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CRYSTAL AND MOLECULAR STRUCTURE OF TETRACARBONYL(3,3,4,4-TETRAMETHYL-3,4-DIHYDRODIAZETE)-TUNGSTEN DIMER, $[W(N_2C_2Me_4)(CO)_4]_2$

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Summary

Crystals of $C_{20}H_{24}N_4O_8W_2$ are orthorhombic, *a* 18.1365(24), *b* 18.6401(6), *c* 15.5086(11) Å; $Z = 8$; space group *Pbca*. The crystal structure has been determined by X-ray diffraction methods and refined to $R = 0.028$ for 2998 independent observed reflections. It consists of discrete dimeric complexes, in which each W atom is bonded to four carbon atoms of carbonyl groups and to two nitrogen atoms of two 3,3,4,4-tetramethyl-1,2-diazetine ligands, in a deformed octahedral coordination. The two metal atoms and the four bridging nitrogen atoms of the ligands form an irregular hexa-atomic ring.

Introduction

Transition-metal complexes of diazenes have been widely investigated [1–15]. Preparations and properties of chromium and tungsten complexes of 1,2-diazetines have been recently reported [15]. In order to account for the different stabilities of these complexes, it seemed of interest to ascertain the interatomic distances and the bond angles in the title compound.

The crystal structure analysis by single crystal X-ray diffraction methods is reported in this paper.

Experimental

The $[W(N_2C_2Me_4)(CO)_4]_2$ complex was prepared by the reaction of $W(CO)_4$(norbornadiene) and 3,3,4,4-tetramethyl-1,2-diazetine in a 1/1 ratio in benzene under argon, with stirring of the solution at room temperature for 15 h. After evaporation of the solvent, the complex was isolated and purified by chromatography on silicagel and crystallization from toluene/petroleum ether mixture. Crystals suitable for a single crystal X-ray diffractometric analysis were obtained by recrystallization from toluene/petroleum ether [15].

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Data collection

A needle-shaped black crystal of the title compound, having approximate dimensions 0.16 × 0.16 × 0.54 mm, was used for data collection. Cell parameters were determined by a least-squares procedure of 2ϑ values for 25 reflections accurately measured on a single-crystal Philips PW 1100 computer controlled diffractometer (using the graphite monochromated Mo-K_α radiation) of Centro di Studio per la Cristallografia strutturale del C.N.R., Pavia, Italy. The intensities of 4613 independent reflections were collected within the angular range $2 \leq \vartheta \leq 25°$. The $\omega/2\,\vartheta$ scan technique was used with a constant scan speed of $0.060° s^{-1}$ in ω. Three standard reflections were measured every 240 min and showed only small random deviations about their mean intensities. 2998 reflections having $I \geq 3\ \sigma(I)$ ($\sigma(I)$ based on counting statistics) were considered observed and employed in the structure analysis. The intensities were corrected for Lorentz and polarization factors and for absorption according to North et al. [16]. An approximate absolute scale and a mean thermal factor were determined by the Wilson's method [17].

Crystal data

$C_{20}H_{24}N_4O_8W_2$, mol.wt 816.16; orthorhombic, a 18.1365(24), b 18.6401(6), c 15.5086(11) Å; V 5242.9 Å^3; $Z = 8$, Dc 2.04 g cm^{-3}; $F(000) = 3072$; λ(Mo-K_α) 0.7107 Å, μ(Mo-K_α) 93.4 cm^{-1}. Systematic absences $hk0$, $h \neq 2n$; $h0l$, $l \neq 2n$; $0kl$, $k \neq 2n$; $h00$, $h \neq 2n$; $0k0$, $k \neq 2n$; $00l$, $l \neq 2n$ defined the space group $Pbca$.

Structure determination and refinement

The structure was solved by Patterson, Fourier and MULTAN-78 methods. The positions of the two unique tungsten atoms were determined by direct methods [18] and confirmed by a three-dimensional Patterson map. Three cycles of full-matrix least-squares refined the positional parameters for the W atoms to give an R index 0.149. The remaining 32 non-hydrogen atoms were located from a three-dimensional difference Fourier map, phased on the W atoms. Two cycles of least-squares refinement, including scale factor and individual isotropic thermal parameters for all atoms reduced the R index to 0.071. After other two refinement cycles with individual anisotropic thermal parameters, the R index dropped to 0.032. At this point a three-dimensional difference Fourier synthesis revealed the approximate positions of the 24 hydrogen atoms. The subsequent least-squares refinement, including the hydrogen atoms with the same isotropic thermal parameters as the atom to which they are attached, reduced the conventional R index down to 0.028 ($R_w = 0.031$) after three cycles.

