

# The synthesis, fluxional properties and X-ray crystal structure of $[\text{W}(\text{CO})(\text{C}_4\text{H}_3\text{N}_2\text{S})(\eta^2\text{-MeC}_2\text{Me})_2]$ (where $[\text{C}_4\text{H}_3\text{N}_2\text{S}]^- = \text{pyrimidine-2-thionate}$ )

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## Abstract

Reaction of  $[\text{W}_2(\text{CO})(\text{NCMe})(\eta^2\text{-MeC}_2\text{Me})_2] \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2$  with one equivalent of  $[\text{K}(\text{C}_4\text{H}_3\text{N}_2\text{S})]$  ( $\text{C}_4\text{H}_3\text{N}_2\text{S} = \text{pyrimidine-2-thionate}$ ) in diethyl ether at room temperature affords the monoiodide product  $[\text{W}(\text{CO})(\text{C}_4\text{H}_3\text{N}_2\text{S})(\eta^2\text{-MeC}_2\text{Me})_2]$  (**1**) in high yield. The molecular structure of **1** has been crystallographically determined and is best described as a distorted octahedron, with one of the but-2-yne ligands lying *trans* to the iodide and both of them occupying the axial positions, and the remaining alkyne, carbon monoxide and the sulphur and nitrogen atoms of the pyrimidine-2-thionate ligand occupying the equatorial positions. Variable-temperature <sup>1</sup>H NMR spectroscopic studies have shown the complex  $[\text{W}(\text{CO})(\text{C}_4\text{H}_3\text{N}_2\text{S})(\eta^2\text{-MeC}_2\text{Me})_2]$  (**1**) to be fluxional. <sup>13</sup>C NMR spectroscopy indicates that the alkyne ligands donate a total of six electrons to the tungsten in **1**.

**Key words:** Tungsten; Iodide; But-2-yne; Pyrimidine-2-thionate; Fluxional properties; Crystal structure

## 1. Introduction

There has been much interest in alkyne complexes of molybdenum(II) and tungsten(II) during the past 30 years [1]. Although a large number of alkyne complexes of molybdenum(II) and tungsten(II) containing dithiocarbamates and related anionic S<sub>2</sub> bidentate donor ligands have been reported [2–11], hitherto no examples of such complexes containing the anionic N<sup>−</sup>S bidentate donor ligand pyrimidine-2-thionate  $[\text{C}_4\text{H}_3\text{N}_2\text{S}]^-$  have been described. In this paper, we describe the synthesis, molecular structure and fluxional properties of the pyrimidine-2-thionate bis(but-2-yne) complex  $[\text{W}(\text{CO})(\text{C}_4\text{H}_3\text{N}_2\text{S})(\eta^2\text{-MeC}_2\text{Me})_2]$  (**1**).

## 2. Results and discussion

The organometallic starting material  $[\text{W}_2(\text{CO})(\text{NCMe})(\eta^2\text{-MeC}_2\text{Me})_2] \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2$  used for this research was prepared by treating  $[\text{W}_2(\text{CO})_3(\text{NCMe})_2]$

with an excess of MeC<sub>2</sub>Me in CH<sub>2</sub>Cl<sub>2</sub> at 0°C [12]. Potassium pyrimidine-2-thionate was prepared by treating pyrimidine-2-thione with an equimolar amount of KOH in methanol. Equimolar quantities of  $[\text{W}_2(\text{CO})(\text{NCMe})(\eta^2\text{-MeC}_2\text{Me})_2] \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2$  and  $[\text{K}(\text{C}_4\text{H}_3\text{N}_2\text{S})]$  suspended in diethyl ether reacted to afford the N<sup>−</sup>S coordinated pyrimidine-2-thionate complex  $[\text{W}(\text{CO})(\text{C}_4\text{H}_3\text{N}_2\text{S})(\eta^2\text{-MeC}_2\text{Me})_2]$  (**1**) in 83% yield after purification. Complex **1** has been fully characterized by elemental analysis (C, H and N), IR, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy (see Section 3). The compound is stable when stored under nitrogen, but decomposes slowly when exposed to air in either the solid state or in solution. It is soluble in CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, NCMe and CH<sub>3</sub>COCH<sub>3</sub> but only slightly soluble in hydrocarbon solvents and diethyl ether.

