

Table 2. Positional parameters ($\times 10^3$) for the hydrogen atoms and isotropic thermal parameters

	x	y	z	B (\AA^2)
H(3)	390 (3)	817 (1)	1061 (3)	4.6 (6)
H(4)	374 (3)	801 (1)	795 (2)	3.3 (5)
H(5)	423 (3)	726 (1)	571 (3)	4.7 (6)
H(6)	519 (3)	612 (1)	469 (3)	4.2 (6)
H(8)	779 (3)	377 (1)	687 (3)	4.3 (6)
H(9)	886 (3)	339 (1)	930 (3)	4.3 (6)
H(10)	945 (3)	357 (1)	1198 (3)	4.5 (6)
H(11)	940 (3)	440 (1)	1406 (3)	4.7 (6)

C–C–C and C–C–O angles at the furan ring are 135.3 (2) and 124.6 (2)°, the endocyclic furan C–C–C and C–C–O angles 105.4 (2) and 112.4 (2)°. The dimensions of the pyran rings are likewise in good agreement with those found in comparable structures such as xanthotoxin (Stemple & Watson, 1972) and 3-(1-phenylpropyl)-4-hydroxycoumarin (Bravic, Gaultier & Hauw, 1971).

In the crystal structure there are small but significant deviations from the formal symmetry expected for such a molecule. Agreement between bond lengths and angles related by the near diad axis passing through O(7) and the mid-point of C(15)–C(16) is good with r.m.s. deviations from the mean values for those not involving hydrogen of 0.004 Å and 0.35°. In terms of the e.s.d.'s quoted there are apparently significant differences between O(7)–C(6a) and O(7)–C(7a), C(5)–C(6) and C(8)–C(9), and O(1)–C(2) and O(13)–C(12). It seems more reasonable to assume that the e.s.d.'s are underestimated than that these differences are real.

The significant deviations from exact C_2 symmetry are in the slightly differing conformations of the pyran rings. The furan ring is rigorously planar, the maxi-

mum deviation of any of its atoms from their least-squares mean plane being 0.006 Å. The deviations of individual atoms in the rest of the molecule from this plane are shown in Fig. 1 which also gives various torsion angles. The C(15) phenyl ring is also planar but the C(17) phenyl ring shows minor distortions from planarity. Each pyran ring is significantly non-planar and the pattern of torsion angles is different in each with the angles at the junction with the phenyl ring being of opposite sign though small. Bond lengths and angles are in Fig. 2.

The O(1)···O(13) separation is 2.852 (2) Å and the overall non-planarity of the molecule presumably arises from lone-pair interactions involving these two atoms. The dihedral angle between the planes of the two phenyl rings is 3°, that between the least-squares mean planes for the pyran rings is 10°.

Intermolecular contacts are of normal van der Waals type with no unusually close approaches.

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Thiomorpholin-3-thione-pentacarbonylungsten

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Abstract. $(\text{CO})_5\text{WS}=\text{C}-\text{NH}-\text{CH}_2-\text{CH}_2-\text{S}-\text{CH}_2$, monoclinic, $P2_1/n$, $a=5.64$ (1); $b=23.17$ (3); $c=10.25$ (2) Å; $\beta=91.7$ (3)°; $D_m=2.24$ g cm $^{-3}$; $Z=4$, $D_c=2.26$ g cm $^{-3}$. The compound was prepared by ultraviolet irradiation of a dry ethyl ether solution of $\text{W}(\text{CO})_6$ and the ligand. The coordination is octahedral, with the heterocyclic ligand bonded through the thioketonic S atom.

Introduction. Crystals suitable for X-ray analysis were obtained by slow evaporation of a methylene chloride–ligroin solution. Cell constants were determined by a least-squares fit of 17 values of θ , χ , ϕ , accurately measured by use of a very narrow counter aperture. Weissenberg photographs showed systematic absences corresponding to space group $P2_1/n$ ($h0l$ with $h+l$ odd and $0k0$ with k odd). The intensities were obtained from a crystal of approximate dimensions $0.01 \times 0.02 \times$

0.04 cm mounted on a Siemens AED diffractometer (Mo $K\alpha$, Zr-filtered, θ - 2θ scan, scintillation counter with pulse-height discrimination). The **a-c** direction of the crystal (its longest dimension) was nearly coincident with the φ axis of the goniostat; 2501 independent reflexions were measured up to 2θ (Mo $K\alpha$) = 52° ; 1919 with $I_o > 3\sigma(I_o)$ were used for the analysis. Absorption [$\mu(\text{Mo } K\alpha) = 93.5 \text{ cm}^{-1}$] and extinction corrections were not applied.

