Notes

Preparation and X-Ray Crystal Structure of the Adduct $WCl_4S{\cdot}S_8$†

David L. Hughes,* Janette D. Lane and Raymond L. Richards
AFRC IPSR, Nitrogen Fixation Laboratory, University of Sussex, Brighton BN1 9RQ, UK

Treatment of $[W(CO)_6]$ with S_2Cl_2 under reflux in CH_2Cl_2 with irradiation gives the dark red complex $WCl_4S{\cdot}S_8$, shown by its X-ray crystal structure to have a monomeric, square-pyramidal WCl_4S unit with apical S [d(W–S) = 2.077(3); mean d(W–Cl) = 2.292(3) Å] and with an S_8 molecule occupying a position below the Cl_4 plane, *trans* to the terminal sulphide ligand.

As part of our studies of metal–sulphur chemistry which has relevance to metal-catalysed processes such as nitrogen fixation[1] and hydrodesulphurisation,[2] we have prepared a variety of disulphur-bridged complexes of molybdenum *e.g.* $[\{MoCl_3(C_4H_4S)\}_2(\mu\text{-}S_2)(\mu\text{-}C_4H_4S)]$ from a starting material derived by treatment of $[Mo(CO)_6]$ with S_2Cl_2.[3] This starting material appears to have the empirical formula $MoCl_3S$, but has not been structurally characterised and in order to help elucidate its structure we attempted to prepare the tungsten analogue by treatment of $[W(CO)_6]$ with S_2Cl_2. This gave a beautifully crystalline, very dark red product which, however, had the empirical formula WCl_4S_9 and has been shown by X-ray crystallography to be the adduct $WCl_4S{\cdot}S_8$, as detailed below.

Results and Discussion

Preparation and Structure of $WCl_4S{\cdot}S_8$.—Treatment of a suspension of $[W(CO)_6]$ in CH_2Cl_2 with S_2Cl_2 at reflux under tungsten-light irradiation gave deep red, air-sensitive crystals as in reaction (1). The empirical formula of the crystals was

$$[W(CO)_6] + S_2Cl_2 \longrightarrow WCl_4S{\cdot}S_8 + 6CO + \text{unidentified products} \quad (1)$$

established by analysis to be WCl_4S_9 and evidence that the compound contained an S_8 ring came from its IR spectrum, which showed absorptions at 467, 379, 307, 269 and 236 cm^{-1} which are close to those of pure S_8 at 465, 389, 306, 270 and 235 cm^{-1}. An absorption at 551 cm^{-1} is assigned to W=S stretching.[4]

The structure of the molecule was established by X-ray crystallography as shown in Fig. 1; bond lengths and angles are in Table 1. The WCl_4S unit is square pyramidal with the sulphur atom at the apical site and the four chlorine atoms lying in a plane 0.45 Å below the tungsten atom. The W–Cl bond lengths and Cl–W–Cl′ angles within the molecule show no significant differences. The Cl–W–S angles are also closely similar to each other.

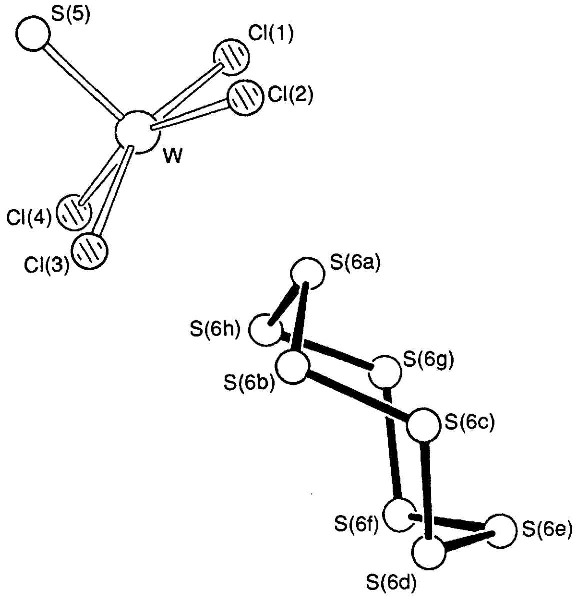

Fig. 1 View of the adduct $WCl_4S{\cdot}S_8$, with the atom labelling scheme

Table 1 Bond dimensions (lengths in Å, angles in °) in neutral forms of WCl_4S with estimated standard deviations (e.s.d.s) in parentheses

