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Tricarbonylbis(4-methyl-1,3-thiazole-2(3*H*)-thionato-*N*,*S*^{2})tungsten(II)

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The title compound, $[W(C_4H_4NS_2)_2(CO)_3]$, consists of a seven-coordinate tungsten centre with three carbonyl ligands and two planar methylthiazole sulfide ligands, both coordinating bidentately to the W atom through the N and sulfide S atoms. The two 4-methylthiazole sulfide ligands are twisted at an angle of 86.98 (15)° with respect to each other.

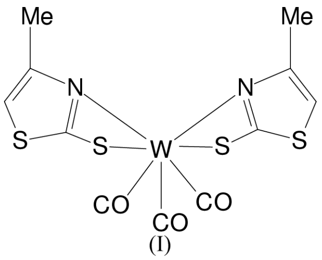
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.013 Å
R factor = 0.036
wR factor = 0.119
Data-to-parameter ratio = 14.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The title compound, (I), represents the first seven-coordinate W^{II} complex synthesized from a neutral W^0 complex and a thiazolyl disulfide. In this process, the disulfide oxidatively substitutes the metal carbonyl, and the N atom of the thiazole moiety coordinates to the metal, as seen in Fig. 1. Similar complexes containing pyridine-2-thionate (Deeming *et al.*, 1990), pyrimidine-2-thionate (Baker *et al.*, 1995) and pyridine-2-selenate (Kienitz *et al.*, 1996) have been obtained previously, but not *via* the same preparative route.



(I)

The coordination sphere of the W atom can be described as a 4:3 piano-stool arrangement, with the three carbonyl ligands forming the legs of the stool (Dreyer *et al.*, 1979). The other four atoms bonded to the W atom form the distorted square base of the piano-stool. Alternatively, the coordination sphere can be viewed as a distorted monocapped trigonal prism, with the C1—O1 carbonyl group in the capping position. The two methylthiazole sulfide ligands are planar [maximum deviations from planarity for the two ligands are 0.096 (4) Å for S1 and −0.065 (6) Å for N2, respectively]. The angle between the two planes is 86.26 (12)°.

There is some evidence for a small difference between the two W—N bond lengths [W1—N2 2.227 (7) Å and W1—N1 2.264 (6) Å], despite the relatively large standard deviations. This observation is similar to the structure of tricarbonylbis(pyrimidine-2-thionato-*S*,*N*)tungsten(II) (Baker *et al.*, 1995), where the difference in W—N bond lengths may be attributed to greater *trans* effect of the two noncapping carbonyl ligands C2—O2 and C3—O3 as opposed to that of

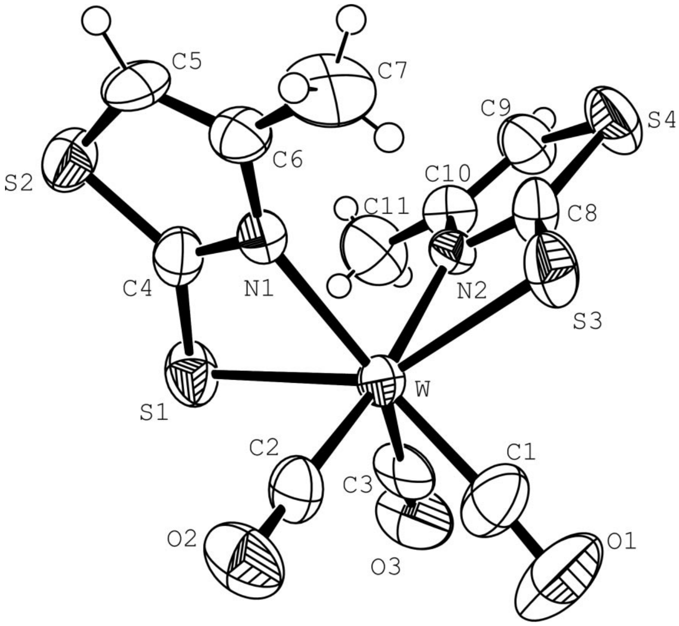


Figure 1
The molecular configuration of the title compound. Ellipsoids are shown at the 50% probability level (Farrugia, 1997).