The positions of W, S(1) and two light atoms were obtained from a three-dimensional Patterson map. The Fourier synthesis calculated with the phases obtained with the contribution of these atoms showed so many spurious peaks that the search for the remaining non-hydrogen atoms proved difficult and time consuming; their coordinates were obtained from a three-dimensional difference synthesis calculated after two cycles of full-matrix least-squares refinement of both positional and isotropic thermal parameters of the four atoms already obtained. After three full-matrix least-squares cycles, refinement converged to $R = 0.10$. A three-dimensional difference Fourier synthesis calculated at this point showed some remarkable peaks of opposite sign close to the positions of the heavy atoms and many other peaks, about $1 \text{ e } \text{Å}^{-3}$ in height, scattered in the cell, of no chemical significance. Refinement was terminated after five block-diagonal least-squares cycles with anisotropic thermal parameters ($R = 0.053$); H atoms were introduced and held fixed at the calculated position ($B = 5.0 \text{ Å}^2$).

The minimized quantity was $\sum w(F_o - F_c)^2$, where $w = 4F_o^2 / [\sigma^2(F_o^2) + (0.12F_o^2)^2]$. A difference electron density map calculated from the final structure factors showed around the W atom the same features as the previous map, but with much lower peak heights ($\approx 3 \text{ e } \text{Å}^{-3}$).

Atomic scattering factors were interpolated from the values given by Cromer & Waber (1965) for W, S, O, N and C and by Stewart, Davidson & Simpson (1965)

for H. The final positional and thermal parameters are given in Table 1.*

Discussion. This structural analysis forms part of an investigation of the competition between Va and VIa donor atoms in the coordination to the metal in compounds of general formula $\text{W}(\text{CO})_5\text{L}$; L is a heterocyclic ligand containing different donor atoms, only one of which is able to coordinate to the metal because of steric hindrance. The crystal structures of $\text{W}(\text{CO})_5\text{tm}$ (tm = $\text{S}-\text{CH}_2-\text{CH}_2\text{NH}-\text{CO}-\text{CH}_2$) (Cannas, Carta, De Filippo, Marongiu & Trogu, 1974) and $\text{W}(\text{CO})_5\text{ttz}$ (ttz = $\text{S}-\text{C}-\text{S}-\text{CH}_2-\text{CH}_2-\text{NH}$) (Cannas, Carta, Marongiu & Trogu, 1974) have been previously reported.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31282 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

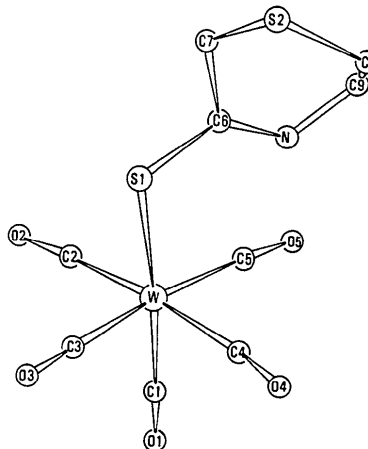


Fig. 1. A perspective view of the molecule of $\text{W}(\text{CO})_5\text{ts}$.

Table 1. Positional and anisotropic thermal parameters ($\times 10^4$), with estimated standard deviations in parentheses

