

molecules from neighbouring sheets mesh together (Fig. 1) and form hydrogen bonds to each other to provide the intersheet linkages.

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The Structure of Pentacarbonyl(5,6-dihydro-4H-1,2-benzodithiole-7-carbothialdehyde-S⁷)tungsten(0), [W(C₈H₈S₃)(CO)₅]

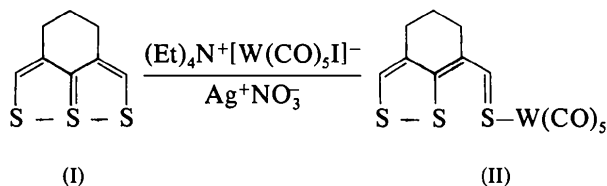
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Abstract. $M_r = 524.24$, triclinic, $P\bar{1}$, $a = 8.337$ (2), $b = 9.039$ (3), $c = 10.962$ (3) Å, $\alpha = 90.83$ (3), $\beta = 91.21$ (3), $\gamma = 100.05$ (3)°, $U = 813.08$ Å³, $D_x = 2.141$ Mg m⁻³ for $Z = 2$, $F(000) = 496$, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 7.828$ mm⁻¹, $R = 0.0454$ for 3503 reflections with $F_o \geq 6\sigma(F_o)$. The S–S and S...S distances of 2.078 (4) and 2.752 (3) Å show that, in the solid state, the compound has a bicyclic structure, not a tricyclic one.

Introduction. Treatment of (I) with $(\text{Et})_4\text{N}^+[\text{W}(\text{CO})_5\text{I}]^-$ in CH_2Cl_2 solution in the presence of aqueous AgNO_3 gave the title compound (II) (Pogorzelec & Reid, 1983). Crystals suitable for X-ray investigation were grown from benzene/hexane solution.



Experimental. Stoe STADI-2 two-circle diffractometer, graphite-crystal-monochromatized Mo $K\alpha$ radiation, crystal dimensions 0.462 × 0.103 × 0.250 mm, bounded by the $\pm(100)$, $\pm(010)$ and $\pm(001)$ faces, and mounted about a ; 3943 reflections collected in the hemisphere $+h, +k, +l$ with $2.5 \leq \theta \leq 30^\circ$, $h = 0-11$ ($0 \leq \mu \leq 27.960^\circ$), $\omega-2\theta$ scan mode, step width of

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0.01° in ω , a time of 1.0s per step, 160 steps per scan; backgrounds measured at both ends of the scan for 80.0s each; standard reflections measured every 50 reflections showed only small random deviations from their means; absorption corrections were applied.

The structure was solved and refined using *SHELX* 76 (Sheldrick, 1976). The W atom position was found on a Patterson synthesis and a subsequent difference synthesis gave the positions of all the other non-H atoms. Least-squares refinement with the matrix blocked so that the W atom refined every cycle, but the CO groups and C₈H₈S₃ group refined in alternate cycles (for computational economy), with anisotropic temperature parameters for all non-H atoms and the H atoms in calculated positions ($d_{\text{C-H}} = 1.08$ Å) with a common isotropic temperature parameter, converged to give an R of 0.0454 and $R_G = (\sum w\Delta^2 / \sum wF_o^2)^{1/2}$ of 0.0566 for 3503 independent reflections with $F_o \geq 6\sigma(F_o)$. In the final cycles 200 parameters were varied, comprising 66 positional coordinates, 132 anisotropic temperature factor components, one common isotropic temperature factor and one overall scale factor: a final difference map showed no significant residual features. Complex neutral-atom scattering factors were used for all atoms (Cromer & Waber, 1974). The reductions in R_G at all stages of the refinement were significant at the 99.5% level (Hamilton, 1965).†

† Lists of structure factors, anisotropic thermal parameters and calculated H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38328 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates ($\times 10^4$, $\times 10^5$ for W) and equivalent isotropic temperature parameters ($\times 10^3$)

The equivalent isotropic temperature parameters are defined as the geometric mean of the diagonal components of the diagonalized matrix of U_{ij} .

