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X-RAY MOLECULAR STRUCTURE OF TETRACARBONYL(S,S-DIMETHYLSULFONIUM 2-PICOLINYLMETHYLIDE)TUNGSTEN(0)

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Summary

The structure of the title compound has been determined by single-crystal X-ray analysis. The crystals contain monomeric units and are of space group $P2_1/c$, with $Z = 4$ in each unit cell of dimensions: $a = 7.658(1)$, $b = 11.881(2)$, $c = 17.233(2)$ Å, $\beta = 103.51(1)°$. The structure was refined to a conventional R factor of 0.042 using 2542 observed ($|F_o| > 3\sigma(F)$) reflections. The ylide ligand coordinates to tungsten through the pyridine nitrogen and carbonyl oxygen atoms, forming a distorted octahedral geometry around the metal atom.

Introduction

Many ylide metal complexes containing ylide carbon-to-metal bonds have been prepared and their structures and properties are of interest. We have recently reported the preparation of palladium(II) and platinum(II) complexes of 2-picolinylmethylides, $MCl_2(C_5H_4NC(O)\overset{-}{C}H\overset{+}{Z})$ (M = Pd, Pt: $\overset{+}{Z}$ = $\overset{+}{N}C_5H_4$-Me-*p*, $\overset{+}{S}Me_2$, and $\overset{+}{P}Ph_3$) and $[Pt(C_5H_4NC(O)\overset{-}{C}H\overset{+}{Z})_2][ClO_4]_2$ (Z = $\overset{+}{N}C_5H_4$-Me-*p*, $\overset{+}{N}C_5H_3$-Me$_2$-*m*,*m*'), which involve chelation of the ylide carbon and 2-picolinyl nitrogen to the metal ions [1,2]. Similar chelation mode has been proposed for $W(CO)_4(C_5H_4NC(O)\overset{-}{C}H\overset{+}{N}C_5H_4$-Me-*p*) [3]. The coordination of ylide carbon to metal in these complexes has been suggested on the basis of markedly high frequency shifts of ν(C=O) upon complex formation. On the other hand, S,S-dimethylsulfonium 2-picolinylmethylide, $C_5H_4NC(O)\overset{-}{C}H\overset{+}{S}Me_2$, exhibited only small frequency shifts of ν(C=O) (+5 cm^{-1} in Nujol mulls and -6 cm^{-1} in THF) upon coordination to the $W(CO)_4$ moiety [3]. In addition, the ^1H NMR spectrum of the complex indicated no coordination of the ylide carbon to tungsten. Thus, spectroscopic techniques have failed to elucidate the mode of coordination in this complex. The present work was therefore undertaken to elucidate the molecular structure of tetracarbonyl(S,S-dimethylsulfonium 2-picolinylmethylide)tungsten(O) by X-ray crystallographic analysis. This paper reports the molecular and crystal structures as well as coordination schemes of the complex.

Experimental

The compound was prepared by the reaction of S,S-dimethylsulfonium 2-picolinylmethylide with $W(CO)_5THF$ [4] in THF as described elsewhere [3]. Recrystallization from a mixture of THF and petroleum ether under a nitrogen atmosphere afforded red single crystals.

The space group and initial unit-cell parameters were determined from oscillation and Weissenberg photographs. Accurate unit-cell parameters were obtained by a least-squares fit of the angular coordinates of 38 reflections with 2θ values from 17° to 27° measured on a computer-controlled Rigaku four-circle diffractometer using graphite-monochromatized Mo-Kα ($\lambda = 0.71069$ Å) radiation.

Crystal data.—— $C_{13}H_{11}NO_5SW$, $M = 477.15$; monoclinic, space group $P2_1/c$; $a = 7.658(1)$, $b = 11.881(2)$, $c = 17.233(2)$ Å, $\beta = 103.51(1)^\circ$; $U = 1524.5(4)$ Å^3; $Z = 4$; $D_x = 2.079$ g cm^{-3}; μ(Mo-Kα) = 78.9 cm^{-1}.

Intensity data of the independent reflections were collected up to $2\theta = 55^\circ$ using the ω-2θ scan technique at a 2θ scan rate of 2° min^{-1}. The scan width in ω was $(0.9 + 0.34\tan\theta)^\circ$, and 30 s background counts were taken on either side of the every scan. Five check reflections were monitored after every 50 reflections. None showed a significant intensity variation during the data collection. The intensities were corrected for the Lorentz and polarization effects. For the sample chosen the transmission coefficients were in the range of 0.46 – 0.74. As the specimen was small (approximately 0.06 × 0.07 × 0.10 mm) and its shape was irregular, no corrections were made for absorption. Of the 3495 independent reflections measured, 2542 had intensities larger than three times their standard deviations, and were used in the subsequent calculations.