The temperature factor is of the form $\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
W	8024 (1)	3285 (0)	5385 (1)	202 (3)	17 (0)	42 (1)	1 (0)	4 (1)	0 (0)
S(1)	5495 (12)	4145 (3)	4636 (6)	375 (23)	19 (1)	58 (5)	22 (4)	-25 (9)	-7 (2)
S(2)	1825 (14)	4716 (4)	1360 (8)	415 (28)	26 (2)	110 (8)	15 (5)	-71 (12)	0 (3)
O(1)	11375 (32)	2341 (9)	6580 (18)	372 (66)	24 (5)	102 (20)	20 (14)	33 (29)	10 (7)
O(2)	11171 (38)	4224 (12)	6898 (22)	425 (79)	39 (7)	143 (27)	-20 (18)	-17 (38)	-24 (10)
O(3)	5031 (38)	3243 (9)	7928 (18)	447 (81)	41 (7)	64 (18)	9 (16)	77 (31)	-7 (8)
O(4)	4890 (33)	2233 (9)	4321 (20)	413 (72)	23 (4)	125 (23)	-25 (13)	20 (32)	-9 (8)
O(5)	11268 (32)	3195 (9)	2925 (18)	290 (59)	34 (6)	73 (18)	-4 (13)	54 (27)	0 (7)
N	5852 (34)	3881 (10)	2162 (17)	311 (68)	25 (5)	42 (16)	12 (14)	-26 (27)	2 (7)
C(1)	10079 (39)	2689 (11)	6146 (19)	304 (75)	19 (5)	42 (19)	1 (15)	17 (31)	4 (7)
C(2)	10043 (42)	3898 (13)	6302 (24)	261 (78)	28 (7)	84 (28)	-1 (18)	-1 (37)	-5 (10)
C(3)	6065 (42)	3261 (11)	7042 (22)	266 (75)	23 (6)	54 (22)	10 (15)	-43 (33)	2 (8)
C(4)	5974 (41)	2636 (11)	4633 (20)	295 (76)	18 (5)	56 (20)	-12 (16)	12 (30)	0 (8)
C(5)	10090 (39)	3256 (11)	3763 (22)	201 (65)	22 (6)	63 (22)	-3 (14)	-9 (31)	-5 (8)
C(6)	5257 (38)	4258 (10)	3035 (21)	242 (71)	17 (5)	62 (22)	-4 (14)	-30 (31)	-6 (8)
C(7)	4233 (53)	4821 (13)	2566 (26)	511 (117)	22 (6)	81 (28)	-5 (22)	-57 (44)	3 (11)
C(8)	2982 (54)	4114 (15)	446 (25)	652 (168)	23 (7)	79 (30)	9 (24)	-33 (56)	0 (10)
C(9)	5533 (58)	3992 (14)	762 (25)	576 (134)	28 (8)	61 (25)	21 (24)	46 (46)	4 (11)

Table 2. Bond distances (Å) and angles (°) with estimated standard deviations in parentheses

W—S(1)	2.556 (8)	S(1)—W—C(1)	172.7 (7)
W—C(1)	1.95 (2)	S(1)—W—C(2)	83.9 (8)
W—C(2)	2.03 (3)	S(1)—W—C(3)	87.7 (7)
W—C(3)	2.05 (2)	S(1)—W—C(4)	99.0 (7)
W—C(4)	2.04 (2)	S(1)—W—C(5)	96.1 (7)
W—C(5)	2.06 (2)	C(1)—W—C(2)	89.5 (11)
C(1)—O(1)	1.17 (3)	C(1)—W—C(3)	88.8 (9)
C(2)—O(2)	1.15 (4)	C(1)—W—C(4)	87.3 (10)
C(3)—O(3)	1.10 (3)	C(1)—W—C(5)	87.5 (9)
C(4)—O(4)	1.15 (3)	C(2)—W—C(3)	86.8 (10)
C(5)—O(5)	1.11 (3)	C(2)—W—C(4)	174.6 (10)
S(1)—C(6)	1.66 (2)	C(2)—W—C(5)	94.2 (10)
S(2)—C(7)	1.83 (3)	C(3)—W—C(4)	88.9 (9)
S(2)—C(8)	1.81 (3)	C(3)—W—C(5)	176.2 (10)
C(6)—N	1.30 (3)	C(4)—W—C(5)	90.0 (9)
C(6)—C(7)	1.50 (4)	W—C(1)—O(1)	177.6 (20)
C(8)—C(9)	1.49 (4)	W—C(2)—O(2)	175.4 (24)
C(9)—N	1.46 (3)	W—C(3)—O(3)	179.2 (23)
		W—C(4)—O(4)	172.7 (20)
		W—C(5)—O(5)	174.0 (21)
		W—S(1)—C(6)	116.6 (9)
		S(1)—C(6)—N	123.8 (19)
		S(1)—C(6)—C(7)	118.2 (18)
		N—C(6)—C(7)	117.9 (21)
		C(6)—C(7)—S(2)	111.9 (20)
		C(7)—S(2)—C(8)	100.4 (14)
		S(2)—C(8)—C(9)	113.1 (21)
		C(8)—C(9)—N	109.6 (23)
		C(9)—N—C(6)	121.9 (22)

