Syntheses, Crystal Structures and Spectroscopic Characterization of Some Confacial Bioctahedral Ditungsten(III) Complexes with Thioether Bridges: $[Cl_3W(\mu\text{-}Et_2S)_3WCl_3]\cdot MeCN$ and $[SMe_3][Cl_3W(\mu\text{-}Me_2S)_2(\mu\text{-}Cl)WCl_3]\cdot EtCN$ †

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Reduction of WCl_4 with 1 equivalent of Na/Hg in a refluxing thioether solution produced $[Cl_3W(\mu\text{-}L)_3WCl_3]$ [L = tetrahydrothiophene(tht) or Et_2S] in *ca.* 80% yields. Subsequent recrystallization from CH_2Cl_2 and MeCN gave $[Cl_3W(\mu\text{-}tht)_3WCl_3]$ **1** and $[Cl_3W(\mu\text{-}Et_2S)_3WCl_3]\cdot MeCN$ **2**, respectively. These complexes can also be prepared, in lower yields, by the same reactions carried out at ambient temperature or by refluxing WCl_4, thioether and Na/Hg in toluene solution. Analogous reactions with Me_2S yield exclusively $[SMe_3][Cl_3W(\mu\text{-}Me_2S)_2(\mu\text{-}Cl)WCl_3]$ which was recrystallized from EtCN to yield the monosolvate, **3**. The structures of **2** and **3** were determined by single-crystal X-ray diffraction, which showed that both complexes possess a confacial bioctahedral framework, with three Et_2S bridges in **2** and two Me_2S and one Cl in **3**. The W–W distances, 2.4990(9) in **2** and 2.4752(8) Å **3** are compatible with triple bond character, while the W–(μ-S) distances are relatively short. The structure of compound **1** was shown spectroscopically to be analogous to that of **2**. Proton NMR spectroscopic studies show that the $W(\mu\text{-thioether})_3W$ unit is resistant to attack by halide ions.

The chemistry of thioether-bridged binuclear complexes containing metal–metal bonds is of interest from several points of view. First, the metal–sulphur bond lengths observed for thioethers in bridging situations have been found by several groups of workers to be shorter than those between metals and terminally bound R_2S ligands.[1–4] This is in contrast to halides, for example, for which the opposite trend in bond lengths is observed. This would suggest that thioethers, like the isoelectronic diarylphosphide ions, might be convenient bridging ligands to employ in situations where metal–metal bonding is sought. Their short M–S bonds should facilitate close metal–metal contacts. This expectation was confirmed in the structures of $[(Me_2S)Cl_2Mo(\mu\text{-}Me_2S)(\mu\text{-}Cl)_2MoCl_2(Me_2S)]$ and the anion $[(Me_2S)Cl_2Mo(\mu\text{-}Cl)_3MoCl_2(Me_2S)]^-$, in which the Mo–Mo distances are 2.462(2) and 2.746(9) Å respectively.[2] Whereas the former is diamagnetic, the latter is antiferromagnetic. More recently we have prepared and obtained crystal structures of $[(tht)_2ClMo(\mu\text{-}Cl)_3MoCl_2(tht)]$ (tht = tetrahydrothiophene) and $[(tht)Cl_2Mo(\mu\text{-}Cl)_2(\mu\text{-}tht)MoCl_2(tht)]$ which display comparable behaviour, in that the former has antiferromagnetic properties and a longer Mo–Mo bond while the latter has a strong Mo≡Mo triple bond and is diamagnetic.[5] The second feature of interest in thioether-bridged complexes is that in spite of the evidence for the strength of the M–(μ-S) bonds, complexes like $[(tht)Cl_2Mo(\mu\text{-}Cl)_2(\mu\text{-}tht)MoCl_2(tht)]$ have been shown to react with certain small molecules. Thus the niobium and tantalum analogues of $[(Me_2S)Cl_2Mo(\mu\text{-}Me_2S)(\mu\text{-}Cl)_2MoCl_2(Me_2S)]$ and $[(tht)Cl_2Mo(\mu\text{-}Cl)_2(\mu\text{-}tht)MoCl_2(tht)]$, first reported by McCarley and wo-workers,[1] were shown by Cotton and Hall[6] to be reactive towards alkynes, a process which appears to involve the displacement of the bridging thioether. Further reaction leads, in some cases, to polymerization of the alkyne. The isolation by Green and co-workers[7] of a dimetallatetrahedrane from the reaction of the $[W_2Cl_7(thf)_2]$ anion with but-2-yne is also noteworthy, since the alkyne displaces a μ-Cl ligand, leaving two terminally bound tetrahydrofuran (thf) molecules. With excess of alkyne, and in the presence of free Cl^- ion in solution, the anionic complex $[(MeC_2Me)Cl_2W(\mu\text{-}Cl)_3WCl_2(MeC_2Me)]^-$ was isolated. In each of these complexes the W≡W structural feature remained intact. The thioether complexes of ditungsten(III) halides have not been reported, and it was therefore of interest to us to follow up our earlier work on the reduction of $[WCl_4(Me_2S)_2]$ with triethylsilane[8] by examining the reactions between WCl_4 and Na/Hg in the presence of an excess of thioether. This preparative procedure has been used extensively by various workers[1,2,9,10] to enter the realm of low-oxidation-state metal halide chemistry. In this paper we report the preparations of two new complexes of general formula $Cl_3W(\mu\text{-thioether})_3WCl_3$, but note that the product with Me_2S is different and involves formation of the trimethylsulphonium cation.