The molecular structure of **1** was determined by X-ray crystallography. The structure obtained is shown in Fig. 1 together with the atomic numbering scheme, and selected bond lengths and angles are listed in Table 1. The structure can be described as a distorted octahedron with both of the coordinated but-2-yne ligands *cis* to each other, and with an iodide and the nitrogen atom of the pyrimidine-2-thionate ligand *trans*

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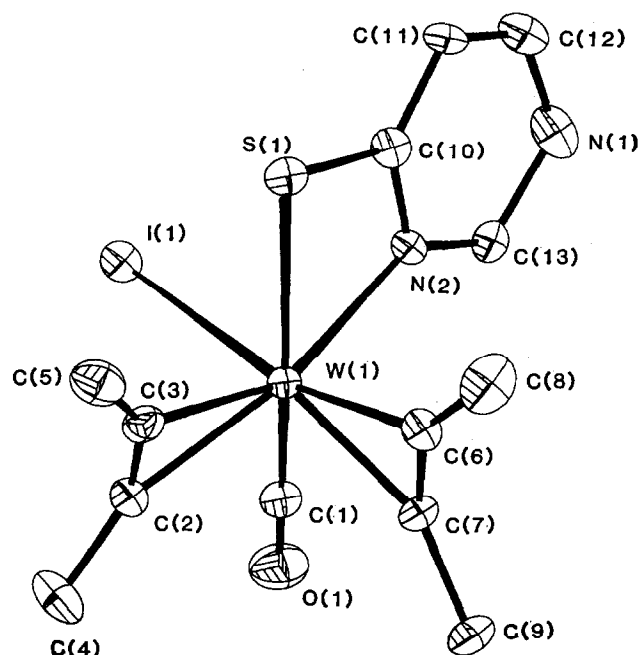


Fig. 1. X-ray crystal structure of  $[\text{W}(\text{CO})(\text{C}_4\text{H}_3\text{N}_2\text{S})(\eta^2\text{-MeC}_2\text{Me})_2]$  (1) with atomic numbering scheme.

to these ligands. The sulphur atom of the pyrimidine-2-thionate and the carbon monoxide ligand occupy the axial positions. It should also be noted that the but-2-yne ligands are parallel and the  $\text{C}\equiv\text{C}$  bonds are also parallel to the  $\text{W}-\text{CO}$  axis. This is commonly observed in  $d^4$  complexes of molybdenum(II) and tungsten(II), since this configuration allows maximum overlap of both  $p\pi$ -orbitals of the coordinated alkynes and thereby optimizes  $\pi$ -acceptor and  $\pi$ -donor properties [1].

The distances from the tungsten atom to the alkyne carbons lie in the range [1] expected for the alkyne acting as an, on average, "three-electron" donor ( $\text{W}-\text{C}(2)$ , 2.139(5) Å;  $\text{W}-\text{C}(3)$ , 2.066(5) Å;  $\text{W}-\text{C}(6)$ , 2.059(5) Å;  $\text{W}-\text{C}(7)$ , 2.086(5) Å). The bend-back angles  $\beta$  [13] of the attached alkynes are not equivalent, indicating a degree of interaction with other ligands ( $\beta$ :  $\text{C}(5)-\text{C}(3)-\text{C}(2)$ , 34.7(3)°;  $\text{C}(4)-\text{C}(2)-\text{C}(3)$ , 31.7(3)°;  $\text{C}(8)-\text{C}(6)-\text{C}(7)$ , 35.0(3)°;  $\text{C}(9)-\text{C}(7)-\text{C}(6)$ , 36.8(3)°). There is also a degree of torsion on the alkyne ligands. The alkyne *trans* to the iodide is twisted by 2.4° and that *cis* to the iodide by 8.1° relative to the  $\text{W}-\text{C}\equiv\text{O}$  axis.

The IR spectrum ( $\text{CHCl}_3$ ) of  $[\text{W}(\text{CO})(\text{C}_4\text{H}_3\text{N}_2\text{S})(\eta^2\text{-MeC}_2\text{Me})_2]$  (1) shows a carbonyl band at 2044  $\text{cm}^{-1}$  which is as expected since the two alkyne ligands are both good  $\pi$ -acceptors and hence there is little electron density on the metal for back-donation to the  $\pi^*$ -orbitals of the carbonyl ligand. There is also a weak  $\nu(\text{C}\equiv\text{C})$  stretching band at 1850  $\text{cm}^{-1}$ , a much lower wavenumber than that observed for the free alkyne,

suggesting weakening of the alkyne bond strength due to back-donation of electron density from the filled metal  $d\pi$ -orbitals into empty  $\pi^*$ -orbitals on the alkyne. This rehybridization of the alkyne triple bond is confirmed by the X-ray crystal structure (Fig. 1) which shows the methyl groups on the alkynes to be bent back away from the  $\text{C}\equiv\text{C}$  moiety.