The crystal structure consists of discrete $W(CO)_5$ ts molecules and all intermolecular contacts appear normal; Fig. 1 is a perspective drawing of an isolated molecule of the complex; bond angles and distances are given in Table 2. The coordination polyhedron is a distorted octahedron with the equatorial plane defined by atoms C(2), C(3), C(4), and C(5); W—C distances in this plane are in the range 2.03–2.06 (2) Å; the apical W—C(1) bond distance [1.95 (2) Å] is significantly shorter, as found in $W(CO)_5$ tm and $W(CO)_5$ ttz, and the hypothesis of a *trans* influence of the W—S(1) bond seems to be confirmed.

Thiomorpholin-3-thione (ts) is bonded to the metal through the thioketonic S atom S(1) and an sp^2 hybridization of this atom would require S(1), C(6), C(7) and

Table 3. Equations of molecular planes, referred to *a*, *b* and *c* axes, with deviations (Å) of atoms from the planes

Plane (a)	C(2) [0.00], C(3) [0.00], C(4) [0.00], C(5) [0.00] $3.3103x - 16.0837y + 4.0903z = -0.3622$
[W	-0.06, O(2) 0.09, O(3) 0.05, O(4) 0.16, O(5) 0.15, S(1) -2.59, C(1) 1.89]
Plane (b)	N[0.01], C(6) [-0.01], C(7) [0.00], C(9) [0.00] $5.1855x + 9.1053y - 0.4375z = 6.4719$
[W	0.44, S(1) -0.05, S(2) -1.29, C(8) -1.20]
Plane (c)	S(2) [0.07], C(7) [-0.04], C(8) [-0.08], C(9) [0.05] $2.0760x + 16.1293y - 6.4273z = 7.0455$
[S(1)	-2.20, N -0.96, C(6) -1.04]

Dihedral angles: planes *a/b* 74.9°, planes *b/c* 128.4°

N to lie on a plane almost perpendicular to the equatorial plane of the polyhedron; a parallel orientation should on the other hand be sterically preferred in order to avoid short intramolecular contacts between the *ortho* atoms of the ligand and the closest equatorial carbonyl groups. The structural situation is a compromise between these two opposing tendencies; the angle between least-squares planes is 75° (Table 3) and intramolecular contacts are lessened by the inclination of the W—S vector with respect to the equatorial plane and by the opening of C(2)—W—C(5) angle (94.5°).

As far as the ligand is concerned, all the distances are very close to those found in tm and ttz molecules; however, the ts and tm molecules have markedly different configurations; ts has an envelope configuration with S(1), C(6), N, C(7) and C(9) as well as C(7), C(9), S(2) and C(8) almost coplanar (Table 3), while tm has a chair conformation with N and S on the opposite side with respect to the plane of the other four atoms; is noteworthy that significant differences in the bond angles involving these two atoms are found in the two molecules.

The structures of $W(CO)_5$ tm, $W(CO)_5$ ttz and $W(CO)_5$ ts show that the ligands are always bonded through sulphur, and in the case of ttz and ts, where two S atoms are present, the preference goes to the thioketonic rather than to the thioetheric one; this choice does not originate from any difference in W—S bond lengths and seems to be sterically unfavourable if we assume that deviations from 90° of the angles at the W atom are a consequence of intramolecular repulsions between the $W(CO)_5$ group and the heterocyclic ligand. The sums of the deviations of the angles from 90° are 27.5, 30.8 and 40.2° in $W(CO)_5$ tm, $W(CO)_5$ ttz and $W(CO)_5$ ts respectively; the difference between the extreme values, which refer to structures with similar ring ligands, one bonded through the thioetheric and the other through the thioketonic sulphur, indicates that the first type of coordination should be sterically favoured. An explanation for the choice could, however, be provided by the HSAB theory (Pearson, 1963), since $W(CO)_5$ is a basic support and sulphur in C=S is to be considered softer than in the C—S—C group.

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