At all stages of the structure analysis, the observed reflections were given unit weights. Attempts to use weights $= \sigma^{-2}$ $(|F_0|)$, made at the end of the refinement, did not lead to better results. Anomalous dispersion effects were included in the scattering factors for W.

The atomic scattering factors for the non-hydrogen atoms were taken from the International Tables [19], while for hydrogen atoms those of Stewart et al. [20] were chosen.

The final atomic coordinates and thermal parameters are listed in Tables 1 and 2. A list of observed and calculated structure factors is available from the author on request.

TABLE 1

FINAL COORDINATES (with e.s.d.'s in parentheses)

Atom	x	y	z
W(1)	0.39055(2)	0.45249(2)	0.23217(2)
W(2)	0.33956(2)	0.24540(2)	0.13791(2)
N(1)	0.3323(3)	0.4144(2)	0.1192(3)
N(2)	0.3189(3)	0.3515(3)	0.0885(3)
N(1′)	0.4551(3)	0.3566(3)	0.2143(3)
N(2′)	0.4401(3)	0.2937(3)	0.1857(4)
C(3)	0.2852(4)	0.3791(4)	0.0055(4)
C(4)	0.2959(4)	0.4548(4)	0.0467(4)
C(5)	0.2074(6)	0.3525(7)	−0.0103(7)
C(6)	0.3344(7)	0.3615(6)	−0.0699(6)
C(7)	0.2261(5)	0.4927(5)	0.0772(6)
C(8)	0.3472(6)	0.5069(5)	0.0009(7)
C(3′)	0.5178(4)	0.2656(4)	0.1931(6)
C(4′)	0.5361(3)	0.3413(4)	0.2263(5)
C(5′)	0.5247(8)	0.2064(8)	0.2581(15)
C(6′)	0.5493(6)	0.2453(14)	0.1095(12)
C(7′)	0.5608(8)	0.3483(10)	0.3167(9)
C(8′)	0.5835(6)	0.3867(8)	0.1685(13)
C(9)	0.4484(6)	0.4874(5)	0.3349(7)
C(10)	0.3329(4)	0.5415(4)	0.2457(6)
C(11)	0.4590(5)	0.5155(4)	0.1601(6)
C(12)	0.3180(5)	0.4105(5)	0.3210(6)
C(13)	0.3634(5)	0.1487(5)	0.1854(7)
C(14)	0.2455(5)	0.2051(4)	0.0900(6)
C(15)	0.3859(6)	0.2085(6)	0.0286(7)
C(16)	0.2752(4)	0.2614(4)	0.2454(6)
O(9)	0.4785(5)	0.5093(5)	0.3936(6)
O(10)	0.3012(4)	0.5946(3)	0.2574(5)
O(11)	0.4955(4)	0.5554(4)	0.1251(6)
O(12)	0.2780(4)	0.3960(4)	0.3751(5)
O(13)	0.3762(4)	0.0932(3)	0.2126(5)
O(14)	0.1921(4)	0.1811(4)	0.0638(5)
O(15)	0.4107(5)	0.1811(5)	−0.0314(6)
O(16)	0.2339(4)	0.2617(4)	0.3005(5)
H(5a)	0.1797(40)	0.3564(41)	0.0472(50)
H(5b)	0.2012(46)	0.3066(44)	−0.0257(57)
H(5c)	0.1844(43)	0.3826(43)	−0.0454(53)
H(6a)	0.3251(44)	0.3181(44)	−0.0782(51)
H(6b)	0.3792(44)	0.3719(46)	−0.0544(53)
H(6c)	0.3206(45)	0.3839(43)	−0.1150(51)
H(7a)	0.1918(38)	0.4552(40)	0.1217(47)
H(7b)	0.2408(42)	0.5373(42)	0.0993(48)
H(7b)	0.1915(43)	0.4985(44)	0.0235(52)
H(8a)	0.3551(42)	0.5432(43)	0.0292(48)
H(8b)	0.3825(46)	0.4834(47)	−0.0143(57)
H(8c)	0.3223(42)	0.5226(40)	−0.0549(51)
H(5′a)	0.4985(60)	0.2161(60)	0.3088(71)
H(5′b)	0.5121(57)	0.1653(56)	0.2314(69)
H(5′c)	0.5815(56)	0.2029(52)	0.2689(67)
H(6′a)	0.5373(60)	0.1985(59)	0.0903(78)
H(6′b)	0.5301(59)	0.2773(62)	0.0664(69)
H(6′c)	0.6061(53)	0.2528(58)	0.1033(63)

(Continued)

TABLE 1 (continued)

