

suggested previously<sup>2a</sup> that bridging through the amide nitrogen more readily takes place in the actinide series than in the early d transition series because of a reduced ligand  $p\pi$  to metal orbital  $\pi$  interaction in the f series. This reduction allows the amide nitrogen atom to more easily become tetrahedral and act as a bridging atom. Consequently the actinide amides may tend to oligomerize and/or be more thermally unstable than analogous d transition compounds. The recent report of the isolation of  $Zr(N(i\text{-Pr})_2)_4$  by sublimation at 120 °C ( $10^{-3}$  mmHg)<sup>11</sup> supports this suggestion since the analogous U compound was not isolated by Jones et al.<sup>2b</sup> nor by our group to date. However, much work remains to be done on these compounds in both f and d transition series.

Registry No.  $U_3(\text{dmed})_6$ , 61202-81-1;  $U(\text{NEt}_2)_4$ , 40678-59-9.

Supplementary Material Available: Listings of structure factors and formulas used in data reduction (10 pages). Ordering information is given on any current masthead page.

## References and Notes

- (1) This work was done with support from the U.S. Energy Research and Development Administration.
- (2) (a) J. G. Reynolds, A. Zalkin, D. H. Templeton, N. M. Edelstein, and L. K. Templeton, *Inorg. Chem.*, **15**, 2498 (1976); (b) R. G. Jones, G. Karmas, G. A. Martin, Jr., and H. Gilman, *J. Am. Chem. Soc.*, **78**, 4285 (1956).
- (3) For a review of metal dialkylamides and the methods of synthesis see D. C. Bradley, *Adv. Inorg. Chem. Radiochem.*, **15**, 259 (1972).
- (4) H. St. Råde, *J. Phys. Chem.*, **77**, 424 (1973).
- (5) L. K. Templeton and D. H. Templeton, Abstracts, American Crystallographic Association Proceedings, Series 2, Vol. 1, 1973, p 143.
- (6) E. Pignataro and B. Post, *Acta Crystallogr.*, **8**, 672 (1955).
- (7) R. D. Burbank, W. E. Falconer, and W. A. Sunder, *Science*, **178**, 1285 (1972).
- (8) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3d ed, Interscience, New York, N.Y., 1972, p 650.
- (9) G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, "Properties of the Thirty-Two Point Groups", M.I.T. Press, Cambridge, Mass., 1963.
- (10) J. G. Reynolds, A. Zalkin, D. H. Templeton, and N. M. Edelstein, to be submitted for publication.
- (11) C. Airolidi and D. C. Bradley, *Inorg. Nucl. Chem. Lett.*, **11**, 155 (1975).

Contribution from the Departments of Chemistry, Princeton University, Princeton, New Jersey 08540, and Texas A&M University, College Station, Texas 77843

## The Tungsten–Tungsten Triple Bond. 6. Hexakis(*N,N*-dimethylcarbamato)ditungsten and Dimethyltetakis(*N,N*-diethylcarbamato)ditungsten. Structures and Dynamical Solution Behavior

MALCOLM H. CHISHOLM,<sup>1a</sup> F. ALBERT COTTON,<sup>1b</sup> MICHAEL W. EXTINE,<sup>1a</sup> and B. RAY STULTS<sup>1b</sup>

Received August 11, 1976

AIC605870

$W_2(\text{NMe}_2)_6$  and  $W_2\text{Me}_2(\text{NEt}_2)_4$  each react with carbon dioxide to give  $W_2(\text{O}_2\text{CNMe}_2)_6$ , I, and  $W_2\text{Me}_2(\text{O}_2\text{CNEt}_2)_4$ , II, respectively. Single-crystal x-ray structural analyses show that both I and II are dinuclear and contain tungsten to tungsten triple bonds ( $W\equiv W_{av} = 2.275 \text{ \AA}$ ) bridged by two dialkylcarbamato,  $\text{O}_2\text{CNR}_2$ , ligands. Crystal parameters are as follows:  $W_2(\text{O}_2\text{CNMe}_2)_6$ ,  $P\bar{1}$ ,  $a = 12.018$  (2)  $\text{ \AA}$ ,  $b = 16.516$  (4)  $\text{ \AA}$ ,  $c = 11.630$  (3)  $\text{ \AA}$ ,  $\alpha = 111.09$  (2)°,  $\beta = 107.26$  (2)°,  $\gamma = 91.00$  (2)°,  $Z = 2$ ;  $R_1 = 0.073$ ; for  $W_2\text{Me}_2(\text{O}_2\text{CNEt}_2)_4$ ,  $P2_1/c$ ,  $a = 16.014$  (4)  $\text{ \AA}$ ,  $b = 10.433$  (4)  $\text{ \AA}$ ,  $c = 18.983$  (5)  $\text{ \AA}$ ,  $\beta = 107.51$  (2)°,  $Z = 4$ ,  $R_1 = 0.040$ . In both compounds each tungsten atom is at the apex of an irregular pentagonal pyramid. The basal vertices of each pyramid are defined by the two oxygen atoms of the bidentate nonbridging carbamato ligand ( $W\text{--}O_{av} = 2.16 \text{ \AA}$ ), one oxygen atom from each of the two bridging carbamato groups ( $W\text{--}O_{av} = 2.08 \text{ \AA}$ ), and either an oxygen atom from the other carbamato ligand ( $W\text{--}O_{av} = 2.07 \text{ \AA}$ ) in compound I or a methyl group ( $W\text{--}C_{av} = 2.20 \text{ \AA}$ ) in compound II. In compound I, the second oxygen atom from the nonbridging carbamato ligand is weakly bonded ( $W\text{--}O_{av} = 2.67 \text{ \AA}$ ) along an extension of the tungsten-to-tungsten triple bond. NMR studies show that, while I and II retain their structures in solution, both molecules are fluxional. The low-temperature  $^1\text{H}$  NMR spectra for  $W_2(\text{O}_2\text{CNMe}_2)_6$  provide a slow-exchange limiting spectrum at  $-60 \text{ }^\circ\text{C}$ , consisting of four signals of relative intensities 4:4:2:2, consistent with the structure found in the solid state which has approximate  $C_{2v}$  symmetry. As the temperature is raised, these four signals are seen to collapse and eventually re-form as a sharp singlet ( $+70 \text{ }^\circ\text{C}$ ) showing that all three ligands undergo rapid scrambling. The low-temperature limiting  $^{13}\text{C}$  NMR spectrum ( $-60 \text{ }^\circ\text{C}$ ) consists of three resonances of relative intensities 1:1:1 assignable to the carboxylic carbons and four resonances of relative intensities 4:4:2:2 assignable to the methyl carbons. As the temperature is raised, three processes are observed, which are, in order of increasing energy, (i) the interchange of proximal and distal methyl groups of the unsymmetrically bonded bidentate  $\text{O}_2\text{CNMe}_2$  ligand, (ii) interchange of the nonbridging ligands, and (iii) interchange of nonbridging and bridging carbamato ligands. Variable-temperature  $^1\text{H}$  NMR studies on  $W_2\text{Me}_2(\text{O}_2\text{CNEt}_2)_4$  indicate that at  $+80 \text{ }^\circ\text{C}$  exchange between bridging and nonbridging carbamato ligands is rapid on the NMR time scale.