Experimental

General Procedures and Techniques.—All manipulations were carried out using standard glove-box and double-manifold vacuum-line techniques under an atmosphere of dry nitrogen. Acetonitrile, diethyl ether, methyl and ethyl sulphide, and tetrahydrothiophene were dried over calcium hydride then distilled under nitrogen before use. Dichloromethane was dried consecutively over phosphorus(V) oxide and calcium hydride before final distillation and degassing. The compound WCl_4 was prepared by a literature method.[11] Elemental analyses (C,H,N) were performed either by the University of Calgary Department of Chemistry Analytical Services Laboratory, or by Canadian Microanalytical Services, Vancouver, BC. Tungsten

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† Tris(μ-diethyl sulphide)-bis[trichlorotungsten(III)]–acetonitrile(1/1) and trimethylsulphonium μ-chloro-bis(μ-dimethyl sulphide)-bis[trichlorotungstate(III)]–propionitrile (1/1).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

analyses were performed in-house as previously described.[12] Proton NMR spectra were obtained using a Bruker ACE-200 spectrometer, IR spectra as Nujol mulls between CsI plates using either a Nicolet 8000 FT or a Perkin-Elmer 467 grating spectrometer and UV–VIS spectra using a Varian 219 spectrophotometer in the range 200–800 nm. Electrochemical measurements were carried out as described in detail by Hinman and co-workers,[13] using a platinum wire and saturated calomel electrode (SCE) as working and reference electrodes. Solutions were prepared in a dry-box, using previously dried and degassed dichloromethane. Argon was bubbled through the solutions immediately after preparation, to ensure complete removal of any traces of oxygen.

Preparations.—$[Cl_3W(\mu\text{-tht})_3WCl_3]$, **1** *Method* (*i*). The compound WCl_4 (4.0 g, 0.0123 mol), Na/Hg, (0.4%, 75 g) and tht (60 cm^3) were placed in a Schlenk tube and heated to the boiling point of the tht and stirred vigorously for 20 min. After cooling to room temperature, the supernatant was decanted and the residue was washed with ether. Extraction and subsequent recrystallization from dichloromethane gave dark red crystals. Yield: 4.2 g, 81% (Found: C, 17.1; H, 2.75; W, 43.3. Calc. for $C_{12}H_{24}Cl_6S_4W_2$: C, 17.1; H, 2.85; W, 43.5%). IR spectrum (Nujol mull, CsI plates, 1500–300 cm^{-1}): 1460s (Nujol), 1439(sh), 1413w, 1377s (Nujol), 1321w, 1302m, 1257w, 1244w, 1189w, 1128s, 1076w, 1068w, 1031w, 952ms, 881s, 873w, 796s, 725w, 672w and 311s (br). ^{1}H NMR (CD_2Cl_2): δ 3.80 (m, 4 H) and 2.45 (m, 4 H).

Method (*ii*). The same reactants and quantities were used, but the reaction mixture was stirred at 22 °C for 24 h. Yield, 3.0 g, 58%. The product was shown by its ^{1}H NMR spectrum to be the same as that from method (*i*).

$[Cl_3W(\mu\text{-}Et_2S)_3WCl_3]\cdot MeCN$ **2**. *Method* (*i*). A mixture of WCl_4 (4 g, 0.01228 mol), Na/Hg (0.4%, 75 g), and Et_2S (60 cm^3) was stirred at reflux temperature in a Schlenk tube for 40 min. The resulting red-brown solid was separated from the supernatant diethyl sulphide solution and extracted with CH_2Cl_2 until no further red colour was discerned in the extractant. The CH_2Cl_2 extracts were then combined and evaporated to dryness to yield 4.4 g of a red crystalline product {77% yield of $[Cl_3W(\mu\text{-}Et_2S)_3WCl_3]\cdot CH_2Cl_2$, based on WCl_4}. Recrystallization from MeCN yielded crystals of high enough quality for an X-ray study, of the acetonitrile solvate, $[Cl_3W(\mu\text{-}Et_2S)_3WCl_3]\cdot MeCN$ (Found: C, 18.85; H, 3.60; W, 41.3. Calc. for $C_{14}H_{33}Cl_6NS_3W_2$: C, 18.85; H, 3.75; W, 41.2%). IR spectrum (CsI plates, Nujol mull, 1500–250 cm^{-1}): 1460s (Nujol), 1448 (sh), 1404ms, 1378s (Nujol), 1268ms, 1251w, 1228w, 1071s, 1046w, 1022w, 976m, 776ms, 766ms, 745ms, 724w, 302vs and 290vs. ^{1}H NMR ($CDCl_3$): δ 3.73 (q, J = 7.4 2 H) and 1.86 (t, J = 7.4 Hz, 3 H).

Method (*ii*). With the same quantities of starting materials as in (*i*) the reaction mixture was stirred at 22 °C for 72 h. Upon working up the product as in (*i*) a 9% yield of the MeCN solvate of **2** was obtained.

Method (*iii*). The compound WCl_4 (2.0 g, 0.0061 mol), Na/Hg (0.4%, 38 g), Et_2S (1.3 cm^3), and toluene (50 cm^3) were stirred at reflux temperature in a Schlenk tube for 24 h. Employing the same isolation procedure as in (*i*) above gave 1.6 g of compound **2** (56% yield).