Atom	x	y	z
H(7'a)	0.5994(60)	0.3125(61)	0.3255(70)
H(7'b)	0.5762(61)	0.3944(65)	0.3343(76)
H(7'c)	0.5231(58)	0.3338(66)	0.3595(71)
H(8'a)	0.5871(63)	0.4313(62)	0.1969(81)
H(8'b)	0.5608(64)	0.3891(69)	0.1046(71)
H(8'c)	0.6310(58)	0.3685(58)	0.1615(69)

Results and discussion

The crystal structure of the $[W(N_2C_2Me_4)(CO)_4]_2$ complex consists of discrete dimeric molecules. Interatomic distances and bond angles, uncorrected for the effects of thermal motion, are given in Table 3. A representation of the molecule with the numbering scheme, drawn with the program ORTEP [21], is shown in Fig. 1.

Each W atom is in a deformed octahedral arrangement, bonded to four carbon atoms of carbonyl groups and to two *cis* nitrogen atoms of two 3,3,4,4-tetramethyl-1,2-diazetine ligands. The metal atoms have virtual C_{2v} symmetry and the whole molecule also has virtual C_{2v} symmetry with a mirror plane passing through W(1) and W(2) atoms and N(1)-N(1′), N(2)-N(2′), C(3)-C(3′) and C(4)-C(4′) midpoints and with an other mirror plane passing through W(1)-W(2), N(1)-N(2), N(1′)-N(2′), C(3)-C(4) and C(3′)-C(4′) midpoints.

In fact the molecule exhibits no crystallographic symmetry and all atoms occupy general positions. This complex shows five carbonyl IR stretching bands [15] instead of the four bands expected for a local C_{2v} symmetry of the two $W(CO)_4$ units, and this suggests that in solution the molecule retains the asymmetrical solid state structure with some interaction between the *cis*-substituted $W(CO)_4$ units. The molecule has a "folded book" shape, with an angle of 131.2° between the planes defined by W(1)–W(2)–N(1)–N(2) and W(1)–W(2)–N(1′)–N(2′), which are at their turn nearly coplanar with the N(1)–N(2)–C(3)–C(4) and N(1′)–N(2′)–C(3′)–C(4′) ligand rings, respectively.

The best planes in the molecule, the displacements of atoms from them (with e.s.d.'s in parentheses) and the dihedral angles are given in Table 4. The quantity $\Sigma(d/\sigma\perp)^2$ distributed like χ^2 $(n = 1)$ for the planes I, II and III is 83.58, 1.17 and 18.90, respectively; the probability (P), that the ligand rings I and II are non-planar is $P > 99\%$ and $P = 72\%$, respectively. Plane III leaves W(1) and W(2) out of this on the same side; the four nitrogen atoms are not coplanar with a probability $P > 99\%$ and their deviations from the best plane III show that the puckering of the hexa-atomic W(1)-N(1)-N(2)-W(2)-N(2′)-N(1′) ring is best regarded as a distorted skew conformation, rather than a boat shape. There is no evidence of W · · · W interaction, since the corresponding distance is 4.230 Å.

The W–N bond lengths (mean value 2.160 Å) are slightly shorter than those in a tungsten complex of substituted formamidine, 2.18(3) Å [22]. These sufficiently long distances, the large W–N–N angles and the acute N–W–N angles (mean values

(Continued on p. 369)