## Introduction

Tungsten, unlike its neighbors molybdenum and rhenium, has not yet been shown conclusively to form compounds containing metal-to-metal quadruple bonds,<sup>2</sup> despite the existence of scores of well-characterized, quadruply bonded compounds for molybdenum and rhenium.<sup>28</sup> However, recent work from our laboratories has shown that there exists an extensive series of compounds containing tungsten-to-tungsten triple bonds, e.g.,  $W_2(\text{NR}_2)_6$ , where  $R = \text{Me}^3$  and  $\text{Et}$ ,<sup>3</sup> and  $W_2(\text{NEt}_2)_4\text{X}_2$ , where  $X = \text{Cl}$ ,<sup>4</sup>  $\text{Br}$ ,<sup>5</sup>  $\text{I}$ ,<sup>5</sup>  $\text{Me}$ ,<sup>6</sup> and  $\text{CH}_2\text{SiMe}_3$ .<sup>5</sup> There is also the compound  $W_2(\text{CH}_2\text{SiMe}_3)_6$  reported first by Wilkinson<sup>7</sup> and recently structurally characterized by us.<sup>8</sup> In addition, the alkoxides  $W_2(\text{OR})_6$ ,<sup>9</sup> where  $R = t\text{-Bu}$  and  $\text{SiMe}_3$ , appear to be members of a structurally related series  $M_2L_6$ ,

where  $M = \text{Mo}$  and  $W$  and  $L = R$  (alkyl),<sup>10</sup>  $\text{NR}_2$ ,<sup>11</sup> and  $\text{OR}$ ,<sup>12</sup> containing metal-to-metal triple bonds unsupported by bridging ligands. In the preceding paper<sup>5</sup> we described chlorine atom substitution reactions involving  $W_2\text{Cl}_2(\text{NEt}_2)_4$ : an extensive chemistry of compounds of the type  $W_2X_2(\text{NEt}_2)_4$  where  $X$  is a univalent anionic ligand was implicated. The transition metal–nitrogen bond in early transition metal dialkylamides,  $M(\text{NR}_2)_n$ , is known to be reactive toward a number of exchange and insertion reactions.<sup>13</sup> Thus an extension of the dinuclear chemistry of trivalent tungsten might be anticipated from the compounds  $W_2(\text{NR}_2)_6$  and  $W_2X_2(\text{NR}_2)_4$ . In this paper we describe our characterization of  $W_2(\text{O}_2\text{CNMe}_2)_6$ , I, and  $W_2\text{Me}_2(\text{O}_2\text{CNEt}_2)_4$ , II, formed by the reactions of carbon dioxide with  $W_2(\text{NMe}_2)_6$  and  $W_2\text{Me}_2(\text{NEt}_2)_4$ , re-

Table I. Positional and Anisotropic Thermal Parameters<sup>a</sup> for the Anisotropically Refined Atoms in W<sub>2</sub>[O<sub>2</sub>CN(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub>