The room-temperature  $^1\text{H}$  NMR spectrum of 1 in  $\text{CD}_3\text{CN}$  shows four singlets corresponding to the different but-2-yne methyl environments, at  $\delta = 3.03$ , 2.99, 2.93 and 2.84 ppm, and also four other resonances shifted slightly downfield, at  $\delta = 3.16$ , 3.13, 3.09 and 3.06 ppm, with an intensity ratio of 3:1 respectively. This might suggest that a mixture of isomers is present at room temperature. Variable-temperature  $^1\text{H}$  NMR studies indicate that at low temperature only one isomer is present. The four singlets at  $\delta = 3.03$ –2.84 ppm

TABLE 1. Bond lengths (Å) and angles (°) of compound 1

Bond lengths			
I(1)–W(1)	2.960(1)	S(1)–W(1)	2.544(4)
N(2)–W(1)	2.210(4)	C(1)–W(1)	2.047(5)
C(2)–W(1)	2.139(5)	C(3)–W(1)	2.066(5)
C(6)–W(1)	2.059(5)	C(7)–W(1)	2.086(5)
C(10)–S(1)	1.739(5)	C(1)–O(1)	1.085(5)
C(12)–N(1)	1.372(6)	C(13)–N(1)	1.414(6)
C(10)–N(2)	1.346(5)	C(13)–N(2)	1.330(5)
C(3)–C(2)	1.229(5)	C(4)–C(2)	1.458(6)
C(5)–C(3)	1.490(5)	C(7)–C(6)	1.278(6)
C(8)–C(6)	1.492(6)	C(9)–C(7)	1.500(7)
C(11)–C(10)	1.347(5)	C(12)–C(11)	1.287(6)
Bond angles			
S(1)–W(1)–I(1)	84.8	N(2)–W(1)–I(1)	78.7(2)
N(2)–W(1)–S(1)	64.4(2)	C(1)–W(1)–I(1)	75.2(2)
C(1)–W(1)–S(1)	155.4(1)	C(1)–W(1)–N(2)	97.2(2)
C(2)–W(1)–I(1)	85.4(2)	C(2)–W(1)–S(1)	116.8(2)
C(2)–W(1)–N(2)	163.9(1)	C(2)–W(1)–C(1)	76.3(2)
C(3)–W(1)–I(1)	94.7(2)	C(3)–W(1)–S(1)	85.2(2)
C(3)–W(1)–N(2)	149.2(1)	C(3)–W(1)–C(1)	110.3(2)
C(3)–W(1)–C(2)	33.9(1)	C(6)–W(1)–I(1)	165.9(1)
C(6)–W(1)–S(1)	85.5(2)	C(6)–W(1)–N(2)	87.8(2)
C(6)–W(1)–C(1)	111.1(2)	C(6)–W(1)–C(2)	108.2(2)
C(6)–W(1)–C(3)	94.8(2)	C(7)–W(1)–I(1)	149.2(1)
C(7)–W(1)–S(1)	120.5(2)	C(7)–W(1)–N(2)	95.9(2)
C(7)–W(1)–C(1)	75.4(2)	C(7)–W(1)–C(2)	96.6(2)
C(7)–W(1)–C(3)	104.1(2)	C(7)–W(1)–C(6)	35.9(1)
C(10)–S(1)–W(1)	81.1(2)	C(13)–N(1)–C(12)	117.0(4)
C(10)–N(2)–W(1)	103.8(3)	C(13)–N(2)–W(1)	137.7(2)
C(13)–N(2)–C(10)	118.5(4)	O(1)–C(1)–W(1)	175.9(3)
C(3)–C(2)–W(1)	69.8(3)	C(4)–C(2)–W(1)	141.9(3)
C(4)–C(2)–C(3)	148.3(3)	C(2)–C(3)–W(1)	76.3(3)
C(5)–C(3)–W(1)	138.3(3)	C(5)–C(3)–C(2)	145.3(3)
C(7)–C(6)–W(1)	73.2(3)	C(8)–C(6)–W(1)	141.7(3)
C(8)–C(6)–C(7)	145.0(3)	C(6)–C(7)–W(1)	70.9(3)
C(9)–C(7)–W(1)	145.4(3)	C(9)–C(7)–C(6)	143.2(3)
N(2)–C(10)–S(1)	110.7(3)	C(11)–C(10)–S(1)	124.4(4)
C(11)–C(10)–N(2)	124.9(4)	C(12)–C(11)–C(10)	116.0(4)
C(11)–C(12)–N(1)	124.5(4)	N(2)–C(13)–N(1)	118.9(4)