TABLE 2

THERMAL PARAMETERS (with e.s.d.'s in parentheses)[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
W(1)	0.00207(1)	0.00194(1)	0.00353(1)	0.00002(1)	−0.00001(1)	−0.00055(1)
W(2)	0.00204(1)	0.00169(1)	0.00405(1)	−0.00018(1)	−0.00003(1)	−0.00021(1)
N(1)	0.0018(1)	0.0017(1)	0.0032(2)	0.0001(1)	0.0004(2)	0.0005(2)
N(2)	0.0022(2)	0.0019(2)	0.0027(2)	−0.0005(1)	−0.0001(2)	0.0001(2)
N(1′)	0.0017(2)	0.0019(2)	0.0042(3)	0.0001(1)	−0.0002(2)	−0.0002(2)
N(2′)	0.0018(2)	0.0021(2)	0.0045(3)	−0.0001(1)	0.0002(2)	0.0001(2)
C(3)	0.0028(2)	0.0032(3)	0.0026(3)	−0.0003(2)	0.0002(2)	0.0004(2)
C(4)	0.0031(2)	0.0024(2)	0.0029(3)	0.0002(2)	−0.0002(2)	0.0003(2)
C(5)	0.0032(4)	0.0052(4)	0.0062(6)	−0.0011(4)	−0.0014(3)	0.0008(4)
C(6)	0.0057(4)	0.0048(4)	0.0032(4)	−0.0007(4)	−0.0001(4)	0.0000(3)
C(7)	0.0036(4)	0.0037(3)	0.0058(5)	0.0009(3)	0.0000(3)	0.0002(3)
C(8)	0.0044(4)	0.0032(3)	0.0059(5)	0.0001(3)	0.0007(4)	0.0020(3)
C(3′)	0.0016(2)	0.0028(3)	0.0102(6)	0.0007(2)	−0.0004(3)	−0.0006(3)
C(4′)	0.0019(2)	0.0031(2)	0.0053(4)	0.0001(2)	−0.0002(2)	0.0004(3)
C(5′)	0.0046(5)	0.0042(5)	0.0303(26)	−0.0005(4)	−0.0070(10)	0.0065(10)
C(6′)	0.0024(4)	0.0185(16)	0.0167(17)	0.0014(8)	0.0003(7)	−0.0119(15)
C(7′)	0.0072(7)	0.0109(9)	0.0090(8)	0.0048(7)	−0.0050(6)	−0.0050(8)
C(8′)	0.0028(4)	0.0065(6)	0.0206(18)	0.0010(4)	0.0038(7)	0.0046(9)
C(9)	0.0039(4)	0.0039(4)	0.0060(6)	−0.0006(3)	−0.0004(4)	−0.0009(4)
C(10)	0.0032(3)	0.0026(3)	0.0052(5)	0.0002(2)	0.0001(3)	−0.0015(3)
C(11)	0.0026(3)	0.0022(3)	0.0071(6)	−0.0002(2)	−0.0006(3)	−0.0012(3)
C(12)	0.0036(3)	0.0030(3)	0.0038(4)	0.0002(2)	−0.0006(3)	−0.0009(3)
C(13)	0.0026(3)	0.0021(3)	0.0078(6)	−0.0002(2)	0.0005(3)	−0.0001(3)

(Continued)

TABLE 2 (continued)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(14)	0.0034(3)	0.0018(2)	0.0074(6)	−0.0004(2)	−0.0005(4)	−0.0001(3)
C(15)	0.0045(4)	0.0045(4)	0.0061(5)	0.0000(4)	0.0005(4)	−0.0017(4)
C(16)	0.0027(3)	0.0016(2)	0.0062(5)	−0.0001(2)	−0.0001(3)	0.0001(3)
O(9)	0.0082(5)	0.0071(4)	0.0073(5)	−0.0010(4)	−0.0029(4)	−0.0033(4)
O(10)	0.0057(3)	0.0033(2)	0.0097(5)	0.0019(2)	0.0005(3)	−0.0018(3)
O(11)	0.0041(3)	0.0033(2)	0.0125(6)	−0.0016(2)	0.0019(3)	0.0005(3)
O(12)	0.0059(4)	0.0067(4)	0.0055(4)	−0.0010(3)	0.0029(3)	−0.0011(3)
O(13)	0.0047(3)	0.0021(2)	0.0097(5)	0.0001(2)	−0.0012(3)	0.0004(2)
O(14)	0.0046(3)	0.0039(3)	0.0113(6)	−0.0022(2)	−0.0033(3)	−0.0001(3)
O(15)	0.0075(5)	0.0081(5)	0.0075(5)	0.0010(4)	0.0017(4)	−0.0039(4)
O(16)	0.0045(3)	0.0036(2)	0.0083(4)	0.0004(2)	0.0032(3)	0.0009(3)

Atom	B (Å^2)	Atom	B (Å^2)	Atom	B (Å^2)
H(5a)	5.81	H(7c)	5.17	H(6′b)	14.96
H(5b)	5.81	H(8a)	5.34	H(6′c)	14.96
H(5c)	5.81	H(8b)	5.34	H(7′a)	11.09
H(6a)	5.74	H(8c)	5.34	H(7′b)	11.09
H(6b)	5.74	H(5′a)	13.71	H(7′c)	11.09
H(6c)	5.74	H(5′b)	13.71	H(8′a)	10.87
H(7a)	5.17	H(5′c)	13.71	H(8′b)	10.87
H(7b)	5.17	H(6′a)	14.96	H(8′c)	10.87

[a] The anisotropic parameters are in the form: exp $-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)$