Atom	x	y	z	β <sub>11</sub>	β <sub>22</sub>	β <sub>33</sub>	β <sub>12</sub>	β <sub>13</sub>	β <sub>23</sub>
W(1)	0.825 02 (4)	0.303 74 (5)	0.099 45 (3)	0.004 96 (3)	0.007 09 (5)	0.002 54 (2)	0.001 22 (6)	0.003 19 (3)	0.000 71 (5)
W(2)	0.683 52 (4)	0.269 84 (5)	0.031 63 (3)	0.005 29 (3)	0.006 73 (4)	0.002 56 (2)	-0.001 37 (6)	0.003 38 (3)	-0.000 57 (5)
O(1)	0.784 9 (6)	0.350 2 (8)	0.190 5 (4)	0.006 3 (5)	0.008 7 (8)	0.002 8 (3)	0.002 (1)	0.004 0 (5)	-0.001 1 (8)
O(2)	0.643 1 (6)	0.328 8 (9)	0.120 6 (5)	0.005 7 (5)	0.011 5 (10)	0.003 2 (3)	-0.003 (1)	0.003 7 (6)	-0.003 0 (9)
O(3)	0.854 8 (6)	0.355 7 (9)	0.003 9 (5)	0.005 9 (5)	0.010 3 (9)	0.003 2 (3)	0.002 (1)	0.004 6 (6)	0.003 3 (9)
O(4)	0.717 1 (6)	0.308 5 (8)	-0.063 4 (5)	0.005 0 (4)	0.010 0 (9)	0.003 1 (3)	-0.001 (1)	0.004 3 (5)	0.001 5 (8)
O(5)	0.853 1 (7)	0.133 0 (9)	0.168 9 (5)	0.010 8 (6)	0.010 1 (10)	0.003 2 (3)	0.007 (1)	0.007 1 (6)	0.001 4 (9)
O(6)	0.899 3 (7)	-0.148 1 (9)	0.074 2 (5)	0.010 0 (6)	0.012 7 (10)	0.003 8 (3)	0.011 (1)	0.008 0 (6)	0.005 9 (10)
O(7)	0.643 2 (7)	0.101 2 (9)	0.077 6 (5)	0.010 5 (6)	0.008 4 (9)	0.003 7 (3)	-0.004 (1)	0.006 6 (7)	-0.002 1 (9)
O(8)	0.683 9 (7)	0.087 5 (8)	-0.021 4 (5)	0.010 3 (6)	0.006 4 (8)	0.004 3 (8)	-0.003 (1)	0.006 8 (7)	-0.000 2 (9)
N(1)	0.675 7 (8)	0.416 (1)	0.235 3 (6)	0.007 7 (7)	0.010 (1)	0.003 5 (4)	0.003 (2)	0.005 6 (8)	0.001 (1)
N(2)	0.813 9 (8)	0.388 (1)	-0.118 1 (6)	0.007 0 (6)	0.009 (1)	0.002 9 (3)	0.003 (1)	0.004 5 (7)	0.002 (1)
N(3)	0.920 9 (11)	-0.040 (1)	0.138 2 (8)	0.022 7 (11)	0.017 (2)	0.005 5 (5)	0.025 (2)	0.016 2 (10)	0.008 (1)
N(4)	0.643 3 (11)	-0.098 (1)	0.024 1 (7)	0.019 5 (11)	0.007 (1)	0.005 1 (5)	-0.009 (2)	0.011 1 (11)	0.001 (1)
C(1)	0.702 5 (9)	0.363 (1)	0.179 7 (6)	0.007 4 (7)	0.007 (1)	0.002 5 (3)	0.001 (2)	0.006 5 (7)	0.000 (1)
C(2)	0.793 3 (9)	0.350 (1)	-0.058 1 (6)	0.006 3 (7)	0.007 (1)	0.002 0 (4)	0.004 (2)	0.003 2 (8)	0.002 (1)
C(3)	0.892 5 (10)	0.081 (1)	0.126 9 (8)	0.008 4 (9)	0.013 (2)	0.003 7 (5)	0.009 (2)	0.005 2 (11)	0.003 (2)
C(4)	0.657 5 (11)	0.029 (1)	0.027 2 (9)	0.008 1 (10)	0.010 (2)	0.005 4 (7)	-0.005 (2)	0.002 7 (13)	-0.002 (2)
C(5)	0.839 9 (10)	0.515 (1)	0.107 1 (8)	0.007 4 (9)	0.008 (1)	0.004 1 (5)	-0.003 (2)	0.004 6 (10)	-0.002 (1)
C(6)	0.625 3 (9)	0.457 (1)	-0.003 7 (9)	0.004 3 (7)	0.009 (1)	0.005 5 (6)	0.000 (2)	0.003 6 (10)	0.000 (2)

<sup>a</sup> Figures in parentheses are the estimated standard deviations in the least significant figures. The form of the anisotropic thermal parameter is  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$ .

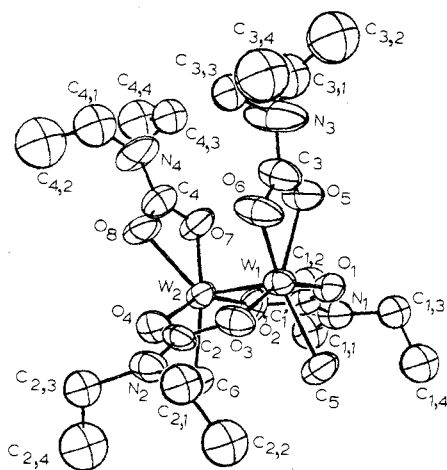


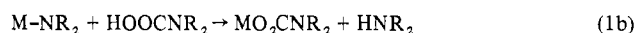
Figure 1. Drawing of the W<sub>2</sub>Me<sub>2</sub>(O<sub>2</sub>CNEt<sub>2</sub>)<sub>4</sub> molecule, II. The atom-numbering scheme is defined. Each atom is represented by a thermal vibration ellipsoid enclosing 50% of its electron density. Hydrogen atoms are omitted and only one of the two orientations of each of the disordered ethyl groups is shown.

spectively. The tungsten-to-tungsten triple bond is maintained in the reaction products. A preliminary report of this work has been published.<sup>14</sup>