Structure analysis.—— The structure was solved by the heavy-atom method. The position of the tungsten atom was determined from a three-dimensional Patterson map. Subsequent cycles of Fourier and diagonal least-squares calculations gave a reasonable set of coordinates and anisotropic thermal factors of all the nonhydrogen atoms. At this stage the residual index, $R = \Sigma|\Delta F|/\Sigma|F_o|$, where $\Delta F = |F_o| - |F_c|$, was 0.044. The least-squares refinement was based on the minimization of $\Sigma w(\Delta F)^2$, where w was the weight given to each reflection. A difference-Fourier map based on anisotropic refinement of all the nonhydrogen atoms contained electron densities in positions which would be attributed to the hydrogen atoms of pyridine ring, ylide, and S-methyl groups. In the final four cycles of the block-diagonal least-squares calculations the weighting scheme, $1/w = \sigma^2(F_o) + 0.0005(F_o)^2$, was used. The final residual indices are: $R = 0.042$ and $R_w = [\Sigma w(\Delta F)^2/\Sigma w|F_o|^2]^{1/2} = 0.045$. A final difference-Fourier map had no positive maxima >le Å^{-3} except in the vicinity of the metal position. Atomic scattering factors used throughout the refinements were those of Cromer and Waber [5] for the nonhydrogen atoms and of Stewart et al. [6] for hydrogen. Anomalous dispersion corrections of the form $f = f_o + \Delta f' + i\Delta f''$ were applied to tungsten and sulfur; $\Delta f' = -1.421$ and $\Delta f'' = 6.872$ for W, $\Delta f' = 0.110$ and $\Delta f'' = 0.124$ for S.

The final atomic positional parameters and their estimated standard deviations are presented in Table 1.
Tables of the anisotropic thermal parameters, and of observed and calculated structure amplitudes are available from NAPS*.

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TABLE 1. FINAL FRACTIONAL ATOMIC COORDINATES (× 10^4; FOR H × 10^3).

ATOM	*x*	*y*	*z*
W	3310.8(5)	1626.1(3)	2569.0(2)
S	1538(3)	3965(2)	4765(1)
N	5235(8)	1075(5)	3700(4)
O(1)	151(12)	5(8)	2777(5)
O(2)	6402(11)	2980(7)	2028(5)
O(3)	4124(10)	-177(6)	1387(4)
O(4)	453(9)	2679(6)	1170(4)
O(5)	2958(8)	2729(5)	3526(3)
C(1)	1311(13)	623(8)	2743(5)
C(2)	5303(12)	2541(8)	2268(5)
C(3)	3794(11)	512(8)	1824(5)
C(4)	1533(12)	2298(8)	1699(5)
C(5)	6437(12)	242(8)	3759(5)
C(6)	7591(11)	-57(8)	4459(5)
C(7)	7532(12)	528(8)	5142(6)
C(8)	6321(12)	1380(8)	5096(5)
C(9)	5177(10)	1657(7)	4381(5)
C(10)	3761(11)	2526(7)	4249(5)
C(11)	3290(12)	3023(8)	4891(5)
C(12)	-328(15)	3294(10)	4118(7)
C(13)	2057(15)	5061(10)	4160(7)
H(5)	638(7)	-6(5)	326(3)
H(6)	834(12)	-52(7)	448(5)
H(7)	835(14)	33(9)	563(6)
H(8)	627(10)	183(6)	550(4)
H(11)	374(7)	289(5)	540(3)
H(12-1)	-38(19)	275(13)	434(8)
H(12-2)	-8(13)	335(7)	364(6)
H(12-3)	-137(14)	391(9)	394(6)
H(13-1)	256(10)	484(7)	376(4)
H(13-2)	296(16)	556(10)	454(7)
H(13-3)	117(8)	544(5)	401(4)

Results and Discussion

Figure 1 shows the crystal structure, in which no unusual intermolecular contacts were found. A perspective view of the molecule and the labelling scheme are shown in Figure 2. Bond lengths and angles with estimated standard deviations are given in Table 2.

The complex contains a hexa-coordinated tungsten atom with four mutually *cis* carbonyl carbon atoms. The ylide ligand