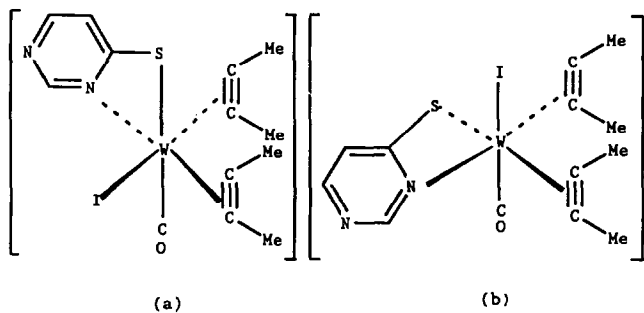


Fig. 2. Proposed isomers of **1** in solution at room temperature from  $^1H$  NMR spectroscopy.

broaden on cooling to 218 K to give three peaks of intensity 1:2:1 at  $\delta = 3.0$ , 2.94 and 2.84 ppm. On warming to 343 K the four methyl resonances at  $\delta = 3.03$ –2.84 ppm collapse to give a singlet at 2.86 ppm. It is likely that the more abundant isomer at room temperature is that shown in Fig. 2(a), *i.e.* the crystallographically observed structure (Fig. 1), and the less prevalent isomer is that shown in Fig. 2(b), which can be obtained from Fig. 2(a) by a simple trigonal twist. It should be noted that the structure for the less abundant isomer (Fig. 2(b)) has been observed previously for the pyrollidine-2-thionate complex  $[W(CO)(NCMe)(S_2CNC_4H_8)(\eta^2-MeC_2Me)_2][BPh_4]$  [14], which has an acetonitrile in place of the iodide ligand in Fig. 2(b). Both isomers (Figs. 2(a) and 2(b)) would be expected to show four but-2-yne methyl resonances in the  $^1H$  NMR spectrum for **1**.

The  $^{13}C$  NMR spectrum for **1** shows the expected features for the complex given in Fig. 1. Alkyne contact carbon resonances for the major isomer occur at 181.79, 167.24, 162.88 and 151.56 ppm which suggests [15] that the but-2-yne ligands are donating an average of three electrons each to the metal centre. This would allow complex **1** to obey the effective atomic number rule.

### 3. Experimental details

The synthesis and purification of  $[W(CO)(C_4H_3N_2S)(\eta^2-MeC_2Me)_2]$  (**1**) were carried out under dry nitrogen by standard Schlenk-line techniques. The compound  $[W_2(CO)(NCMe)(\eta^2-MeC_2Me)_2] \cdot \frac{1}{2}CH_2Cl_2$  was prepared by the published method [12]. The potassium salt of pyrimidine-2-thione was prepared by the action of KOH in methanol with one equivalent of the thione. Concentration of the solution afforded a yellow solid which was washed with diethyl ether and dried in a vacuum oven. All other chemicals were purchased from commercial sources. The solvent  $CH_2Cl_2$  was distilled over  $P_4O_{10}$  and diethyl ether was dried over sodium wire before use.

The elemental analysis (C, H and N) was determined with a Carlo Erba Elemental Analyser MOD 1106 (using helium as the carrier gas). The IR spectrum was recorded on a Perkin-Elmer 1600 FTIR spectrophotometer.  $^1H$  and  $^{13}C$  NMR spectra were recorded on either a Bruker CP/MAS AC 250 ( $^1H$ ) or a Bruker WH 400 ( $^{13}C$ ) NMR spectrometer. All NMR spectra were calibrated against tetramethylsilane.