$[SMe_3][Cl_3W(\mu\text{-}Me_2S)_2(\mu\text{-}Cl)WCl_3]\cdot EtCN$ **3**. *Method* (*i*). The compound WCl_4 (4.0 g, 0.0128 mol), Na/Hg (0.4%, 76 g), and dimethyl sulphide (70 cm^3) were introduced into a pressure bottle which was flushed with nitrogen and sealed. The contents were stirred and heated to 100 °C for 30 min. The bottle was cooled to room temperature and the Me_2S solution was separated from the residual solid. This was washed with diethyl ether and then extracted with acetonitrile (2 × 150 cm^3). Pumping this solution to dryness gave red crystals of $[SMe_3][Cl_3W(\mu\text{-}Me_2S)_2(\mu\text{-}Cl)WCl_3]\cdot MeCN$. Yield: 3.6 g, 68% based on WCl_4. Recrystallization from propionitrile yielded high-quality crystals of the EtCN solvate, one of which was used for an X-ray study (Found: C, 13.95; H, 3.00; N, 1.80; W, 42.35. $C_{10}H_{26}Cl_7NS_3W_2$ requires C, 13.75; H, 3.00; N, 1.60; W, 42.15%). IR spectrum (2500–250 cm^{-1}, Nujol mull, CsI plates): 2204s, 1459s (Nujol), 1414ms, 1404m (sh), 1377s (Nujol), 1353w, 1315m, 1296w, 1094w, 1075w, 1049ms, 1023s, 972w, 943w, 918w, 786w, 722w, 303vs and 286vs. ^{1}H NMR (CD_3CN): δ 3.47 (s, 6 H), 3.07 (s, 6 H), 2.80 (s, 9 H), 2.37 (q) and 1.21 (t).

Method (*ii*). Using the same reagents and quantities as in (*i*), the mixture was heated, with vigorous stirring, to the boiling point of the dimethyl sulphide at atmospheric pressure, rather than in a sealed system. The same product resulted as in (*i*), and in similar yield (3.3 g, 62%).

Method (*iii*). Even when the reaction temperature was restricted to 22 °C, using otherwise identical conditions to those in (*ii*), the same product, $[SMe_3][Cl_3W(\mu\text{-}Me_2S)_2(\mu\text{-}Cl)WCl_3]\cdot MeCN$, was produced, although in somewhat lower yield (2.6 g, 49%). This product was recrystallized from EtCN as in (*i*).

X-Ray Crystal Structures of Compounds **2** *and* **3**.—Crystals of the two compounds were mounted on glass fibres, and then on an Enraf-Nonius CAD4 diffractometer. Unit-cell parameters were derived from the setting angles of 25 automatically centred reflections in the range $7.39 < \theta < 15.74°$, **2** and $8.38 < \theta < 13.99°$, **3**. Intensities were recorded in the ω–2θ scan mode with graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å) as previously described in detail.[14] The data were corrected for absorption using the program DIFABS,[15] after isotropic refinement. The structures were solved by locating the W atoms in an E map with phases derived from symbolic addition.[16] The remaining non-hydrogen atoms were located in difference maps after refining scale and thermal parameters. Neutral atom scattering factors were used with anomalous dispersion corrections applied.[17] No corrections for extinction were made. For the final, full-matrix, refinement cycles a weighting scheme with $w = 1/\sigma^2(F)$ was used. All calculations were carried out at Montana State University using the program package XTAL2.6,[18] on a micro Vax cluster.

Crystal data for $[Cl_3W(\mu\text{-}Et_2S)_3WCl_3]\cdot MeCN$ **2**. Opaque, dark red blocks, $C_{14}H_{33}Cl_6NS_3W_2$, M = 891.99, orthorhomhombic, space group *Pbcb* (equivalent to no. 54), a = 11.644(2), b = 14.806(2), c = 31.861(4) Å, U = 5492.99 Å^3, $F(000)$ = 3376, μ(Mo-Kα) = 93.04 cm^{-1}, D_m = 2.3(1) g cm^{-3}, Z = 8, D_c = 2.154 g cm^{-3}.

Crystal dimensions: 0.41 × 0.30 × 0.28 mm. Total data recorded 9523, unique 7988, observed [$F > 3.0\sigma(F)$] 4851 [sin θ/λ (max.) = 0.7033 Å^{-1}]. Number of parameters refined 235. Final R = 0.066, $R' = \Sigma w(||F_o| - |F_c||)/\Sigma w|F_o|$ = 0.048. Hydrogen atoms could not be reliably located, but they were calculated in idealized positions with fixed thermal parameters which were not refined. Final fractional atomic coordinates are given in Table 1.

Crystal data for $[SMe_3][Cl_3W(\mu\text{-}Me_2S)_2(\mu\text{-}Cl)WCl_3]\cdot EtCN$ **3**. Dark red, transparent blocks, $C_{10}H_{26}Cl_7NS_3W_2$, M = 872.35, monoclinic, space group $P2_1/c$, a = 11.546(2), b = 13.423(3), c = 17.462(4) Å, β = 107.38(2)°, U = 2582.55 Å^3, $F(000)$ = 1632, μ(Mo-Kα) = 99.89 cm^{-1}, D_m = 2.23(3), Z = 4, D_c = 2.244 g cm^{-3}.

Crystal dimensions: 0.35 × 0.35 × 0.38 mm. Total data recorded 8123, unique 7505, observed [$F > 3.0\sigma(F)$] 6072 [sin θ/λ (max) = 0.7032 Å^{-1}]. Number of parameters refined 208. Final R = 0.052, R' = 0.042. Hydrogen atoms could not be reliably located and were not included in any calculations. Final fractional atomic coordinates are given in Table 2.

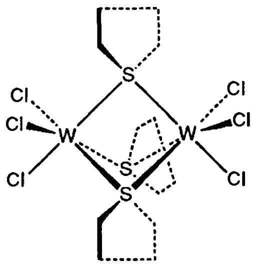
Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates for compound **2**, thermal parameters for **2** and **3**, and remaining bond lengths and angles.