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} (\AA^2)
W	29615 (5)	14667 (5)	35438 (4)	38 (1)
S(1)	3440 (3)	3051 (3)	1652 (2)	47 (1)
S(2)	3120 (3)	3332 (3)	-834 (2)	47 (1)
S(3)	2759 (5)	3541 (4)	-2700 (2)	62 (2)
C(1)	2804 (14)	4719 (11)	1756 (9)	46 (5)
C(2)	2477 (11)	5540 (10)	766 (8)	39 (4)
C(3)	2557 (10)	5044 (11)	-455 (8)	39 (4)
C(4)	2139 (13)	5864 (12)	-1471 (9)	48 (5)
C(5)	2173 (15)	5239 (15)	-2585 (9)	57 (5)
C(6)	1937 (15)	7046 (12)	977 (10)	52 (5)
C(7)	2396 (18)	8102 (13)	-64 (11)	61 (6)
C(8)	1613 (15)	7389 (13)	-1255 (11)	55 (6)
C(11)	4450 (14)	148 (12)	2824 (10)	52 (5)
O(11)	5283 (12)	-615 (11)	2420 (9)	73 (6)
C(12)	1497 (15)	2835 (12)	4233 (9)	50 (5)
O(12)	705 (12)	3608 (11)	4623 (8)	70 (6)
C(13)	1011 (14)	267 (11)	2600 (10)	48 (5)
O(13)	-99 (12)	-379 (10)	2079 (10)	72 (6)
C(14)	4859 (14)	2682 (13)	4534 (9)	50 (5)
O(14)	5889 (11)	3362 (11)	5124 (8)	73 (5)
C(15)	2466 (14)	84 (13)	4921 (9)	52 (5)
O(15)	2126 (13)	-742 (11)	5695 (8)	75 (6)

The common isotropic temperature factor for H = 0.09 (2) \AA^2 .

Table 2. Bond lengths (\AA) and angles ($^\circ$)

<i>a</i> 2.752 (3)	<i>b</i> 2.078 (4)	<i>c</i> 1.68 (1)	<i>d</i> 1.74 (1)	<i>e</i> 1.69 (1)
<i>f</i> 1.37 (1)	<i>g</i> 1.41 (1)	<i>h</i> 1.52 (2)	<i>i</i> 1.42 (1)	<i>j</i> 1.34 (2)
<i>k</i> 1.53 (2)	<i>l</i> 1.51 (2)	<i>m</i> 1.53 (2)	<i>n</i> 2.536 (3)	
<i>o</i> 2.03 (1)	<i>p</i> 2.03 (1)	<i>q</i> 2.04 (1)	<i>r</i> 2.04 (1)	<i>s</i> 1.98 (1)
<i>t</i> 1.15 (2)	<i>u</i> 1.13 (2)	<i>v</i> 1.14 (1)	<i>w</i> 1.15 (1)	<i>x</i> 1.15 (1)
<i>nc</i> 114.3 (3)	<i>bd</i> 94.6 (3)	<i>be</i> 94.9 (4)		
<i>cf</i> 123.9 (8)	<i>fg</i> 123.6 (9)	<i>fh</i> 119.1 (9)	<i>gh</i> 117.3 (8)	
<i>dg</i> 122.4 (7)	<i>dl</i> 114.3 (7)	<i>gi</i> 123.3 (9)	<i>ij</i> 117.9 (11)	
<i>ik</i> 119.2 (9)	<i>jk</i> 122.9 (10)	<i>ej</i> 118.3 (9)	<i>hl</i> 111.8 (10)	
<i>lm</i> 109.7 (9)	<i>km</i> 109.5 (10)			
<i>no</i> 87.4 (3)	<i>np</i> 91.1 (3)	<i>nq</i> 86.1 (3)	<i>nr</i> 95.0 (3)	
<i>os</i> 174.6 (3)	<i>op</i> 178.4 (4)	<i>oq</i> 90.6 (4)	<i>or</i> 91.1 (5)	
<i>os</i> 90.9 (5)	<i>pq</i> 89.8 (4)	<i>pr</i> 88.5 (5)	<i>ps</i> 90.7 (5)	
<i>qr</i> 178.0 (4)	<i>qs</i> 88.9 (4)	<i>rs</i> 90.1 (4)	<i>ot</i> 179.2 (9)	
<i>pu</i> 178.9 (10)	<i>qu</i> 178.5 (10)	<i>rw</i> 177.6 (10)	<i>sx</i> 177.4 (10)	