			Tetramer[c]	
	S_8 adduct[a]	Dimer[b]	A	B
W–Cl(1)	2.285(2)	2.366(10)	2.296(9)	2.341(12)
W–Cl(2)	2.291(2)	2.273(12)	2.265(12)	2.251(12)
W–Cl(3)	2.295(2)	2.267(12)	2.282(9)	2.243(13)
W–Cl(4)	2.297(3)	2.291(13)	2.280(12)	2.433(12)
W–S(5)	2.077(3)	2.098(8)	2.076(13)	2.076(11)
Cl(1)–W–Cl(2)	87.8(1)	87.5(4)	87.5(4)	89.1(4)
Cl(1)–W–Cl(3)	157.5(1)	157.9(3)	155.1(4)	157.7(4)
Cl(2)–W–Cl(3)	87.4(1)	88.9(4)	87.4(4)	91.8(5)
Cl(1)–W–Cl(4)	88.7(1)	86.2(4)	87.7(4)	84.8(4)
Cl(2)–W–Cl(4)	157.2(1)	158.9(3)	155.6(4)	160.9(3)
Cl(3)–W–Cl(4)	87.3(1)	89.4(5)	86.9(4)	87.1(4)
Cl(1)–W–S(5)	101.1(1)	99.7(4)	102.5(4)	99.9(5)
Cl(2)–W–S(5)	102.3(1)	100.3(4)	102.2(5)	101.7(4)
Cl(3)–W–S(5)	101.3(1)	102.4(4)	102.4(4)	101.7(5)
Cl(4)–W–S(5)	100.4(1)	100.6(4)	102.2(5)	97.2(4)

[a] This work. [b] See text and ref. 4. [c] See text and ref. 5.

Two structural determinations of WCl_4S have already been published. One, by Drew and Mandyczewsky,[4] defined a dimeric unit formed by weak intermolecular W–Cl bonds about a centre of symmetry, thus conferring an octahedral environment on the co-ordinatively unsaturated tungsten. The second structure, by Cotton *et al.*,[5] defined tetrameric units, also formed by weak intermolecular W–Cl bonds. Two WCl_4S units (B in Table 1) of the tetramer form a centrosymmetric dimer essentially as found by Drew and this is linked to two separate

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† Tetrachloro(sulphido)tungsten(VI)–cyclooctasulphur (1/1).

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

Table 2 Cyclooctasulphur and its lattice adducts, with selected structural parameters (lengths in Å, angles in °); e.s.d.s are in parentheses

Compound	S_8 category	Mean dimensions S–S	Mean dimensions S–S–S	Ref.
$[Cu(phen)_2I]I{\cdot}S_8$	Lattice adduct	2.029(10)	107.2(3)	7
$2S_8{\cdot}SnI_4$	Weak $S\cdots I$ interaction			8
$[PPh_4]_4[Ag_2S_{20}]{\cdot}S_8$	Lattice adduct			9
$[N(PPh_3)_2][Ag(S_9)]{\cdot}S_8$	Lattice adduct	2.027(5)	107.6(3)	10
$[Ag(S_8)_2]AsF_6$	Ligand			11
$WCl_6{\cdot}S_8$	Lattice adduct	2.044(1)	107.9(1)	12
$WCl_4S{\cdot}S_8$	Weak $S\cdots Cl$ interaction	2.054(4)	107.2(3)	This work
α-S_8	Elemental S, orthorhombic form	2.060(1)	108.0(4)	13
γ-S_8	Elemental S, monoclinic form	2.060(4)	107.7(2)	14

Dimensions of the S_8 molecule in $WCl_4S{\cdot}S_8$

S(6a)–S(6b)	2.043(4)	S(6b)–S(6a)–S(6h)	108.8(1)
S(6b)–S(6c)	2.058(5)	S(6a)–S(6b)–S(6c)	106.1(2)
S(6c)–S(6d)	2.059(5)	S(6b)–S(6c)–S(6d)	107.9(2)
S(6d)–S(6e)	2.047(5)	S(6c)–S(6d)–S(6e)	107.1(2)
S(6e)–S(6f)	2.055(4)	S(6d)–S(6e)–S(6f)	107.1(2)
S(6f)–S(6g)	2.062(4)	S(6e)–S(6f)–S(6g)	106.5(2)
S(6g)–S(6h)	2.036(4)	S(6f)–S(6g)–S(6h)	107.6(2)
S(6h)–S(6a)	2.063(3)	S(6a)–S(6h)–S(6g)	106.6(2)

Table 3 Final atomic coordinates (fractional $\times 10^4$) for $WCl_4S{\cdot}S_8$. E.s.d.s are in parentheses

Atom	x	y	z
W	1401.3(2)	2159.9(2)	850.5(4)
Cl(1)	545(2)	1089(2)	1027(3)
Cl(2)	389(2)	2954(2)	1636(3)
Cl(3)	1948(1)	3307(1)	−6(3)
Cl(4)	2115(2)	1449(1)	−643(3)
S(5)	2129(2)	1993(2)	2431(3)
S(6a)	205(1)	2365(2)	−1493(2)
S(6b)	433(2)	3512(2)	−2094(3)
S(6c)	−598(2)	3895(2)	−2995(3)
S(6d)	−422(2)	3778(2)	−4919(3)
S(6e)	−991(2)	2743(2)	−5472(3)
S(6f)	−128(2)	1859(2)	−5583(2)
S(6g)	−209(2)	1202(2)	−3929(3)
S(6h)	702(2)	1567(2)	−2771(3)

WCl_4S units (A in Table 1) by longer, unreciprocated $W\cdots Cl$ interactions.