Results and Discussion

X-Ray Structures.—The important bond length and angle

Table 1 Fractional coordinates of atoms with standard deviations for complex **2**

Atom	*x*	*y*	*z*
W(1)	0.151 23(5)	0.305 13(3)	0.140 65(2)
W(2)	0.347 86(5)	0.237 65(3)	0.138 50(2)
S(1)	0.256 0(3)	0.273 2(3)	0.204 19(9)
C(11)	0.313(1)	0.361 0(9)	0.237 2(4)
C(12)	0.226(2)	0.394(1)	0.270 8(5)
C(13)	0.207(1)	0.190(1)	0.241 1(4)
C(14)	0.294(2)	0.159(1)	0.271 8(5)
S(2)	0.306 0(3)	0.380 7(2)	0.106 1(1)
C(21)	0.366(1)	0.486 1(9)	0.125 8(4)
C(22)	0.298(2)	0.566(1)	0.109 4(5)
C(23)	0.314(2)	0.394(1)	0.049 9(4)
C(24)	0.432(2)	0.419(1)	0.032 4(5)
S(3)	0.185 3(3)	0.158 4(2)	0.110 4(1)
C(31)	0.166(2)	0.136(1)	0.055 1(4)
C(32)	0.044(2)	0.106(1)	0.041 1(6)
C(33)	0.126(1)	0.057 1(9)	0.134 9(4)
C(34)	0.191(1)	−0.029(1)	0.119 7(5)
Cl(1)	0.043 5(3)	0.342 0(3)	0.079 0(1)
Cl(2)	−0.014 3(4)	0.239 3(3)	0.172 4(1)
Cl(3)	0.105 0(3)	0.446 5(2)	0.171 7(1)
Cl(4)	0.441 1(3)	0.194 9(3)	0.074 7(1)
Cl(5)	0.517 2(4)	0.309 5(3)	0.164 3(1)
Cl(6)	0.406 5(3)	0.098 6(2)	0.170 9(1)
C(2)	0.741(2)	0.288(1)	0.060 4(9)
C(1)	0.750(2)	0.358(1)	0.031 4(5)
N(1)	0.756(2)	0.411(1)	0.007 9(5)



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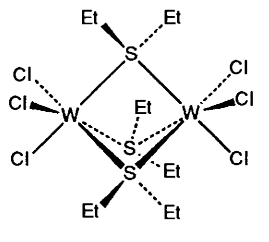

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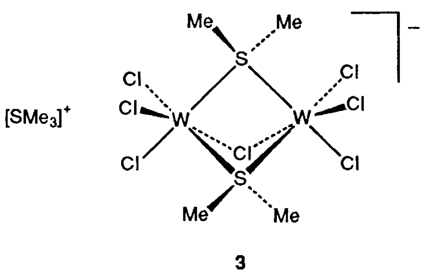

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Table 2 Fractional coordinates of atoms with standard deviations for compound **3**

Atom	*x*	*y*	*z*
W(1)	0.810 96(4)	0.737 75(3)	0.090 82(3)
W(2)	0.643 39(4)	0.792 15(3)	0.142 36(2)
S(1)	0.843 5(2)	0.768 1(2)	0.229 8(2)
S(2)	0.698 4(2)	0.885 0(2)	0.041 5(2)
Cl(3)	0.629 7(2)	0.629 4(2)	0.071 5(2)
Cl(11)	0.791 0(3)	0.696 5(2)	−0.045 5(2)
Cl(12)	0.926 0(3)	0.587 0(2)	0.131 3(2)
Cl(13)	0.989 0(3)	0.833 9(2)	0.102 7(2)
Cl(21)	0.436 5(2)	0.813 3(2)	0.062 7(2)
Cl(22)	0.575 6(3)	0.701 2(2)	0.238 3(2)
Cl(23)	0.640 5(3)	0.946 8(2)	0.208 7(2)
C(11)	0.885(1)	0.667 7(8)	0.304 5(6)
C(12)	0.938 2(9)	0.870 2(8)	0.286 1(7)
C(21)	0.770(1)	1.008 3(7)	0.059 6(7)
C(22)	0.599(1)	0.890(1)	−0.060 8(6)
S(3)	0.205 2(3)	0.565 1(2)	0.098 8(2)
C(31)	0.240(1)	0.662 1(8)	0.172 5(6)
C(32)	0.132(1)	0.631(1)	0.007 0(7)
C(33)	0.352(1)	0.538 0(9)	0.088 2(7)
N(1)	0.781(2)	0.236(1)	0.147(1)
C(1)	0.708(2)	0.296(2)	0.154(1)
C(2)	0.627(2)	0.369(2)	0.170(2)
C(3)	0.670(2)	0.422(1)	0.240(1)