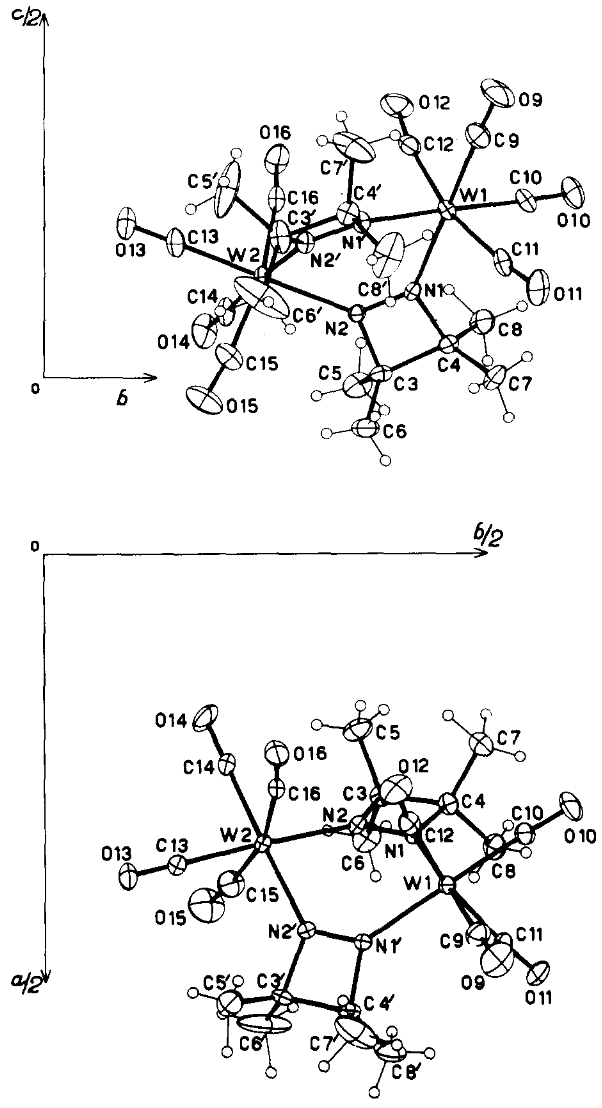

Fig. 1 ORTEP representations and numbering scheme of atoms, down *a* and *c* axes of cell. Thermal ellipsoids enclose 20% of the electron density.

133.0 and 83.5°, respectively) together ensure adequate separation of the two $W(CO)_4$ units; the shortest intramolecular contact $O(12)\cdots O(16)$ is thus 2.871 Å. All the carbonyl groups are terminal; the W–C bond lengths (mean value 2.020 Å) can be compared with known values: 2.01 [23], 2.00 [24], 1.976 [25] and 1.97 Å [26].

When the W–CO bonds in *trans* positions to the nitrogen atoms are compared with those in *cis* positions, it is seen that the former bonds are significantly shortened (1.997 vs. 2.043 Å). There is an evident *trans*-effect of the diazetine ligand, which is a stronger σ-donor than CO groups (and so a poorer π-acceptor): the π back-bonds are stronger for W–CO in *trans* positions to the nitrogen atoms and

TABLE 3

INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) (with e.s.d.'s in parentheses)