### Results and Discussion

**Syntheses.** The preparation of W<sub>2</sub>(O<sub>2</sub>CNMe<sub>2</sub>)<sub>6</sub>, I, and W<sub>2</sub>Me<sub>2</sub>(O<sub>2</sub>CNEt<sub>2</sub>)<sub>4</sub>, II, from the reaction between carbon

dioxide and W<sub>2</sub>(NMe<sub>2</sub>)<sub>6</sub> and W<sub>2</sub>Me<sub>2</sub>(NEt<sub>2</sub>)<sub>4</sub>, respectively, has been described in detail elsewhere.<sup>15</sup> The mechanism of the carbon dioxide insertion reaction involving mononuclear early transition metal dialkylamides, M(NR<sub>2</sub>)<sub>n</sub> + nCO<sub>2</sub> → M-(O<sub>2</sub>CNR<sub>2</sub>)<sub>n</sub>, was also studied and was shown to involve catalysis by the fortuitous presence of amine in solutions of M(NR<sub>2</sub>)<sub>n</sub> according to the sequence



In the absence of HNEt<sub>2</sub>, W<sub>2</sub>Me<sub>2</sub>(NEt<sub>2</sub>)<sub>4</sub> did not react with CO<sub>2</sub>.<sup>16</sup> It is also interesting to note that the weak acid Et<sub>2</sub>NCOOH attacks preferentially, if not exclusively, the tungsten-nitrogen bond. The reaction W-Me + HOOCNEt<sub>2</sub> → WO<sub>2</sub>CNEt<sub>2</sub> + CH<sub>4</sub> would quench the catalytic cycle (1).

**Structural Results.** W<sub>2</sub>(O<sub>2</sub>CNEt<sub>2</sub>)<sub>4</sub>Me<sub>2</sub>. The crystal is composed of discrete molecules. All atoms of the molecule occupy positions of general crystallographic symmetry in space group P2<sub>1</sub>/c and there is no crystallographic symmetry imposed on the molecules. However, each molecule has approximate C<sub>2v</sub> symmetry if the orientations of the ethyl groups are ignored.

A perspective drawing of the molecule along with the atom-labeling scheme is shown in Figure 1. A stereoview of a single molecule is shown in Figure 2. A listing of atomic coordinates and thermal parameters for those atoms refined anisotropically is given in Table I, while Table II contains the atomic coordinates and the refined isotropic thermal pa-

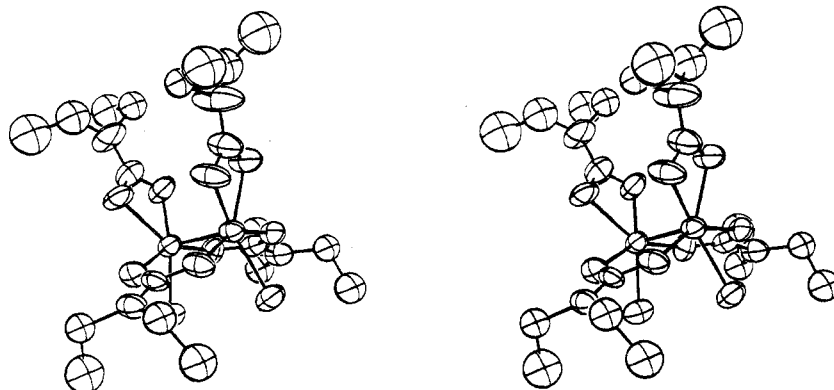


Figure 2. Stereoview of the W<sub>2</sub>Me<sub>2</sub>(O<sub>2</sub>CNEt<sub>2</sub>)<sub>4</sub> molecule, II.

**Table II.** Positional and Isotropic Thermal Parameters<sup>a</sup> for the Isotropically Refined Atoms in  $W_2[O_2CN(C_2H_5)_2]_4(CH_3)_2$ 

Atom	x	y	z	$B_{iso}, \text{Å}^2$
C(1,1)	0.5780 (11)	0.438 (2)	0.2248 (10)	7.2 (5)
C(1,2)	0.5472 (14)	0.327 (2)	0.2657 (13)	9.7 (6)
C(1,3)	0.7434 (10)	0.456 (1)	0.3039 (9)	5.5 (3)
C(1,4)	0.7727 (12)	0.594 (2)	0.2999 (10)	7.4 (5)
C(2,1)	0.9012 (10)	0.442 (1)	-0.1112 (9)	5.4 (3)
C(2,2)	0.9096 (12)	0.582 (2)	-0.0861 (10)	7.0 (4)
C(2,3)	0.7432 (9)	0.388 (1)	-0.1932 (8)	4.9 (3)
C(2,4)	0.6884 (13)	0.506 (2)	-0.2045 (12)	8.8 (6)
C(3,1)	0.8885 (13)	-0.131 (2)	0.1925 (11)	8.4 (5)
C(3,2)	0.9712 (16)	-0.170 (3)	0.2433 (14)	11.0 (7)
C(3,3)	0.9393 (18)	-0.106 (3)	0.0749 (15)	4.7 (6)
C(3,4)	1.0306 (28)	-0.098 (4)	0.0867 (24)	9.7 (12)
C(3,5)	0.9986 (21)	-0.078 (3)	0.0947 (18)	5.8 (8)
C(3,6)	0.9227 (27)	-0.147 (4)	0.0359 (24)	9.0 (11)
C(4,1)	0.6738 (13)	-0.175 (2)	-0.0338 (11)	8.1 (5)
C(4,2)	0.5889 (17)	-0.186 (3)	-0.0953 (15)	12.1 (8)
C(4,3)	0.6421 (21)	-0.169 (3)	0.0942 (18)	5.9 (7)
C(4,4)	0.5558 (28)	-0.200 (4)	0.0749 (25)	9.3 (12)
C(4,5)	0.5688 (20)	-0.137 (3)	0.0739 (17)	5.6 (7)
C(4,6)	0.6279 (24)	-0.229 (4)	0.1286 (22)	7.1 (9)

<sup>a</sup> Figures in parentheses are the estimated standard deviations in the least significant figures.