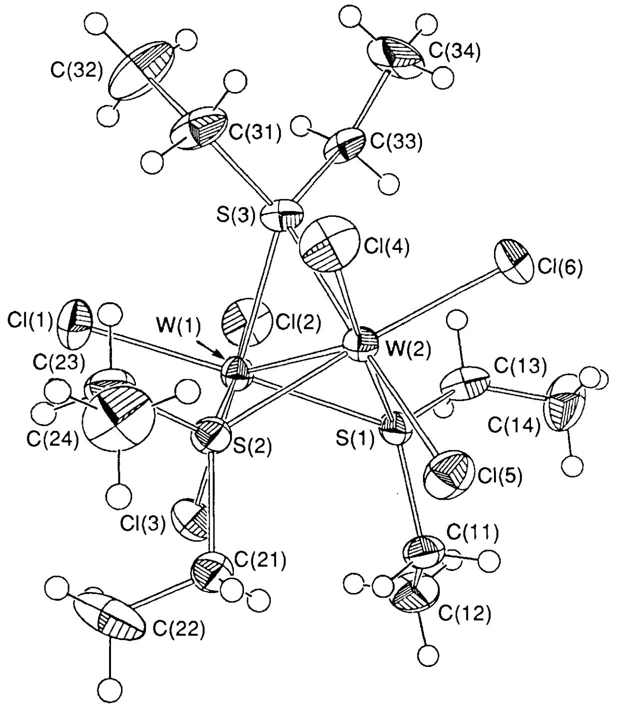

Fig. 1 Structure of complex **2**

data for compounds **2** and **3** are presented in Tables 3 and 4 respectively, with the atom numbering schemes shown in the ORTEP plots in Figs. 1 and 2 respectively. The most notable feature of both structures is that they possess the commonly encountered confacial bioctahedral geometry which pervades the chemistry of bis[tungsten(III)] complexes. The symmetric nature of **2**, as detected by ^{1}H NMR spectroscopy, is retained in the solid state, although the molecule deviates from having pure three-fold symmetry. The W–W bond length, 2.4990(9) Å, is almost 0.1 Å longer than that observed in the $[W_2Cl_9]^{3-}$ anion (2.409 Å),[19] but the other structural indicators suggest that there is still very strong metal–metal interaction.[20] Most significantly, the angles subtended at the μ-S atoms are much smaller (*ca.* 62.5°) than the 70.5° value required for a pure confacial bioctahedral structure with no metal–metal interaction. Concomitant expansion of the S–W–S bond angles (from 90°) is observed. The complex, and its tht analogue, is diamagnetic as expected for a strongly spin-coupled system. Although **1** and **2** are the first neutral complexes of this symmetric structure to be reported, the anions $[M_2Cl_6(tht)_3]^{2-}$ (M = Nb or Ta) were recently reported by Cotton *et al.*[9] These anions are isoelectronic with **1** and **2**, hence it is of interest to compare their structural parameters with those of **2**. The metal–metal bond distances in the anions spanned the narrow range 2.607–2.632 Å, and the M–S–M bond angles averaged to 65.7°. As in the structures of **2** and **3** the M–S bond lengths are relatively short, a commonly encountered feature in the chemistry of bridging thioether complexes. A Fenske-Hall calculation by Cotton on these systems showed that there is

Table 3 Selected bond distances (Å) and angles (°) for compound **2**

W(1)–Cl(3)	2.376(4)	W(2)–Cl(5)	2.387(4)	S(1)–C(11)	1.80(1)	S(3)–C(31)	1.80(1)
W(1)–Cl(2)	2.384(4)	W(2)–Cl(4)	2.390(4)	C(11)–C(12)	1.56(2)	S(3)–C(33)	1.82(1)
W(1)–S(2)	2.389(4)	W(2)–S(3)	2.401(4)	C(13)–C(14)	1.48(2)	C(31)–C(32)	1.56(2)
W(1)–Cl(1)	2.393(4)	W(2)–Cl(6)	2.402(4)	S(2)–C(23)	1.81(1)	C(33)–C(34)	1.56(2)
W(1)–S(3)	2.410(3)	W(2)–S(2)	2.405(4)	S(2)–C(21)	1.82(1)	C(2)–C(1)	1.40(3)
W(1)–S(1)	2.410(3)	W(2)–S(1)	2.409(3)	C(21)–C(22)	1.51(2)	C(1)–N(1)	1.09(3)
W(1)–W(2)	2.4990(9)	S(1)–C(13)	1.79(2)	C(23)–C(24)	1.53(2)		
Cl(3)–W(1)–Cl(2)	90.1(1)	Cl(1)–W(1)–S(3)	87.9(1)	C(23)–S(2)–C(21)	103.1(7)	Cl(4)–W(2)–S(2)	87.8(1)
Cl(3)–W(1)–S(2)	87.1(1)	S(3)–W(2)–S(1)	94.6(1)	C(23)–S(2)–W(1)	123.2(6)	Cl(4)–W(2)–S(1)	177.1(1)
Cl(3)–W(1)–Cl(1)	91.2(1)	S(3)–W(2)–W(1)	58.89(9)	Cl(1)–W(1)–S(1)	177.6(1)	Cl(4)–W(2)–W(1)	123.1(1)
Cl(3)–W(1)–S(3)	176.2(1)	Cl(6)–W(2)–S(2)	175.1(1)	Cl(1)–W(1)–W(2)	123.3(1)	S(3)–W(2)–Cl(6)	88.0(1)
Cl(3)–W(1)–S(1)	86.5(1)	Cl(6)–W(2)–S(1)	86.6(1)	S(3)–W(1)–S(1)	94.4(1)	S(3)–W(2)–S(2)	96.4(1)
Cl(3)–W(1)–W(2)	124.8(1)	Cl(6)–W(2)–W(1)	126.2(1)	S(3)–W(1)–W(2)	58.52(9)	C(23)–S(2)–W(2)	120.8(5)
Cl(2)–W(1)–S(2)	175.0(1)	S(2)–W(2)–S(1)	95.2(1)	S(1)–W(1)–W(2)	58.74(9)	C(21)–S(2)–W(1)	122.1(5)
Cl(2)–W(1)–Cl(1)	91.0(1)	S(2)–W(2)–W(1)	58.28(9)	Cl(5)–W(2)–Cl(4)	92.0(1)	C(21)–S(2)–W(2)	122.0(5)
Cl(2)–W(1)–S(3)	86.2(1)	S(1)–W(2)–W(1)	58.79(9)	Cl(5)–W(2)–S(3)	176.3(1)	W(1)–S(2)–W(2)	62.83(9)
Cl(2)–W(1)–S(1)	88.5(1)	C(13)–S(1)–C(11)	103.2(7)	Cl(5)–W(2)–Cl(6)	90.0(1)	C(31)–S(3)–C(33)	102.7(7)
Cl(2)–W(1)–W(2)	126.1(1)	C(13)–S(1)–W(2)	124.1(5)	Cl(5)–W(2)–S(2)	85.6(1)	C(31)–S(3)–W(2)	123.5(6)
S(2)–W(1)–Cl(1)	84.9(1)	C(13)–S(1)–W(1)	121.7(5)	Cl(5)–W(2)–S(1)	88.3(1)	C(31)–S(3)–W(1)	122.4(5)
S(2)–W(1)–S(3)	96.5(1)	C(11)–S(1)–W(2)	120.1(5)	Cl(5)–W(2)–W(1)	124.7(1)	C(33)–S(3)–W(2)	122.6(5)
S(2)–W(1)–S(1)	95.5(1)	C(11)–S(1)–W(1)	122.4(5)	Cl(4)–W(2)–S(3)	84.9(1)	C(33)–S(3)–W(1)	120.5(5)
S(2)–W(1)–W(2)	58.90(9)	W(2)–S(1)–W(1)	62.47(7)	Cl(4)–W(2)–Cl(6)	90.5(1)	W(2)–S(3)–W(1)	62.59(9)