W(1)···W(2)	4.230(1)		
In the coordination octahedra			
W(1)–N(1)	2.165(5)	W(2)–N(2)	2.154(5)
W(1)–N(1′)	2.155(5)	W(2)–N(2′)	2.165(5)
W(1)–C(9)	2.016(10)	W(2)–C(13)	1.995(9)
W(1)–C(10)	1.972(8)	W(2)–C(14)	2.006(10)
W(1)–C(11)	2.043(9)	W(2)–C(15)	2.012(11)
W(1)–C(12)	2.059(9)	W(2)–C(16)	2.057(9)
N(1)–W(1)–N(1′)	83.6(2)	N(2)–W(2)–N(2′)	83.5(2)
N(1)–W(1)–C(10)	96.0(3)	N(2)–W(2)–C(14)	93.7(3)
N(1)–W(1)–C(11)	92.4(3)	N(2)–W(2)–C(15)	95.0(3)
N(1)–W(1)–C(12)	96.0(3)	N(2)–W(2)–C(16)	93.2(2)
N(1′)–W(1)–C(9)	95.0(3)	N(2′)–W(2)–C(13)	93.9(3)
N(1′)–W(1)–C(11)	94.3(3)	N(2′)–W(2)–C(15)	94.5(4)
N(1′)–W(1)–C(12)	96.8(3)	N(2′)–W(2)–C(16)	98.1(3)
C(9)–W(1)–C(10)	85.4(4)	C(13)–W(2)–C(14)	89.0(3)
C(9)–W(1)–C(11)	86.0(4)	C(13)–W(2)–C(15)	84.9(4)
C(9)–W(1)–C(12)	85.8(4)	C(13)–W(2)–C(16)	87.4(4)
C(10)–W(1)–C(11)	84.1(3)	C(14)–W(2)–C(15)	85.1(4)
C(10)–W(1)–C(12)	84.8(3)	C(14)–W(2)–C(16)	82.7(4)
In the carbonyls			
C(9)–O(9)	1.137(14)	C(13)–O(13)	1.142(11)
C(10)–O(10)	1.160(10)	C(14)–O(14)	1.141(12)
C(11)–O(11)	1.134(11)	C(15)–O(15)	1.154(14)
C(12)–O(12)	1.143(12)	C(16)–O(16)	1.136(11)
W(1)–C(9)–O(9)	176.8(9)	W(2)–C(13)–O(13)	179.3(7)
W(1)–C(10)–O(10)	176.5(8)	W(2)–C(14)–O(14)	178.8(8)
W(1)–C(11)–O(11)	173.7(8)	W(2)–C(15)–O(15)	173.7(9)
W(1)–C12)–O(12)	171.0(8)	W(2)–C(16)–O(16)	169.8(7)
In the 3,3,4,4-tetramethyl-3,4-dihydrodiazete ligands			
N(1)–N(2)	1.288(7)	N(1′)–N(2′)	1.282(7)
N(1)–C(4)	1.506(8)	N(1′)–C(4′)	1.508(8)
N(2)–C(3)	1.514(8)	N(2′)–C(3′)	1.508(9)
C(3)–C(4)	1.561(10)	C(3′)–C(4′)	1.539(11)
C(3)–C(5)	1.515(13)	C(3′)–C(5′)	1.500(20)
C(3)–C(6)	1.508(13)	C(3′)–C(6′)	1.466(21)
C(4)–C(7)	1.525(11)	C(4′)–C(7′)	1.477(17)
C(4)–C(8)	1.521(12)	C(4′)–C(8′)	1.503(17)
C(5)–H(5a)	1.03(8)	C(5′)–H(5′a)	0.94(11)
C(5)–H(5b)	0.90(8)	C(5′)–H(5′b)	0.90(11)
C(5)–H(5c)	0.89(8)	C(5′)–H(5′c)	1.05(10)
C(6)–H(6a)	0.84(8)	C(6′)–H(6′a)	0.95(11)
C(6)–H(6b)	0.87(8)	C(6′)–H(6′b)	0.96(11)
C(6)–H(6c)	0.85(8)	C(6′)–H(6′c)	1.04(10)
C(7)–H(7a)	1.16(7)	C(7′)–H(7′a)	0.98(11)
C(7)–H(7b)	0.94(8)	C(7′)–H(7′b)	0.94(12)
C(7)–H(7c)	1.05(8)	C(7′)–H(7′c)	0.99(11)
C(8)–H(8a)	0.82(8)	C(8′)–H(8′a)	0.94(12)
C(8)–H(8b)	0.81(9)	C(8′)–H(8′b)	1.07(11)
C(8)–H(8c)	1.02(8)	C(8′)–H(8′c)	0.93(11)
W(1)–N(1)–N(2)	133.6(4)	W(1)–N(1′)–N(2′)	133.4(4)
W(2)–N(2)–N(1)	132.1(4)	W(2)–N(2′)–N(1′)	132.7(4)
W(1)–N(1)–C(4)	130.8(4)	W(1)–N(1′)–C(4′)	132.1(4)

TABLE 3 (continued)