the capping carbonyl ligand C1—O1. A similar effect was observed in the structure of dicarbonyldimethylphenylphosphinebis(pyridine-2-thionato-*S*,*N*)tungsten(II) (Deeming *et al.*, 1990), where the difference in W—N bond lengths is a result of the *trans* ligands [$P(CH_3)_2(C_6H_5)$ and CO] having different *trans* influences. The W—S [W1—S3 2.515 (2) Å and W1—S1 2.546 (2) Å] bond lengths also differ, in contrast to the two comparable thionate structures, where the difference in W—S bond lengths is less than 0.02 Å. This is as a result of the constraints of the four-membered W—N—C—S rings, where the differing W—N bond lengths result in differing W—S bond lengths. The three W—C(carbonyl) bond lengths are the same within experimental error. The bond angles around the tungsten do not differ significantly from those observed in the comparable tricarbonylbis(pyrimidine-2-thionato-*N*,*S*)-tungsten(II) (Baker *et al.*, 1995).

No significant intermolecular interactions were observed.

Experimental

Oxidation of 4-methylthiazol-2-thione [prepared by reacting 4-methylthiazol-2-yllithium with sulfur at 195 K and then water, Gundermann & Hümke (1985)] at 306 K in 0.2 *M* phosphate buffer (pH 7.6) with an NaI/I_2 solution (2:1, *w*/*w*) yields di-4-methylthiazole 2-disulfide (Doerr *et al.*, 1961). A solution of di-4-methylthiazolyl 2-disulfide in THF (20% excess) was added to $W(CO)_5$(thf) [obtained by UV-irradiation of $W(CO)_6$ in THF as described by Werner *et al.* (1969)] and stirred for 1 h. Stripping of solvent *in vacuo* followed by flash chromatography (258 K, 8:5 diethyl ether/hexane eluent) afforded orange microcrystalline (I). Single crystals formed from a concentrated diethyl ether solution layered with pentane at 253 K.

Crystal data

$[W(C_4H_4NS_2)_2(CO)_3]$
$M_r = 528.28$
Monoclinic, $P2_1/c$
$a = 9.6233$ (9) Å
$b = 10.2686$ (8) Å
$c = 16.272$ (2) Å
$\beta = 97.672$ (11)°
$V = 1593.5$ (3) Å^3
$Z = 4$

$D_x = 2.202$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 46 reflections
$\theta = 4.5$–17.7°
$\mu = 7.78$ mm^{-1}
$T = 293$ (2) K
Plate, orange-red
0.25 × 0.23 × 0.10 mm

Data collection

Philips PW1100 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.160$, $T_{\max} = 0.459$
2993 measured reflections
2817 independent reflections
2259 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.069$
$\theta_{\max} = 25.0°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 12$
$l = -19 \rightarrow 19$
3 standard reflections every 50 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.119$
$S = 1.07$
2817 reflections
192 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0809P)^2 + 1.9916P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.20$ e Å^{-3}
$\Delta\rho_{\min} = -2.28$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

W1—C1	1.950 (10)	W1—N1	2.264 (6)
W1—C3	1.982 (10)	W1—S3	2.517 (2)
W1—C2	1.973 (9)	W1—S1	2.545 (2)
W1—N2	2.227 (7)		
C1—W1—C3	74.0 (4)	N1—W1—S3	87.35 (17)
C1—W1—C2	74.6 (4)	N2—W1—S1	94.95 (18)
C3—W1—C2	103.3 (4)	N1—W1—S1	65.07 (16)
N2—W1—N1	85.1 (2)	S3—W1—S1	147.86 (8)
N2—W1—S3	65.09 (18)		

The positions of the H atoms could be identified from difference density maps; however, they were calculated geometrically and constrained to ride on the atoms to which they were attached. Their isotropic displacement parameters were fixed at 1.2 or 1.5 (for methyl groups) times the equivalent isotropic displacement parameters of their parent atoms. The highest peak and deepest hole in the final difference density map were 0.92 Å from W1 and 1.08 Å from W1, respectively.

Data collection: *PWPC* (Gomm, 1998); cell refinement: *PWPC*; data reduction: *Xtal*3.4 (Hall *et al.*, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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