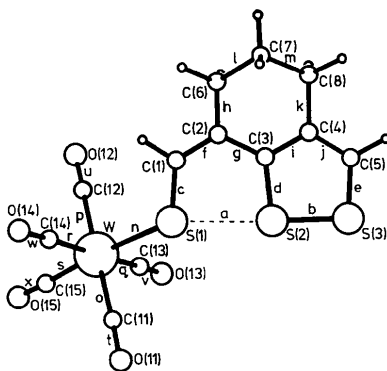


Fig. 1. The molecule showing the labelling scheme for atoms and bonds.

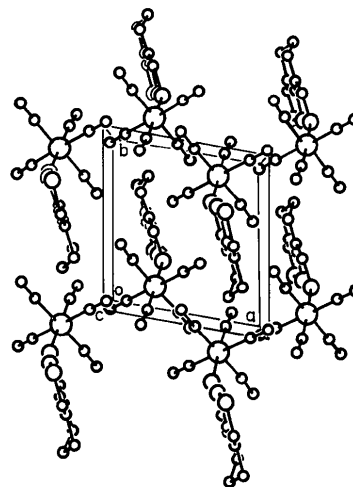
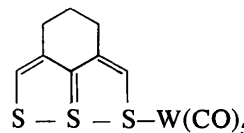


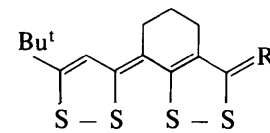
Fig. 2. View of the unit-cell contents down *c*: all molecules whose centres lie in the range -0.5 to $+1.5$ in *x* and *y*, and 0 to 1 in *z* are shown.

Discussion. The final atomic coordinates are given in Table 1. These together with the covariance matrix were used to calculate the bond lengths and bond angles given in Table 2. Fig. 1 shows the molecule with the labelling scheme for atoms and bonds; Fig. 2 shows the unit-cell contents.

The S—S and S...S distances of 2.078 (4) and 2.752 (3) \AA show that, in the solid state, the compound should be represented as bicyclic (II), rather than as tricyclic (III): in solution, it exhibits fluxional behaviour with the $W(CO)_5$ group migrating between S(1) and S(3) (Pogorzelec & Reid, 1983). In the free ligands (I) the S—S distances are 2.300 (7) and 2.385 (7), and 2.276 (7) and 2.412 (7) \AA for two crystallographically independent molecules (Johnson, Llaguno & Paul, 1976).



(III)

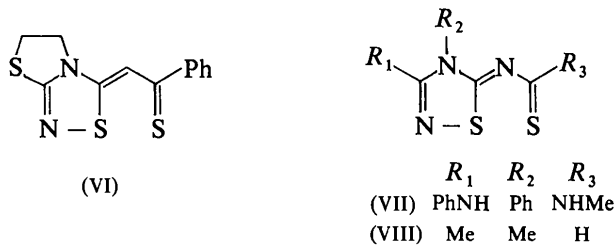


(IV) R=S

(V) R=PhCOCH

The S—S distance found here is similar to those in (IV) [2.063 (3) and 2.062 (3) \AA (Sletten, 1972)] and (V) [2.064 (1) and 2.110 (1) \AA (Sletten & Velsvik, 1973)] and also to those found in a number of 3*H*-1,2-dithiole derivatives containing S—S...O chains (see Glidewell & Liles, 1981*b*). The exocyclic S...S distance is slightly shorter than those in (IV) [2.863 (3) \AA] and (V) [2.856 (1) \AA] but is similar to those in (VI) [2.750 (5) \AA (Glidewell, Holden & Liles, 1980)], (VII) [2.822 (5) \AA (Cuthbertson & Glidewell, 1981)] and (VIII) [2.817 (5) \AA (Glidewell & Liles,