Table 4 Selected bond distances (Å) and angles (°) for compound **3**

W(1)–S(1)	2.378(3)	W(1)–Cl(3)	2.487(3)	S(1)–C(11)	1.84(1)	S(3)–C(33)	1.79(1)
W(1)–S(2)	2.381(3)	W(2)–S(1)	2.380(2)	S(1)–C(12)	1.84(1)	S(3)–C(32)	1.81(1)
W(1)–Cl(13)	2.383(3)	W(2)–Cl(23)	2.382(3)	S(2)–C(22)	1.81(1)	N(1)–C(1)	1.20(3)
W(1)–Cl(11)	2.387(3)	W(2)–Cl(22)	2.387(3)	S(2)–C(21)	1.83(1)	C(1)–C(2)	1.44(3)
W(1)–Cl(12)	2.407(3)	W(2)–S(2)	2.393(3)	S(3)–C(31)	1.79(1)	C(2)–C(3)	1.37(3)
W(1)–W(2)	2.4752(8)	W(2)–Cl(2)	2.395(2)				
S(1)–W(1)–S(2)	97.5(1)	Cl(11)–W(1)–W(2)	125.30(8)	S(2)–W(2)–W(1)	58.52(7)	S(1)–W(2)–Cl(23)	87.60(9)
S(1)–W(1)–Cl(11)	175.2(1)	Cl(11)–W(1)–Cl(3)	84.4(1)	C(12)–S(1)–C(11)	100.4(5)	S(1)–W(2)–Cl(22)	86.52(9)
S(1)–W(1)–Cl(12)	86.5(1)	Cl(12)–W(1)–Cl(13)	92.5(1)	C(12)–S(1)–W(2)	123.3(3)	S(1)–W(2)–Cl(21)	175.7(1)
S(1)–W(1)–Cl(13)	87.1(1)	Cl(12)–W(1)–W(2)	124.32(9)	C(12)–S(1)–W(1)	124.0(4)	S(1)–W(2)–S(2)	97.05(9)
S(1)–W(1)–W(2)	58.71(6)	Cl(12)–W(1)–Cl(3)	85.20(9)	C(11)–S(1)–W(2)	123.4(4)	S(1)–W(2)–W(1)	58.60(7)
S(1)–W(1)–Cl(3)	96.23(9)	Cl(23)–W(2)–Cl(21)	91.3(1)	C(11)–S(1)–W(1)	121.8(4)	Cl(23)–W(2)–Cl(22)	92.8(1)
S(2)–W(1)–Cl(11)	87.3(1)	Cl(23)–W(2)–S(2)	87.1(1)	W(2)–S(1)–W(1)	62.70(6)	C(21)–S(2)–W(1)	121.2(3)
S(2)–W(1)–Cl(12)	175.9(1)	Cl(23)–W(2)–W(1)	124.04(8)	C(22)–S(2)–C(21)	104.8(6)	C(21)–S(2)–W(2)	123.2(4)
S(2)–W(1)–Cl(13)	86.9(1)	Cl(22)–W(2)–Cl(21)	89.4(1)	C(22)–S(2)–W(1)	120.3(4)	W(1)–S(2)–W(2)	62.46(7)
S(2)–W(1)–W(2)	59.02(8)	Cl(22)–W(2)–S(2)	176.42(9)	C(22)–S(2)–W(2)	121.1(4)	C(31)–S(3)–C(33)	101.9(6)
S(2)–W(1)–Cl(3)	95.17(9)	Cl(22)–W(2)–W(1)	124.08(7)	Cl(13)–W(1)–W(2)	123.79(8)	C(31)–S(3)–C(32)	103.0(6)
Cl(11)–W(1)–Cl(12)	89.2(1)	Cl(21)–W(2)–S(2)	87.1(1)	Cl(13)–W(1)–Cl(3)	175.8(1)	C(33)–S(3)–C(32)	102.5(6)
Cl(11)–W(1)–Cl(13)	92.1(1)	Cl(21)–W(2)–W(1)	125.16(8)	W(2)–W(1)–Cl(3)	60.29(7)		

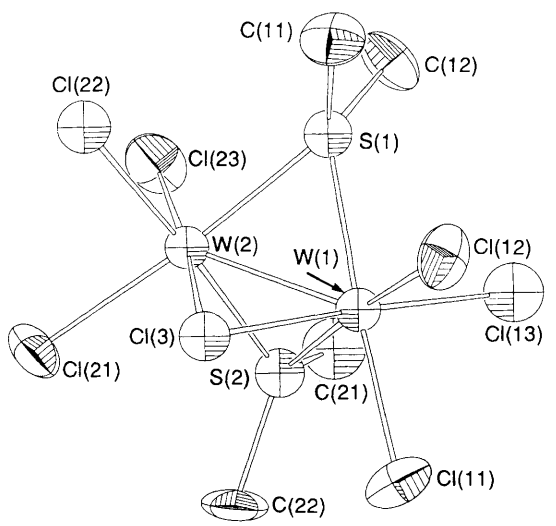

Fig. 2 Structure of the anion of compound **3**

essentially metal–metal triple bonding. As has frequently been pointed out, however, the presence of the three bridging ligands precludes assigning exact bond orders to systems of this sort.[21]