W(2)–N(2)–C(3)	133.2(4)	W(2)–N(2′)–C(3′)	131.9(4)
N(1)–N(2)–C(3)	94.7(5)	N(1′)–N(2′)–C(3′)	95.4(5)
N(2)–C(3)–C(4)	84.8(5)	N(2′)–C(3′)–C(4′)	84.7(5)
C(3)–C(4)–N(1)	84.7(5)	C(3′)–C(4′)–N(1′)	85.5(5)
C(4)–N(1)–N(2)	95.5(5)	C(4′)–N(1′)–N(2′)	94.4(5)
N(1)–C(4)–C(7)	111.3(6)	N(1′)–C(4′)–C(7′)	113.3(8)
N(1)–C(4)–C(8)	113.6(6)	N(1′)–C(4′)–C(8′)	112.1(7)
C(7)–C(4)–C(8)	110.9(7)	C(7′)–C(4′)–C(8′)	110.1(1.0)
C(3)–C(4)–C(7)	116.2(6)	C(3′)–C(4′)–C(7′)	117.6(9)
C(3)–C(4)–C(8)	117.6(6)	C(3′)–C(4′)–C(8′)	116.0(9)
N(2)–C(3)–C(5)	113.8(6)	N(2′)–C(3′)–C(5′)	112.6(8)
N(2)–C(3)–C(6)	110.3(7)	N(2′)–C(3′)–C(6′)	112.8(8)
C(5)–C(3)–C(6)	110.8(8)	C(5′)–C(3′)–C(6′)	111.9(1.3)
C(4)–C(3)–C(5)	118.5(7)	C(4′)–C(3′)–C(5′)	115.5(1.0)
C(4)–C(3)–C(6)	116.1(7)	C(4′)–C(3′)–C(6′)	116.7(1.1)
C(3)–C(5)–H(5a)	107(4)	C(3′)–C(5′)–H(5′a)	112(7)
C(3)–C(5)–H(5b)	118(5)	C(3′)–C(5′)–H(5′b)	107(7)
C(3)–C(5)–H(5c)	109(5)	C(3′)–C(5′)–H(5′c)	104(6)
H(5a)–C(5)–H(5b)	104(7)	H(5′a)–C(5′)–H(5′b)	115(10)
H(5a)–C(5)–H(5c)	105(7)	H(5′a)–C(5′)–H(5′c)	112(9)
H(5b)–C(5)–H(5c)	112(8)	H(5′b)–C(5′)–H(5′c)	106(9)
C(3)–C(6)–H(6a)	102(6)	C(3′)–C(6′)–H(6′a)	115(7)
C(3)–C(6)–H(6b)	107(6)	C(3′)–C(6′)–H(6′b)	108(7)
C(3)–C(6)–H(6c)	111(6)	C(3′)–C(6′)–H(6′c)	116(6)
H(6a)–C(6)–H(6b)	117(8)	H(6′a)–C(6′)–H(6′b)	106(10)
H(6a)–C(6)–H(6c)	107(8)	H(6′a)–C(6′)–H(6′c)	109(9)
H(6b)–C(6)–H(6c)	113(8)	H(6′b)–C(6′)–H(6′c)	102(9)
C(4)–C(7)–H(7a)	110(4)	C(4′)–C(7′)–H(7′a)	107(6)
C(4)–C(7)–H(7b)	107(5)	C(4′)–C(7′)–H(7′b)	116(7)
C(4)–C(7)–H(7c)	107(4)	C(4′)–C(7′)–H(7′c)	114(6)
H(7a)–C(7)–H(7b)	118(6)	H(7′a)–C(7′)–H(7′b)	112(10)
H(7a)–C(7)–H(7c)	102(6)	H(7′a)–C(7′)–H(7′c)	102(9)
H(7b)–C(7)–H(7c)	112(6)	H(7′b)–C(7′)–H(7′c)	105(10)
C(4)–C(8)–H(8a)	113(5)	C(4′)–C(8′)–H(8′a)	105(7)
C(4)–C(8)–H(8b)	106(6)	C(4′)–C(8′)–H(8′b)	111(7)
C(4)–C(8)–H(8c)	108(4)	C(4′)–C(8′)–H(8′c)	113(7)
H(8a)–C(8)–H(8b)	118(8)	H(8′a)–C(8′)–H(8′b)	115(10)
H(8a)–C(8)–H(8c)	107(7)	H(8′a)–C(8′)–H(8′c)	108(10)
H(8b)–C(8)–H(8c)	105(8)	H(8′b)–C(8′)–H(8′c)	105(9)

there is a corresponding shortening of these W–CO distances.

The W–C–O angles are in the range 179.3–169.8°, but those of the groups *cis* are quite deformed compared with those *trans* to the nitrogen atoms. This bending of the former angles can be attributed to repulsions between non-bonded atoms.

The C–O bond lengths are in the range 1.160–1.134 Å (mean value 1.143 Å) and can be compared with known values: 1.148 [23] and 1.149 Å [25]. The structural details of the ligand ring are similar to those found in the complex (3,3,4,4-tetramethyl-1,2-diazetine) $Fe_2(CO)_7$ [14]. The N–N bond length (1.285 Å) is greater than that for a localized double bond. The two nitrogen lone-pairs of the ligand contribute to the whole ring bonding, and when the ligand coordinates to metals by σ-donation a weakening of the N–N bond occurs; there is also a weak π-backbon-