The monomeric nature of the WCl_4S unit as determined in the present study results from the presence of the S_8 unit in the lattice, although there do not appear to be any strong interactions between the S_8 molecule and the WCl_4S unit. The bond dimensions of the WCl_4S units in the three separate structures are shown in Table 1; they show clearly the effects of the various interactions between the units.

The $W\cdots S(6a)$ distance of 3.189(2) Å in $WCl_4S{\cdot}S_8$ is close to the sum of the metallic radius for W(1.37 Å) and the van der Waals radius for S(1.85 Å), at 3.22 Å; this contact is therefore a normal crystal-packing interaction. Of rather more significance are the short interatomic distances between Cl(3) and S(6b) (3.36 Å) and between Cl(4) and S(6h) (3.25 Å). Both of these distances are significantly shorter than the $Cl\cdots S$ van der Waals sum of 3.65 Å and are suggestive of weak interactions between the S_8 ring and the WCl_4S unit. Furthermore, the distances between S(6a) and both Cl(1) and Cl(2) are quite short (3.44 and 3.45 Å respectively) again suggestive of weak interactions.

The S_8 molecule occupies the site *trans* to the terminal sulphide of WCl_4S thus conferring essentially octahedral geometry to the tungsten and preventing the weak $W\cdots Cl$ interactions observed in the dimeric[4] and tetrameric[5] structures.

A number of inorganic species containing the cyclooctasulphur moiety (S_8) are known. In this range of compounds, S_8 can act as a neutral ligand co-ordinating metal centres at one or more atoms on the sulphur ring; it can form lattice adducts in which it has no significantly close contacts with any other atom within the crystal lattice; or it can take part in charge-transfer interactions *e.g.* in CHI_3–S_8.[6]

The S_8 molecule in $WCl_4S{\cdot}S_8$ is essentially a lattice adduct and, apart from the bond distance similarities with other lattice adducts which are noted in Table 2, it also has S_8 bond angles which are all close to 108° (Table 2) in common with the other lattice S_8 molecules. In the normal crown-shaped S_8 ring the torsion angles have values, alternately + and −, in the range 98.5(2)–101.7(2)°.

Potential Use of $WCl_4S{\cdot}S_8$.—Although the preparation of $WCl_4S{\cdot}S_8$ reported here is very simple and convenient compared to some routes to WCl_4S,[4,5] it does require a relatively expensive starting material, $[W(CO)_6]$, and we have found the presence of the lattice S_8 to be a hindrance in using the adduct as a source of WCl_4S for further reactions; products were generally contaminated with variable amounts of sulphur which were difficult to remove. We attempted to remove the S_8 from the adduct by sublimation, but were unsuccessful; the adduct melts at 120 °C. Various solvent systems were also used in an attempt to precipitate preferentially the S_8 but reliably quantitative removal was not achieved.

Experimental

The compounds $[W(CO)_6]$ and S_2Cl_2 were used as commercially supplied (Aldrich) and solvents were dried and distilled under N_2 before use. Elemental analyses were by Butterworth Laboratories and IR spectra were obtained using a Perkin-Elmer 883 spectrometer.

Tetrachloro(sulphido)tungsten(VI)*-Cyclooctasulphur* (1/1), $WCl_4S{\cdot}S_8$.—The compound $[W(CO)_6]$ (16.04 g, 0.045 mol) was suspended in CH_2Cl_2 (100 cm^3) and S_2Cl_2 (18.2 cm^3, 5 mol equivalents) was added. The mixture was heated to reflux and irradiated with a 150 W tungsten-filament lamp at 25 cm. After 3.5 h the dark red solution was allowed to cool at room temperature, when dark red crystals separated, which were filtered off under dry N_2, washed quickly with dry CH_2Cl_2 (2×10 cm^3) and dried in a vacuum. Yield 23.8 g (85%) of essentially pure crystalline material (Found: Cl, 23.0; S, 47.0. Cl_4S_9W requires Cl, 23.1; S, 46.9%).