Syntheses.—The synthetic chemistry for the reduction of WCl_4 by Na/Hg in the presence of thioether is summarized in equations (1)–(3). It is noteworthy that the tungsten starting material appears to be critical in determining the products, since

$$WCl_4 + Na/Hg \xrightarrow[(b)\,CH_2Cl_2]{(a)\,tht} [Cl_3W(\mu\text{-tht})_3WCl_3] \quad (1)$$

1

$$WCl_4 + Na/Hg \xrightarrow[(b)\,MeCN]{(a)\,Et_2S} [Cl_3W(\mu\text{-}Et_2S)_3WCl_3]\cdot MeCN \quad (2)$$

2

$$WCl_4 + Na/Hg \xrightarrow[\substack{(b)\,MeCN\\(c)\,EtCN}]{(a)\,Me_2S} [SMe_3][Cl_3W(\mu\text{-}Me_2S)_2(\mu\text{-}Cl)WCl_3]\cdot EtCN \quad (3)$$

3

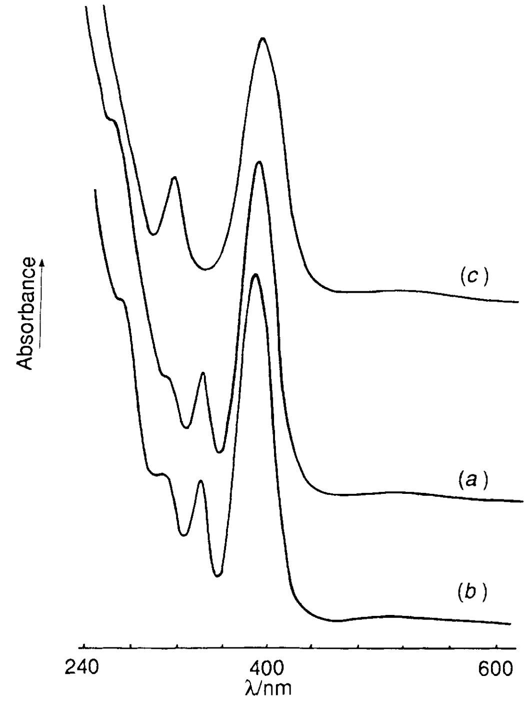

Fig. 3 Electronic absorption spectra of compounds **1** (*a*) and **2** (*b*) in dichloromethane and **3** (*c*) in acetonitrile solution

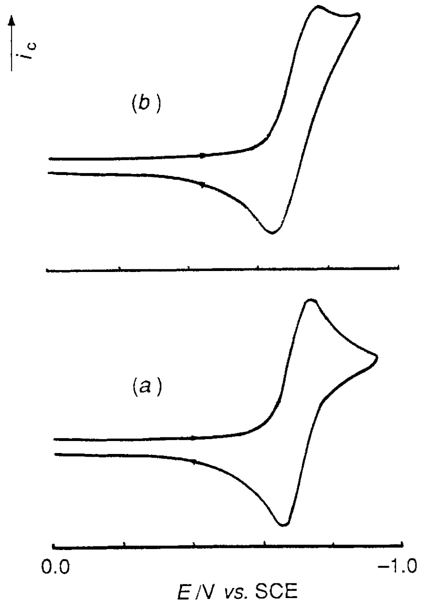

Fig. 4 Cyclic voltammograms of compounds **1** (*a*) and **2** (*b*) in dichloromethane *vs.* SCE (scan rate = 100 mV s^{-1})

Table 5 Electronic absorption data for selected d^3–d^3 confacial bioctahedral complexes

Compound	$\lambda_{max.}$/nm	ν/cm^{-1}	ε/dm^3 mol^{-1} cm^{-1}
$[Cl_3W(\mu\text{-tht})_3WCl_3]$[a]	520	19 200	140
	390	25 600	11 600
	341	29 300	4 380
	311(sh)	32 100	4 210
	260(sh)	38 500	13 160
$[Cl_3W(\mu\text{-SEt}_2)_3WCl_3]$[a]	520	19 200	200
	395	25 300	8 880
	342	29 300	4 800
	311(sh)	32 500	5 100
	272(sh)	36 800	11 100
$[SMe_3][Cl_3W(\mu\text{-Me}_2S)_2(\mu\text{-Cl})WCl_3]$[a]	530	18 900	360
	395	25 300	8 880
	319	31 300	4 060
$K_3[Cl_3W(\mu\text{-Cl})_3WCl_3]$[b]	758	13 190	50
	628	15 900	160
	457	21 900	4 730
	380(sh)	26 300	1 200
$Na[W_2Cl_7(thf)_2]$[c]	754	13 300	150
	634	15 800	290
	450	22 200	3 800
$Na_2[Nb_2Cl_6(tht)_3]$[d]	535w	18 700	
	410s	24 400	

[a] This work. [b] Ref. 23. [c] Ref. 10. [d] Ref. 9.