**Table III.** Bond Distances<sup>a</sup> (Å) within  $W_2[O_2CN(C_2H_5)_2]_4(CH_3)_2$ 

W(1)–W(2)	2.272 (1)	N(1)–C(1,1)	1.53 (1)
W(1)–O(1)	2.074 (9)	–C(1,3)	1.48 (2)
–O(3)	2.080 (8)	N(2)–C(2,1)	1.48 (2)
–O(5)	2.181 (9)	–C(2,3)	1.53 (2)
–O(6)	2.150 (9)	N(3)–C(3,1)	1.60 (2)
–C(5)	2.216 (13)	–C(3,3)	1.49 (4)
W(2)–O(2)	2.076 (9)	–C(3,5)	1.73 (5)
–O(4)	2.072 (8)	N(4)–C(4,1)	1.56 (2)
–O(7)	2.148 (9)	–C(4,3)	1.53 (4)
–O(8)	2.154 (9)	–C(4,5)	1.78 (4)
–C(6)	2.185 (13)	C(1,1)–C(1,2)	1.56 (3)
C(1)–O(1)	1.28 (2)	C(1,3)–C(1,4)	1.52 (2)
–O(2)	1.28 (2)	C(2,1)–C(2,2)	1.53 (2)
–N(1)	1.37 (2)	C(2,3)–C(2,4)	1.49 (2)
C(2)–O(3)	1.29 (2)	C(3,1)–C(3,2)	1.44 (3)
–O(4)	1.27 (2)	C(3,3)–C(3,4)	1.41 (6)
–N(2)	1.34 (2)	C(3,5)–C(3,6)	1.56 (6)
C(3)–O(5)	1.28 (2)	C(4,1)–C(4,2)	1.51 (3)
–O(6)	1.25 (2)	C(4,3)–C(4,4)	1.36 (6)
–N(3)	1.34 (2)	C(4,5)–C(4,6)	1.52 (5)
C(4)–O(7)	1.29 (2)		
–O(8)	1.28 (2)		
–N(4)	1.34 (2)		

<sup>a</sup> Figures in parentheses are the estimated standard deviations of the least significant figures.

rameters for the ethyl carbon atoms. The bond distances and bond angles for  $W_2(O_2CNEt_2)_4Me_2$  are given in Tables III and IV, respectively. Some pertinent molecular planes are described in Table V.

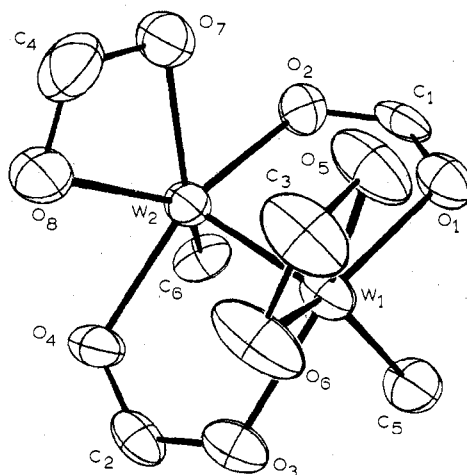
The only unusual feature within the molecule is the disorder observed for two of the ethyl groups, one bonded to N(3) and the other to N(4). For each of the nonbridging bidentate carbamate ligands one of the two ethyl groups is disordered (50:50) in such a way that the dihedral angle between N(3)–C(3,1)–C(3,3) and N(3)–C(3,1)–C(3,5) is 37.1° and the angle between the planes N(4)–C(4,1)–C(4,3) and N(4)–C(4,1)–C(4,5) is 46.2° (see Table V). No unusual short intermolecular contacts were observed.

Figure 3 shows just the central skeleton of the molecule and is helpful in examining the coordination about the metal atoms. The virtual  $C_{2v}$  symmetry is quite obvious in this representation. One symmetry plane contains C(3), C(4), W(1), W(2), C(5), and C(6), while the other contains C(1) and C(2) and is perpendicular to the W(1)–W(2) bond. The W–O bond lengths fall into two groups. For oxygen atoms belonging to