1981a)]. Although it is too long to be regarded as a bond the S...S distance is shorter than the sum of the van der Waals radii for two S atoms [3.6 Å (Bondi, 1964)].



The heterocyclic ring and the S(1)—C(1)—C(2) side chain are not exactly coplanar. The dihedral angle between the least-squares planes of the heterocycle and the S(1)—C(1)—C(2)—C(3)—S(2) group is 2.6 (1)°. The W atom lies 1.103 (5) Å out of the plane of the heterocycle and 0.90 (1) Å out of the plane of the side chain. The torsion angle W—S(1)—C(1)—C(2) is -159.3 (5)°.

The W—S distance of 2.536 (3) Å, the mean W—C distance for the carbonyls *cis* to the S of 2.036 (8) Å and the W—C distance for the carbonyl *trans* to the S of 1.978 (11) Å are similar to those reported in a number of other S-ligand—W(CO)₅ complexes; some recent examples are: W—S 2.543 (2), W—C(*cis*) 2.04 (1) and W—C(*trans*) 1.97 (1) (Barnett, Cooper, McPartlin & Robertson, 1978); 2.586 (4), 2.002 (6) and 1.935 (12) (Cooper, Duckworth, Saporta & McPartlin, 1980); 2.560 (3), 2.03 (2) and 1.99 (1) (Balbach, Koray, Okur, Wulknitz & Ziegler, 1981); 2.555 (2), 2.034 (8) and 1.972 (9) Å (Pickering, Jacobson & Angelici, 1981). The shorter W—C bond *trans* to the S ligand is a general feature of these complexes attributable to the competition of the mutually *trans* carbonyl ligand for electron density from the W atom (Barnett *et al.*, 1978; Cooper *et al.*, 1980).

The bond lengths within the unsaturated portion of the heterocyclic ligand (Table 2) make it difficult to draw a satisfactory bond structure within the classical valence rules. We have investigated further the bonding in this fragment by means of MNDO calculations (Dewar & Thiel, 1977; Thiel, Weiner, Stewart & Dewar, 1981) on the model compound (IX). Table 3 give the calculated distances for (IX), and the bond orders both for the optimized geometry and for a configuration corresponding to that found in (II). The overall agreement between the pattern of distances found in (II) and calculated in (IX) is good, and the two skeletal structures give closely similar bond orders. These confirm the high bond order, greater than 1.5, in the bonds *f* and *j*: since no atom in (IX) carries a charge greater than ±0.2 e, no single classical structure can be drawn.

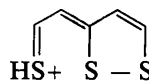
Table 3. Distances and bond orders for compound (IX)

Bond*	Distance (Å)†	Bond order†	Bond order‡
<i>a</i>	3.052	0.041	0.050
<i>b</i>	1.952	1.002	0.962
<i>c</i>	1.653	1.183	1.165
<i>d</i>	1.677	1.188	1.160
<i>e</i>	1.667	1.151	1.144
<i>f</i>	1.382	1.561	1.575
<i>g</i>	1.421	1.246	1.256
<i>i</i>	1.444	1.206	1.211
<i>j</i>	1.378	1.630	1.635

* Labelling of bonds as in (II).

† Optimized geometry.

‡ For geometry as found in (II).



(IX)

There are no short contacts between the molecules: the molecules are assembled (Fig. 2) so that parallel to a there are alternate ribbons consisting of W(CO)₅ groups and of heterocyclic ligands, which are themselves oriented almost perpendicular to a.

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