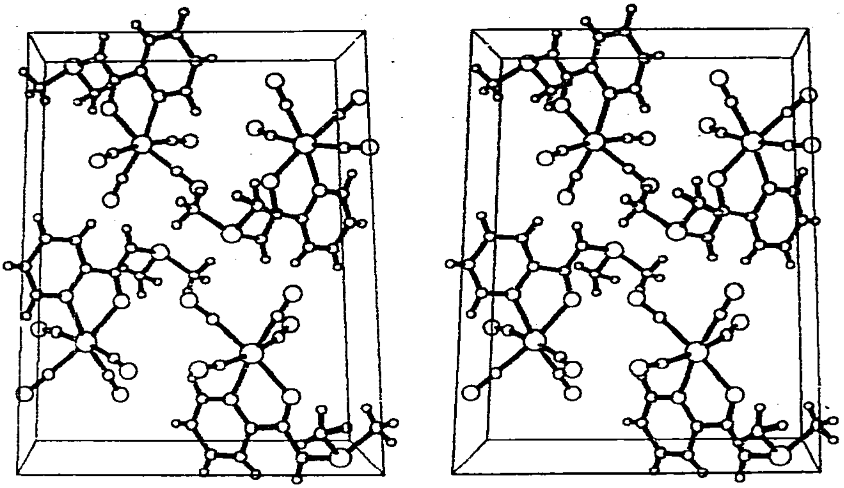


Figure 1. Stereoview of the crystal structure of tetracarbonyl(S,S-dimethylsulfonium 2-picolinylmethylide)-tungsten(0) in the unit cell. The view is approximately along *a*, with *b* horizontal and *c* vertical in the plane of the sheet.

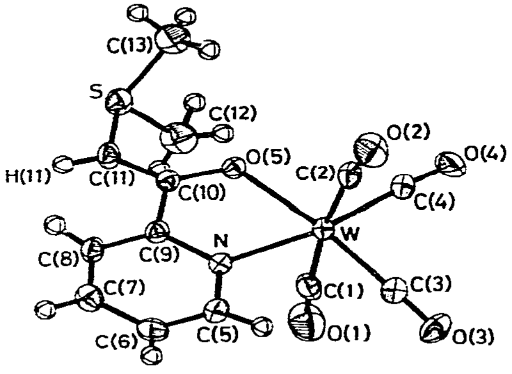


Figure 2. Perspective view of the molecular structure of tetracarbonyl(S,S-dimethylsulfonium 2-picolinylmethylide)-tungsten(0) showing the labelling scheme. Thermal ellipsoids are drawn at the 30 % probability level except those for hydrogen atoms, which are represented by spheres having an arbitrary radius.

TABLE 2. BOND LENGTHS (IN Å) AND ANGLES (IN DEGREES)

BOND	LENGTH	BOND	LENGTH	BOND	LENGTH
W — C(1)	2.017(10)	C(3) — O(3)	1.18(1)	C(5) — N	1.34(1)
W — C(2)	2.036(10)	C(4) — O(4)	1.17(1)	C(5) — C(6)	1.37(1)
W — C(3)	1.939(10)	C(9) — C(10)	1.48(1)	C(6) — C(7)	1.38(1)
W — C(4)	1.945(8)	C(10) — C(11)	1.37(1)	C(7) — C(8)	1.36(1)
W — N	2.249(6)	C(10) — O(5)	1.277(9)	C(8) — C(9)	1.38(1)
W — O(5)	2.173(6)	C(11) — S	1.72(1)	C(9) — N	1.37(1)
C(1) — O(1)	1.17(1)	C(12) — S	1.78(1)		
C(2) — O(2)	1.15(1)	C(13) — S	1.77(1)		

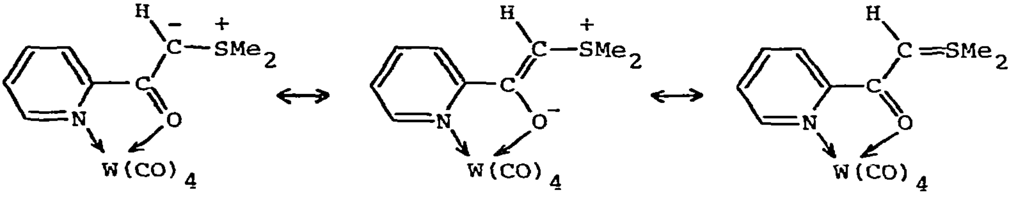
BOND	ANGLE	BOND	ANGLE
W — C(1) — O(1)	174.0(9)	C(4) — W — N	170.5(3)
W — C(2) — O(2)	172.5(8)	C(4) — W — O(5)	98.5(3)
W — C(3) — O(3)	178.2(7)	N — W — O(5)	71.9(2)
W — C(4) — O(4)	178.5(8)	W — N — C(9)	116.7(5)
C(1) — W — N	93.8(3)	W — O(5) — C(10)	120.7(5)
C(1) — W — O(5)	90.6(3)	N — C(9) — C(10)	113.0(6)
C(1) — W — C(2)	173.2(4)	C(9) — C(10) — O(5)	116.8(8)
C(1) — W — C(3)	87.9(4)	O(5) — C(10) — C(11)	123.1(8)
C(1) — W — C(4)	86.4(4)	C(10) — C(11) — S	121.5(6)
C(2) — W — N	89.9(3)	C(10) — C(11) — H(11)	127(4)
C(2) — W — O(5)	96.0(3)	H(11) — C(11) — S	111(4)
C(3) — W — N	100.8(3)	C(11) — S — C(12)	106.0(5)
C(3) — W — O(5)	172.5(3)	C(11) — S — C(13)	106.1(5)
C(3) — W — C(4)	88.7(4)	C(12) — S — C(13)	102.6(5)