**Table IV.** Bond Angles<sup>a</sup> (deg) within  $W_2[O_2CN(C_2H_5)_2]_4(CH_3)_2$ 

W(2)–W(1)–O(1)	90.2 (3)	C(1)–O(1)–W(1)	116.9 (8)
–O(3)	89.9 (3)	–O(2)–W(2)	117.5 (8)
–O(5)	102.8 (3)	C(2)–O(3)–W(1)	118.1 (9)
–O(6)	106.3 (3)	–O(4)–W(2)	119.5 (8)
–C(5)	105.1 (4)	C(3)–O(5)–W(1)	91.0 (8)
W(1)–W(2)–O(2)	89.7 (3)	–O(6)–W(1)	93.1 (9)
–O(4)	89.3 (3)	C(4)–O(7)–W(2)	92.0 (9)
–O(7)	105.5 (3)	–O(8)–W(2)	92.1 (9)
–O(8)	105.1 (3)	O(1)–C(1)–O(2)	125 (1)
–C(6)	107.2 (4)	O(3)–C(2)–O(4)	123 (1)
O(1)–W(1)–O(3)	151.0 (3)	O(5)–C(3)–O(6)	116 (1)
–O(5)	75.3 (3)	O(7)–C(4)–O(8)	115 (1)
–O(6)	133.9 (3)	N(1)–C(1)–O(1)	118 (1)
–C(5)	76.5 (4)	–O(2)	118 (1)
O(3)–W(1)–O(5)	132.8 (3)	N(2)–C(2)–O(3)	117 (1)
–O(6)	73.4 (3)	–O(4)	121 (1)
–C(5)	75.5 (4)	N(3)–C(3)–O(5)	120 (1)
O(5)–W(1)–O(6)	59.4 (3)	–O(6)	123 (1)
–C(5)	140.8 (5)	N(4)–C(4)–O(7)	123 (2)
O(6)–W(1)–C(5)	135.2 (5)	–O(8)	122 (2)
O(2)–W(2)–O(4)	151.3 (4)	N(1)–C(1,1)–C(1,2)	101 (2)
–O(7)	72.9 (4)	–C(2,3)–C(1,4)	112 (1)
–O(8)	133.5 (4)	N(2)–C(2,1)–C(2,2)	112 (1)
–C(6)	77.0 (5)	–C(2,3)–C(2,4)	112 (1)
O(4)–W(2)–O(7)	134.6 (3)	N(3)–C(3,1)–C(3,2)	101 (2)
–O(8)	74.2 (3)	–C(3,3)–C(3,4)	107 (4)
–C(6)	75.9 (5)	–C(3,5)–C(3,6)	86 (4)
O(7)–W(2)–O(8)	60.7 (3)	N(4)–C(4,1)–C(4,2)	101 (2)
–C(6)	134.9 (5)	–C(4,3)–C(4,4)	99 (3)
O(8)–W(2)–C(6)	135.1 (5)	–C(4,5)–C(4,6)	97 (3)
C(1)–N(1)–C(1,1)	120 (1)	C(1,1)–N(1)–C(1,3)	121 (1)
–C(1,3)	118 (1)	C(2,1)–N(2)–C(2,3)	120 (1)
C(2)–N(2)–C(2,1)	121 (1)	C(3,1)–N(3)–C(3,3)	115 (2)
–C(2,3)	119 (1)	–C(3,5)	126 (2)
C(3)–N(3)–C(3,1)	120 (1)	C(3,3)–N(3)–C(3,5)	33 (2)
–C(3,3)	117 (2)	C(4,1)–N(4)–C(4,3)	117 (2)
–C(3,5)	113 (2)	–C(4,5)	131 (2)
C(4)–N(4)–C(4,1)	117 (2)	C(4,3)–N(4)–C(4,5)	40 (2)
–C(4,3)	119 (2)		
–C(4,5)	110 (2)		

<sup>a</sup> Figures in parentheses are the estimated standard deviations in the least significant figures.

**Figure 3.** Central skeleton of the  $W_2Me_2(O_2CNEt_2)_4$  molecule.

bridging  $O_2CNEt_2$  groups, the distances are shorter, ranging from 2.072 to 2.080 Å, with an average value of  $2.075 \pm 0.003$  Å. The other four W–O distances are appreciably longer, ranging from 2.148 to 2.181 Å, with an average value of  $2.158 \pm 0.011$  Å. This difference of ca. 0.08 Å is probably attributable to the fact that the oxygen atoms of the bridging carbamate groups can form bonds to the tungsten atoms along very favorable directions whereas the formation of four-membered rings by the nonbridging carbamate ligands leads

Table V. Unit-Weighted Mean Planes<sup>a</sup> for  $W_2[O_2CN(C_2H_5)_2]_4(CH_3)_2$ 

Plane	Atoms in plane	Equation of mean plane			
		A	B	C	D
I	O(1)-O(2)-C(1)-N(1)-C(1,1)-C(1,3)	0.1676	0.9057	-0.3893	3.8768
II	O(3)-O(4)-C(2)-N(2)-C(2,1)-C(2,3)	0.3557	-0.9223	-0.1509	1.4281
III	O(5)-O(6)-C(3)-N(3)	-0.7388	-0.3372	-0.5835	-11.6364
IV	O(7)-O(8)-C(4)-N(4)	-0.8136	0.1425	-0.5637	-8.6644
V	W(1)-W(2)-O(1)-O(2)	0.0458	0.9559	-0.2902	3.0512
VI	W(1)-W(2)-O(3)-O(4)	0.2791	-0.9559	-0.0919	0.2976
VII	N(3)-C(3,1)-C(3,3)	-0.5075	-0.3652	-0.7804	-8.8843
VIII	N(3)-C(3,1)-C(3,5)	-0.8197	0.1421	-0.5548	-12.8895
IX	N(4)-C(4,1)-C(4,3)	-0.8496	-0.2801	-0.4470	-8.5457
X	N(4)-C(4,1)-C(4,5)	-0.5560	0.3892	-0.7344	-6.3681

Displacement of Atoms from Mean Plane, Å			
Plane I	O(1)	0.015	
	O(2)	-0.009	
	C(1)	-0.002	
	N(1)	-0.015	
	C(1,1)	0.016	
Plane III	O(5)	0.005	
	O(6)	0.005	
	C(3)	-0.015	
	N(3)	0.005	
	Plane V	W(1)	-0.034
W(2)		0.034	
O(1)		-0.034	
O(2)		0.034	
Plane II	O(3)	0.000	
	O(4)	-0.010	
	C(2)	0.001	
	N(2)	0.036	
	C(2,1)	-0.017	
Plane IV	O(7)	0.004	
	O(8)	0.004	
	C(4)	-0.011	
	N(4)	0.004	
	Plane VI	W(1)	-0.037
W(2)		0.037	
O(3)		-0.037	
O(4)		0.037	

Dihedral Angles between Planes, Deg			
I-II	135.8	I-V	9.5
V-VI	137.5	II-VI	5.8
VII-VIII	37.1	IX-X	46.2

<sup>a</sup> The equation for the plane is of the form:  $Ax + By + Cz - D = 0$ .

to strain and hence weakening of the W-O bonds.