#### 3.1. Preparation of $[W(CO)(C_4H_3N_2S)(\eta^2-MeC_2Me)_2]$ (**1**)

To a suspension of  $[W_2(CO)(NCMe)(\eta^2-MeC_2Me)_2] \cdot \frac{1}{2}CH_2Cl_2$  (1.0 g, 1.521 mmol) in diethyl ether (30 cm<sup>3</sup>) under a stream of dry nitrogen was added  $K[C_4H_3N_2S]$  (0.229 g, 1.521 mmol). After 18 h stirring, the green solution was syringed off and the precipitate was washed with further 10 cm<sup>3</sup> portions of diethyl ether until all the green colour had disappeared. The crude product was dissolved in  $CH_2Cl_2$  and the solution was filtered to remove the KI. Removal of the solvent *in vacuo* afforded a pale green solid  $[W(CO)(C_4H_3N_2S)(\eta^2-MeC_2Me)_2]$  (**1**), which was recrystallized by dissolving in a minimum volume of NCMe and keeping the solution at  $-25^\circ C$  for 24 h. This afforded suitable single crystals for X-ray crystallography. Yield of pure product = 0.71 g, 83%. Anal. Found: C, 28.2; H, 2.8; N, 5.0;  $C_{13}H_{15}N_2OSIW$  calc.: C, 28.0; H, 2.7; N, 5.0%. IR ( $CHCl_3$ ):  $\nu(C=O)$  2044s,  $\nu(C\equiv C)$  1850vw cm<sup>-1</sup>.  $^1H$  NMR ( $CD_3CN$ ,  $+25^\circ C$ ) spectral data for the major isomer: 8.51 (brs, 1H, NCHN); 8.02 (brm, 1H, NCHNCH); 6.80 (t,  $J_{H-H} = 7.15$  Hz, 1H, SCCH); 3.03, 2.99, 2.93, 2.84 (4s, 12H,  $MeC_2$ ) ppm.  $^{13}C$  NMR ( $CD_2Cl_2$ ,  $+25^\circ C$ ) spectral data for the major isomer: 209.17 (s,  $C=O$ ); 193.62 (s, NCHN); 181.79, 167.24, 162.88, 151.56 (4s,  $C\equiv C$ ); 157.55 (brs, NCS); 155.30 (brs, NCHNCH); 115.26 (brs, SCCH); 19.99, 18.22, 18.07, 15.76 (4s,  $MeC_2$ ) ppm.

#### 3.2. Crystal structure analysis of $[W(CO)(C_4H_3N_2S)(\eta^2-MeC_2Me)_2]$ (**1**)

The single crystal used for the X-ray examination was sealed under nitrogen in a capillary. Crystallographic data were obtained using a CAD 4 diffractometer, operating in the  $\omega-2\theta$  scan mode and using graphite-monochromated Mo  $K\alpha$  radiation as described previously [16].

#### 3.3. Crystal data for **1**

Crystals of **1** were prepared as described above:  $C_{13}H_{15}N_2OSIW$ ,  $M = 558.10$ , monoclinic, space group  $P2_1/c$ ,  $a = 8.25(1)$ ,  $b = 13.54(1)$ ,  $c = 14.66(1)$  Å,  $\beta = 91.61(1)^\circ$ ,  $U = 1645.62$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 2.25$  g cm<sup>-3</sup>,  $\lambda(Mo-K\alpha) = 0.71069$  Å,  $\mu(Mo-K\alpha) = 91.45$  cm<sup>-1</sup>,

TABLE 2. Fractional atomic coordinates ( $\times 10^4$ ) for compound 1

Atom	x	y	z
W(1)	2052(1)	751(1)	2140(1)
I(1)	4756(1)	2000(1)	2828(1)
S(1)	566(2)	1397(2)	3512(1)
O(1)	5010(8)	21(5)	1039(5)
N(1)	3641(11)	-938(6)	4692(6)
N(2)	2665(7)	25(4)	3453(4)
C(1)	4022(10)	275(6)	1449(6)
C(2)	2063(9)	1679(6)	962(5)
C(3)	900(9)	1878(6)	1433(5)
C(4)	2982(13)	1884(8)	150(7)
C(5)	-585(11)	2493(8)	1506(7)
C(6)	155(9)	-225(6)	1992(6)
C(7)	1264(9)	-525(6)	1470(5)
C(8)	-1479(10)	-443(8)	2349(9)
C(9)	1627(14)	-1263(7)	742(7)
C(10)	1761(9)	508(6)	4057(6)
C(11)	1785(9)	338(5)	4961(5)
C(12)	2730(11)	-357(7)	5246(6)
C(13)	3620(10)	-700(5)	3754(6)

$F(000) = 1032$ . Cell dimensions were obtained by least-squares refinement on setting angles of 25 well-spaced reflections with  $10.0^\circ < \theta < 12.0^\circ$ . The intensity data were corrected for absorption empirically using  $\psi$  scan profiles. Of the 6636 intensities measured, 2804 were unique and 2266 observed ( $F_o > 6\sigma F_o$ ).

The structure was solved via the heavy atom method and refined by full-matrix least squares. Only the W, S, N and O atoms were refined anisotropically, the remaining non-hydrogens isotropically; hydrogens were not located or included. Computations were made with SHELX 80 [17] using inlaid scattering factors (for C, H, S, N and O) or as given in ref. 18 (for W). The final  $R$  and  $R^1$  factors were 0.035 and 0.051 respectively, for 187 parameters, with weights of  $w = 1/[\sigma(F_o) + 0.016181F_o]$  giving flat agreement analyses.

The final atomic positions are given in Table 2. Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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