coordinates to tungsten through the pyridine nitrogen and carbonyl oxygen atoms. The octahedral geometry around the metal is greatly distorted, since the angle N-W-O(5) is necessarily small (71.9(2)°) owing to the relative rigidity of the 2-picolinyl ligand and large covalent radius of tungsten. W, N, O(5), C(3), and C(4) are coplanar (to within ±0.02 Å), and W-C(3)-O(3) and W-C(4)-O(4) are almost linear, whereas the remaining W-C-O linkages are bent, as seen in several carbonyl tungsten(0) complexes with the angles at carbonyl carbon ranging from 169 to 176° [7].

The bond distances of W-C(3) and W-C(4) are considerably shorter than those of W-C(1) and W-C(2). These differences can be explained in terms of metal-to-ligand π back-bonding. The available 5d electrons on the metal atom are equally accepted by empty π^* orbitals of the C(1)-O(1) and C(2)-O(2) groups which are mutually *trans*. On the other hand, there is metal-to-ligand π donation in the case of the *cis*-carbonyl pair (C(3)-O(3) and C(4)-O(4)). The nitrogen and oxygen atoms of the ylide ligand opposed to these carbonyl groups seem to act as σ-donors to the tungsten atom, their π-acceptor property being small [3]. Similar *trans* effect shortening of the W-C distance for carbonyl groups which are opposite to ligating nitrogen and sulfur atoms also were reported for some tetracarbonyltungsten(0) complexes [7-10].

The W-N bond distance is close to those of (octakisdimethylaminocyclotetraphosphazene)tetracarbonyltungsten(0) (2.33(2), 2.37(1) Å) [7] and (di-*t*-butyl sulfurdimine)tetracarbonyltungsten(0) (2.16, 2.18 Å) [8]. Although structures of zerovalent tungsten complexes with coordinating oxygen have been scarcely studied, the W-O bond length is close to that of tris(methyl vinyl ketone)tungsten(0) (2.11(2) Å) [11].

The C(11)-S bond (1.72(1) Å) which exhibits a partial double bond is appreciably shorter than C(12)-S and C(13)-S bonds (1.78(1) and 1.77(1) Å, respectively), and longer than C(sp^2)=S double bond (1.66 Å) in tetraethylthiuramdisulfide [12]. It is very close to ylide carbon-to-sulfur bond distances (1.70 – 1.73 Å) of some sulfur ylides, whose X-ray structure analyses have been reported [13-16]. The partial double bond character of the C(11)-S bond is explained by assuming the resonance hybrid of canonical structures (I) – (III) in the present ylide.



(I) (II) (III)

The contribution from these canonical structures is supported by the significantly short C(10)-C(11) distance (1.37(1) Å) compared with the C(9)-C(10) distance (1.48(1) Å).

A pyramidal configuration is observed around the sulfur atoms; the C(11)-S-C(12), C(11)-S-C(13), and C(12)-S-C(13) angles are 106.0(5), 106.1(5), and 102.6(5)°, respectively. This configuration is very similar to those observed in dimethylsulfonium ylides, such as 2-dimethylsulfuranylidene-malononitrile [13] and thiophenium bismethoxycarbonylmethylide [15]. S-Methyl groups are oriented towards the C(10)-O(5) group, avoiding any repulsion between sulfur and carbonyl oxygen. C(10), C(11), H(11), and S lie almost on a plane; H(11) deviates 0.06 Å from the S-C(10)-C(11) plane. The ylide carbon, C(11), adopts a sp^2 configuration, which would be expected also in the free ylide molecule.

The ylide carbonyl distance (C(10)-O(5), 1.277(9) Å) is lengthened as compared to the C=O distance as predicted on the basis of double-bond radii of carbon and oxygen atoms (1.20 Å) [17]. This is rationalized in terms of the contribution from the canonical structure (II). The elongated carbonyl bond length stands in contrast to the C-O distance of the ylide ligand ($PhC(O)\overset{-}{C}H\overset{+}{S}Me_2$) in (di-*t*-butyl nitroxide)-(S,S-dimethylsulfonium phenacylide)chloropalladium(II) (1.19(2) Å) and (dimethylphenylphosphine)(S,S-dimethylsulfonium phenacylide)dichloroplatinum(II) (1.23(2) Å), in which the ylide carbon atoms coordinate to the metal ions [18].

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