The W-C distances, with a mean value of  $2.201 \pm 0.015$  Å, are slightly longer than those previously found in  $W_2-(NEt_2)_4Me_2$  (2.17 Å) and  $W_2(CH_2SiMe_3)_6$  (2.14 Å), a result probably attributable to the higher coordination number of the metal atom in the present case.

The W-W-O angles also vary depending on whether the O atom belongs to a bridging or nonbridging carbamate group. For those involving the bridging groups, the angles average  $89.8 \pm 0.3^\circ$ , while the other four angles average  $104.9 \pm 0.8^\circ$ . The W-W-C angles average  $106.1 \pm 0.6^\circ$ . Thus, the set of five ligand atoms about each tungsten atom deviate considerably from coplanarity.

As expected, the O-W-O angles subtended by the pairs of oxygen atoms belonging to the nonbridging carbamate ligands are relatively small,  $60.0 \pm 0.6^\circ$ , whereas the other O-W-O and O-W-C angles are approximately  $75^\circ$ .

The W-W distance, 2.272 (1) Å, is typical of those found in related compounds containing the W-W triple bond. These others range from 2.254 Å in  $W_2(CH_2SiMe_3)_6$  to 2.301 Å in  $W_2Cl_2(NEt_2)_4$ .<sup>4</sup>

The angle between the planes defined by the W-W bond and each of the pairs of oxygen atoms of bridging carbamate groups, planes V and VI in Table V, is  $137.5^\circ$ .

$W_2(O_2CNMe_2)_6 \cdot C_7H_8$ . This crystalline compound is composed of discrete molecules but contains in addition one toluene molecule ( $C_7H_8$ ), as solvent of crystallization, for each ditungsten molecule. Again, while there is no imposed crystallographic symmetry, the molecule has virtual  $C_{2v}$  symmetry.

A perspective drawing of the molecule showing the atom-labeling scheme as well as the labeling scheme for the toluene molecule is shown in Figure 4. A stereoscopic drawing is presented in Figure 5. The refined positional and thermal parameters for all atoms are given in Table VI. The bond distances are reported in Table VII and the bond angles are

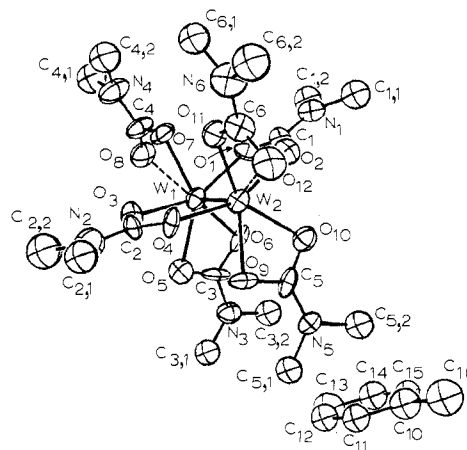


Figure 4. Drawing of the  $W_2(O_2CNMe_2)_6$  molecule, I. The atom-numbering scheme is defined. Each atom is represented by a thermal vibration ellipsoid enclosing 50% of its electron density. Hydrogen atoms are omitted. Also shown is the molecule of toluene of crystallization with its numbering scheme defined.

given in Table VIII. Pertinent least-squares mean planes are given in Table IX. Again, no short intermolecular contacts were observed.

Figure 6 presents a view of the central skeleton of the molecule and facilitates inspection of the coordination geometry. It is apparent that the general arrangement is nearly identical with that in  $W_2(O_2CNEt_2)_4Me_2$ , except that the two methyl groups are here replaced by oxygen atoms from two additional carbamate ligands. The W-O distances to the latter, averaging  $2.065 \pm 0.015$  Å, are similar to the W-O distances involving the bridging carbamates,  $2.08 \pm 0.03$  Å, and shorter than those to oxygen atoms of the nonbridging carbamates,  $2.16 \pm 0.015$  Å. The W-W distance here, 2.279 Å, is very similar to that, 2.272 Å, in the dimethyl compound.

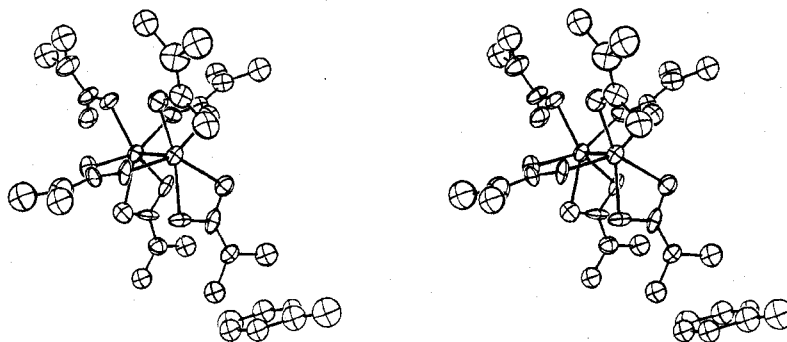


Figure 5. Stereoview of the  $W_2(O_2CNMe_2)_6$  molecule, I, and its accompanying toluene of crystallization.