reduction of $[WCl_4(Me_2S)_2]$ under the same conditions failed to produce the same reaction products. The isomers reported here for **1** and **2** were the only ones detected, there being no evidence for analogues of the molybdenum species $[(Me_2S)Cl_2Mo(\mu\text{-Me}_2S)(\mu\text{-Cl})_2MoCl_2(Me_2S)]$ **4**, $[(Me_2S)Cl_2Mo(\mu\text{-Cl})_3MoCl(MeS)_2]$ **5**, $[(tht)_2ClMo(\mu\text{-Cl})_3MoCl_2(tht)]$ **6** and $[(tht)Cl_2Mo(\mu\text{-Cl})_2(\mu\text{-tht})MoCl_2(tht)]$ **7**. A subtle difference between reaction (**1**) and (**2**) is that at room temperature the production of compound **1** is faster, and gives a higher yield, than that of **2**. The symmetric nature of the tris(thioether) bridging region in the structures of **1** and **2** was revealed in the ^1H NMR spectra, wherein only one environment was detected for the analogous halves of the ligating molecules (*i.e.* all Et groups are equivalent in **2**). The reproducibility of the syntheses of **1** and **2** made the production of the sulphonium salt **3** totally unexpected. Despite numerous attempts to change the course of the reaction by varying the conditions, **3** was the only product to be isolated. The anion has been reported by us previously,[22] from the reaction of either the neutral complex $[Cl_3W(\mu\text{-Me}_2S)_2(\mu\text{-H})WCl_2(Me_2S)]$ **8**, or its derived anion $[Cl_3W(\mu\text{-Me}_2S)_2(\mu\text{-H})WCl_3]^-$ **9**, with a chlorocarbon at elevated temperature. In the specific case of the reaction between **8** and $PhCH_2Cl$ the product is $[SMe_2(CH_2Ph)][Cl_3W(\mu\text{-Me}_2S)_2(\mu\text{-Cl})WCl_3]$, and hence is extremely similar to **3**. The proposed mechanism for its formation was the exchange of μ-H by Cl, producing toluene, and the alkylation of terminally co-ordinated Me_2S to give the sulphonium cation. The precise mechanism by which **3** is produced is more problematical. We have observed previously[8] that terminal and bridging Me_2S exchange rapidly at room temperature in compound **8** and also that under more vigorous conditions C–S bond cleavage and reforming can occur. For example, direct reaction between Me_2S and WCl_6 results[12] in the formation of $[SMe_3]_2[WCl_6]$. However, for the activation of the C–S bond towards cleavage, an oxidizing metal centre is usually required, the converse of the conditions of our reaction. The dealkylated thioether, *i.e.* MeS^-, might be expected to be involved in the redox reaction, through the reductive elimination of Me_2S_2, but this product has not been identified in the case of reaction (3). It may be of importance that $[WCl_4(Me_2S)_2]$ cannot replace WCl_4 as the starting material for the synthesis of **3** and hence is probably not an intermediate in the reaction. Proton NMR spectra of the reaction solution contained a large number of weak peaks in the region normally associated with co-ordinated MeS^-, but we were unable to isolate any products containing this species.

Electronic Structure and Physical and Chemical Properties.— Based on the calculations reported by Cotton *et al.*,[9] and related earlier reports,[21] the frontier orbitals of $M_2Cl_6(\mu\text{-R}_2S)_3$ are: (I) a_1' (σ bonding), e′ (δ/π bonding), e″ (δ/π antibonding), a_2'' (σ antibonding) (all deriving from the t_{2g} metal orbitals); (II) e′(π/δ bonding), e″(π/δ antibonding) (both deriving from the metal e_g orbitals, which being M–L antibonding in character, are generally higher in energy than the orbitals derived from the t_{2g} set). The exact interpretation of the spectra of compounds of this type remains doubtful, since the higher-energy transitions are usually obscured by charge-transfer bands. In addition, the relative separations of the t_{2g} and e_g derived subsets will be dependent upon the bridging and terminal ligand sets, as well as the specific metal atoms in the complex. The spectra of compounds **1**–**3** are shown in Fig. 3, and the data compared with related data in Table 5. By comparison with the assignments of Trogler[23] for the $[W_2Cl_9]^{3-}$ ion, and Cotton *et al.*[9] for the $[Nb_2Cl_6(tht)_3]^{2-}$ ion, the most intense absorption band in the visible region of the spectra, at 25 300 cm^{-1}, of **1** and **2** might be the $a_1' \longrightarrow a_2''$ transition, with the weaker absorption at 19 200 cm^{-1} assigned to $a_1' \longrightarrow e'(e_g)$. However, due to the complexity of our spectra these assignments are tentative. This assignment would be compatible with the presence of a band of similar intensity and energy in the spectrum of compound **3**, as might be expected for an ion with similar W–W bond length. The σ–σ^* transition would be the least likely to be affected by mixing with ligand orbitals. Transitions to the $e'(e_g)$ orbitals would, conversely, be expected to show more dependence on the ligands present.

Cyclic Voltammetry.—The electrochemical behaviour of the neutral complexes **1** and **2** was investigated in dichloromethane solution (1 mmol dm^{-3}) using 0.1 mol dm^{-3} NBu_4ClO_4 as supporting electrolyte. The plots (Fig. 4) show that a reversible one-electron reduction occurs at $E_{\frac{1}{2}} = -0.715$ and -0.717 V *vs.* SCE for **1** and **2** respectively. These waves are independent of sweep rate. There was no evidence of a reversible oxidation reaction, although this might have been anticipated, based on the isolation of $[W_2Cl_9]^{2-}$ and $[W_2Br_9]^{2-}$ complexes.[1] The addition of an electron to the lowest unoccupied molecular orbital, known to be δ/π^* in nature, would obviously weaken the metal–metal interaction in these systems, and a further reduction would probably lead to destabilization of the bridging region and production of quadruply bonded bis[tungsten(II)] species. This step could not be observed within the range of potentials studied.

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