Crystal Structure Analysis of $WCl_4S{\cdot}S_8$.—*Crystal data.* Cl_4S_9W, $M = 614.2$, tetragonal, space group $P\bar{4}2_1c$ (no. 114), $a = b = 16.606(5)$, $c = 10.546(4)$ Å, $U = 2908.2$ Å^3, $Z = 8$, $D_c = 2.805$ g cm^{-3}, $F(000) = 2288$, μ(Mo-Kα) = 100.7 cm^{-1}, λ(Mo-K$\bar{\alpha}$) = 0.710 69 Å.

The crystals are very dark red-brown needles and are very moisture sensitive. Several were mounted in glass capillaries and, after photographic examination, one (0.35 × 0.21 × 1.05 mm) was transferred to our Enraf-Nonius CAD4 diffractometer for determination of accurate cell parameters (from the goniometer settings of 25 reflections having θ *ca.* 14.5°) and measurement of diffraction intensities (to $\theta_{max} = 25°$).

During processing, intensity data were corrected for Lorentz-polarisation effects, absorption (from semiempirical ψ-scan methods) and to eliminate negative intensities (by Bayesian statistical methods). No correction for crystal deterioration was necessary.

1455 Independent reflections (of which only 43 had $I < 2\sigma_I$) were input to the SHELX system,[15] and the structure was determined by the automated Patterson routines in SHELXS.[16] Full-matrix least-squares refinement, with all atoms allowed anisotropic thermal parameters, converged rapidly to $R = 0.035$, $R_g = 0.046$[15] for all data weighted $w = (\sigma_F{}^2 + 0.002\,03F^2)^{-1}$. A final difference map showed no features of significance. Final atomic coordinates are in Table 3. Corresponding refinement of the opposite structure (all atoms at $-x$, $-y$, $-z$) gave $R = 0.067$ and $R_g = 0.103$: we believe, therefore, that the correct absolute structure has the coordinates of Table 3.

Scattering factors for neutral atoms were from ref. 17. Computer programs have been noted above and in Table 4 of ref. 18, and were run on the VAX 11/750 and MicroVAX II computers at the Agriculture and Food Research Council Institute of Horticultural Research Littlehampton Laboratory (Glasshouse Crops Research Institute) and our Laboratory respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

References

1 R. Chianelli, *Catal. Rev. Sci. Eng.*, 1984, **26**, 361.
2 R. L. Richards, *Chem. Br.*, 1988, 29.
3 D. L. Hughes, R. L. Richards and C. Shortman, *J. Chem. Soc., Chem. Commun.*, 1986, 1731.
4 M. G. B. Drew and R. Mandyczewsky, *J. Chem. Soc. A*, 1970, 2815.
5 F. A. Cotton, P. A. Kibala and R. B. W. Sandor, *Inorg. Chem.*, 1989, **28**, 2485.
6 T. Björvatten, *Acta Chem. Scand.*, 1962, **16**, 749.
7 T. W. Hambley, C. L. Raston and A. H. White, *Aust. J. Chem.*, 1977, **30**, 1965.
8 R. Laitinen, J. Steidel and R. Steudel, *Acta Chem. Scand., Ser. A*, 1980, **34**, 687.
9 A. Müller, R. Römer, H. Bögge, E. Kricklmeyer, F. W. Baumann and E. Schmitz, *Inorg. Chim. Acta*, 1984, **89**, L7.
10 A. Müller, R. Römer, H. Bögge, E. Kricklmeyer and M. Zimmerman, *Z. Anorg. Allg. Chem.*, 1986, **534**, 69.
11 H. W. Roesky, M. Thomas, J. Schrimkowiak, P. G. Jones, W. Pinkert and G. M. Sheldrick, *J. Chem. Soc., Chem. Commun.*, 1982, 895.
12 F. A. Cotton, P. A. Kibala and R. B. W. Sandor, *Acta Crystallogr., Sect. C*, 1989, **45**, 1287.
13 A. Caron and J. Donohue, *Acta Crystallogr.*, 1965, **18**, 1287.
14 Y. Watanabe, *Acta Crystallogr., Sect. B*, 1974, **30**, 1396.
15 G. M. Sheldrick, SHELX 76, Program for crystal structure determination, University of Cambridge, 1976.
16 G. M. Sheldrick, in *Crystallographic Computing 3*, eds. G. M. Sheldrick, C. Krüger and R. Goddard, Oxford University Press, 1985, p. 175.
17 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, pp. 99 and 149.
18 S. N. Anderson, R. L. Richards and D. L. Hughes, *J. Chem. Soc., Dalton Trans.*, 1986, 245.

Received 19*th November* 1990; *Paper* 0/05206J