TABLE 4

LEAST-SQUARES PLANES AND DIHEDRAL ANGLES

Plane	Equation	Atoms	Displacements (Å)
I	$0.8907X + 0.0338Y - 0.4534Z - 4.7709 = 0$	W(1)	0.1904(3)
		W(2)	−0.1009(3)
		N(1) [a]	0.020(5)
		N(2) [a]	−0.020(5)
		C(3) [a]	0.036(7)
		C(4) [a]	−0.032(7)
II	$0.1829X + 0.3059Y - 0.9343Z - 0.4407 = 0$	W(1)	0.0710(3)
		W(2)	0.0867(3)
		N(1′) [a]	−0.002(5)
		N(2′) [a]	0.003(6)
		C(3′) [a]	−0.006(9)
		C(4′) [a]	0.004(8)
III	$0.6065X + 0.1726Y - 0.7761Z - 3.5637 = 0$	W(1)	−0.6062(3)
		W(2)	−0.6988(3)
		N(1) [a]	−0.010(5)
		N(2) [a]	0.010(5)
		N(1′) [a]	0.011(5)
		N(2′) [a]	−0.013(5)
		C(3)	0.726(7)
		C(4)	0.592(7)
		C(3′)	0.663(9)
		C(4′)	0.708(7)

Dihedral angles (°)

I/II	126.6	I/III	153.9	II/III	152.7

[a] These atoms were included in the calculation of the plane.

ding from metal to vacant π^* molecular orbital of the ligand. The bond lengths in the ligand rings, 1.509 Å for C–N and 1.550 Å for C–C, are consistent with single bonds. Steric strain in the ligand rings affects the geometry around nitrogen atoms, which deviates remarkably from the virtual sp^2 hybridization (95.0, 132.0 and 133.0 vs. 120°) and the geometry of carbon atoms, which deviates remarkably from the virtual sp^3 hybridization (84.9, 110.9, 111.9, 113.0, 116.6 and 116.9 vs. 109.5°). The C–H distances in the methyl groups show an average value of 0.95 Å, in agreement with known values. The symmetrical coordination of the two ligands to the $W(CO)_4$ units affords only a single signal in the ^{1}H NMR spectrum for all hydrogen atoms at δ 0.9 ppm, very close to the signal for the free ligand at δ 0.95 ppm [15]. The thermal motion of C(5), C(6), C(7) and C(8) atoms appears to be significantly smaller than that of the corresponding carbon atoms of the second ligand.

The packing of the molecules in the crystal is determined by O···O Van der Waals approaches; no hydrogen atom is closer than 2.6 Å to atoms in other molecules. The shortest intermolecular approach distances are listed in Table 5.

The oxidation number of W in this diazene σ-complex is 0. The W atoms have

TABLE 5

SHORTEST INTERMOLECULAR CONTACT DISTANCES (Å)

C(7)····O(13)(i)	3.371	O(10)···C(16)(i)	3.408
C(8)····O(14)(i)	3.465	O(10)···O(16)(i)	3.248
O(9)····O(13)(ii)	3.478	O(11)···C(5')(ii)	3.367
O(10)···C(13)(i)	3.341	O(11)···O(13)(ii)	3.498
O(10)···O(13)(i)	3.291	C(12)···O(15)(iv)	3.313
O(10)···C(14)(i)	3.419	O(12)···C(8)(iii)	3.499
O(10)···O(14)(i)	3.410	O(12)···O(15)(iv)	3.155

Symmetry code

(i)	$-x+1/2$	$y+1/2$	z
(ii)	$-x+1$	$y+1/2$	$-z+1/2$
(iii)	$-x+1/2$	$-y+1$	$z+1/2$
(iv)	x	$-y+1/2$	$z+1/2$

nine valence-shell orbitals, but they make major use of only six in the complexes, to give σ-bonds. Diazetine bridging the two W atoms acts as bidentate four electron ligand (one lone pair for each nitrogen atom). The frontier molecular orbitals of an N=N group arise from the two "lone pairs" localized on each nitrogen atom and the π-bonding pair: in the sequence of increasing energy, these frontier orbitals are $n_2^2\, \pi^2\, n_1^2\, \pi^\star$, where the lone pairs contribute essentially to the n_2 and n_1 orbitals and the shared pair contributes essentially to the π orbital. Both n_2 and n_1 orbitals are involved in the complex formation, while the vacant $\pi^\star$ orbital, whose energy lies in the region of the vacant antibonding metal levels ($d^\star_{x^2-y^2}$, $d^\star_{z^2}$), allows a weak π back-bonding from the occupied nonbonding metal levels (d_{xz}, d_{yz}). The lower the energy of the ligand vacant $\pi^\star$ orbital, the greater the double bond character of the M–N bond. This π acceptor capability of diazetine is greater than that of five- to seven-membered diazenes, since for the latter ones an increasing localization of the lone pairs on the N=N group is expected (with better σ-donor properties and stronger M–N bonds); on the contrary, diazetine exhibits smaller π-acceptor capability than three-membered diazenes, which are poorer σ-donors [15].

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