groups on each half of the molecule being approximately equally distributed on both sides of the W(1)-S-W(2) plane, and with the pentachlorophenyl group almost perpendicular to this plane. However there is a definite rotation of the carbonyl groups on W(1) away from this eclipsed conformation, which reduces the overall symmetry to C_1. Whereas the angles between the *cis*-W(2)-C bonds and the W(1)-S-W(2) plane are in the range 44.5—47.0° (Table 4) those between the *cis*-W(1)-C bonds and this plane are in the range 33.0—55.7°. The angle between the pentachlorophenyl ring and the W(1)-S-W(2) plane is 85.8° and Cl(5) is slightly closer to W(2) than to W(1). The distortion from ideal C_{2v} symmetry shown in these angles minimises contact between the carbonyl groups on the two halves of the anion and the bulky penta-

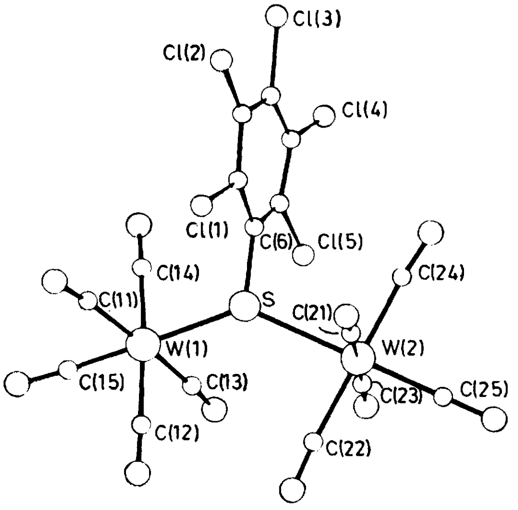

FIGURE 1 Structure of the $[W_2(CO)_{10}(SC_6Cl_5)]^-$ anion

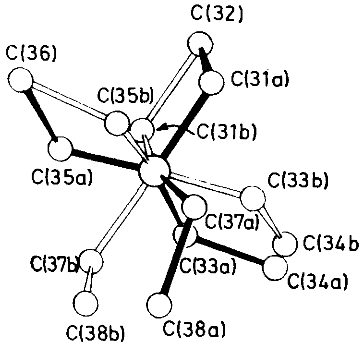

FIGURE 2 The two orientations of the tetraethylammonium cation

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

chlorophenyl group.* The shortest intramolecular non-bonded contacts are O(12) ··· O(22) 3.19, O(13) ··· O(23) 3.24, and Cl(5) ··· O(21) 3.27 Å (Table 3).

The i.r. spectrum of the compound in tetrahydrofuran solution shows six definite carbonyl-stretching frequencies (Table 5) appropriate to the bent W–S–W arrangement. Of the three symmetrical ways of arranging the carbonyl groups with respect to the W–S–W plane, two eclipsed (C_{2v}) and one staggered (C_s), the minimum number of carbonyl stretches arises for the C_{2v} structure in which none of the *cis* carbonyls lies in the W–S–W plane. In this case eight bands are predicted ($3A_1 + 2B_1 + 3B_2$). Accidental degeneracies should therefore occur at 1 941 and 1 876 cm^{-1} if this is the structure of the molecule in solution.

TABLE 5

Carbonyl-stretching bands (cm^{-1}) of thiophenolate-bridged metal pentacarbonyl complexes [a]

Complex	
$[N(PPh_3)_2][W_2(CO)_{10}(SC_6H_5)]$ [b]	2 055w, 2 040m, 1 973w (sh), 1 927vs, 1 908m, 1 869s
$[NEt_4][W_2(CO)_{10}(SC_6H_5)]$ [c]	2 066w, 2 054m, 1 968m (sh), 1 935.5vs, 1 908m, 1 869s
$[NEt_4][W_2(CO)_{10}(SC_6Cl_5)]$ [c]	2 073w, 2 062m, 1 976m (sh), 1 940vs, 1 915s, 1 876s

[a] Solvent in all cases was thf. [b] Ref. 3. [c] This work.

In spite of the large W(1)–S–W(2) angle, the bonds around the bridging sulphur atom are not coplanar, the S atom being 0.3 Å above the best (least-squares) plane through W(1), W(2), C(6), and S. In a binuclear thallium(III) complex the bridging thiophenolate ligand has approximately tetrahedral angles around the S atoms corresponding to sp^3 hybridisation of the sulphur-atom orbitals, whereas in contrast two analogous phenolate complexes have planar co-ordination around the bridging oxygen atoms attributable to sp^2 hybridisation resulting from the π bonding between the oxygen atom and the phenyl ring.[8] The distortion of the W(1)–S–W(2) angle in the present complex from the tetrahedral value to the very large value of 132.1(1)° may be mainly due to the necessity of minimising the contacts between the carbonyl groups on the two bridged tungsten atoms.

The W–S bond lengths are both 2.586(4) Å similar to the mean value of 2.58(1) Å for the W^0–S bonds in $[(\eta\text{-}C_5H_5)_2W^{IV}(\mu\text{-}SC_6H_5)_2W^0(CO)_4]$ the only other sulphur-bridged tungsten complex whose structure has been reported.[9] Although the W–S bond lengths in our complex (1) are shorter than the sum of the previously reported [10] covalent radii of 2.65 Å for these atoms, they are significantly longer than the W–S bond length of 2.543(2) Å found in the pentacarbonyl[trifluoro(monothiothenoyl)acetonato]tungstate(0) † complex anion (2) in which there was evidence of considerable π character in the W–S bond.[2] This may be due to the bridging role of the sulphur atom in (1) but is also consistent with reduced π character in the W–S bond.

The tungsten–carbonyl bond lengths in the bridged complex (1) are shorter than in (2). The *cis*-W–C bond lengths average 2.002(6) in (1) and 2.04(1) Å in (2) and the corresponding *trans*-W–C bonds average 1.935(2) and 1.97(1) Å respectively. This shortening of the W–C bond lengths in (1) is consistent with the reduced π character of the W–S bond which would enhance the metal-to-carbonyl back bonding.

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* We have recently synthesised the anions $[M(CO)_5(SH)]^-$ and $[(OC)_5M\text{–}SH\text{–}M(CO)_5]^-$, where M = Cr, Mo, or W. Any distortions in the latter species should arise primarily from carbonyl interactions.

† Pentacarbonyl[1,1,1-trifluoro-4(2-thienyl)-4-thioxobutan-2-onato-*S*]tungstate(0).

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