Table VI. Refined Positional and Thermal Parameters<sup>a</sup> for  $W_2(O_2CNMe_2)_6$

Atom	x	y	z	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
W(1)	0.237 07 (9)	0.298 61 (7)	0.278 33 (9)	0.006 12 (8)	0.004 81 (5)	0.009 09 (9)	0.0009 (1)	0.0033 (1)	0.007 26 (9)
W(2)	0.071 78 (8)	0.300 68 (7)	0.120 73 (9)	0.004 94 (8)	0.004 61 (4)	0.009 88 (9)	0.0010 (1)	0.0040 (1)	0.006 94 (9)
O(1)	0.289 (1)	0.206 (1)	0.130 (2)	0.007 (1)	0.003 8 (8)	0.011 (2)	0.002 (2)	0.004 (3)	0.003 (2)
O(2)	0.129 (1)	0.210 (1)	-0.015 (2)	0.007 (1)	0.005 7 (9)	0.011 (2)	-0.001 (2)	0.001 (3)	0.004 (2)
O(3)	0.146 (2)	0.333 (1)	0.411 (2)	0.010 (2)	0.006 9 (10)	0.010 (2)	0.001 (2)	0.009 (2)	0.006 (2)
O(4)	-0.015 (1)	0.339 (1)	0.260 (1)	0.010 (1)	0.007 8 (9)	0.011 (1)	0.003 (2)	0.015 (2)	0.012 (2)
O(5)	0.285 (1)	0.436 (1)	0.396 (2)	0.006 (1)	0.005 9 (9)	0.013 (2)	-0.001 (2)	0.007 (2)	0.005 (2)
O(6)	0.373 (1)	0.375 (1)	0.255 (1)	0.008 (1)	0.006 8 (8)	0.012 (1)	-0.001 (2)	0.005 (2)	0.014 (1)
O(7)	0.191 (2)	0.179 (1)	0.285 (2)	0.011 (2)	0.004 4 (7)	0.014 (2)	-0.001 (2)	0.009 (3)	0.009 (2)
O(8)	0.368 (2)	0.216 (1)	0.420 (2)	0.013 (2)	0.006 6 (9)	0.014 (2)	0.003 (2)	0.002 (3)	0.012 (2)
O(9)	0.071 (1)	0.441 (1)	0.176 (2)	0.009 (2)	0.002 2 (6)	0.013 (2)	0.001 (2)	0.004 (3)	0.004 (2)
O(10)	0.138 (1)	0.367 (1)	0.022 (2)	0.008 (1)	0.005 3 (8)	0.013 (2)	0.003 (2)	0.009 (2)	0.008 (2)
O(11)	-0.018 (2)	0.184 (1)	0.088 (2)	0.009 (2)	0.006 0 (9)	0.012 (2)	0.003 (2)	0.007 (3)	0.008 (2)
O(12)	-0.142 (2)	0.236 (1)	-0.047 (2)	0.007 (2)	0.008 5 (12)	0.015 (2)	-0.003 (2)	0.000 (3)	0.006 (3)
N(1)	0.264 (2)	0.128 (1)	-0.074 (2)	0.009 (2)	0.004 7 (10)	0.016 (3)	0.002 (2)	0.008 (4)	0.007 (2)
N(2)	-0.012 (2)	0.381 (2)	0.464 (2)	0.012 (2)	0.007 7 (14)	0.017 (3)	0.001 (3)	0.010 (4)	0.010 (3)
N(3)	0.423 (2)	0.520 (1)	0.367 (2)	0.009 (2)	0.004 7 (10)	0.012 (2)	0.001 (2)	0.003 (4)	0.005 (2)
N(4)	0.264 (3)	0.098 (2)	0.394 (2)	0.015 (3)	0.006 5 (11)	0.020 (3)	0.001 (3)	0.003 (5)	0.015 (2)
N(5)	0.149 (2)	0.517 (1)	0.086 (2)	0.008 (2)	0.004 3 (9)	0.012 (2)	0.001 (2)	0.007 (3)	0.008 (2)
N(6)	-0.191 (2)	0.099 (2)	-0.043 (3)	0.005 (2)	0.008 6 (15)	0.021 (3)	-0.001 (3)	0.006 (4)	0.009 (3)
C(1)	0.226 (2)	0.184 (2)	0.019 (2)	0.004 (2)	0.005 0 (12)	0.009 (2)	-0.000 (3)	0.002 (3)	0.004 (3)
C(2)	0.039 (2)	0.351 (2)	0.374 (2)	0.013 (2)	0.004 7 (13)	0.010 (2)	0.003 (3)	0.018 (3)	0.003 (3)
C(3)	0.357 (3)	0.443 (1)	0.341 (2)	0.012 (3)	0.001 5 (9)	0.010 (3)	0.001 (3)	-0.010 (5)	0.000 (3)
C(4)	0.279 (2)	0.166 (2)	0.369 (2)	0.008 (2)	0.005 0 (11)	0.014 (2)	-0.001 (3)	-0.003 (4)	0.012 (2)
C(5)	0.122 (2)	0.445 (2)	0.093 (2)	0.005 (2)	0.007 7 (12)	0.012 (2)	0.002 (2)	0.009 (3)	0.014 (2)
C(6)	-0.118 (2)	0.175 (2)	-0.005 (3)	0.005 (2)	0.006 2 (14)	0.013 (3)	0.002 (3)	0.002 (4)	0.006 (3)

Atom	x	y	z	$B, \text{\AA}^2$	Atom	x	y	z	$B, \text{\AA}^2$
C(1,1)	0.194 (3)	0.100 (2)	-0.213 (3)	7.2 (9)	C(6,1)	-0.162 (3)	0.028 (2)	0.009 (3)	6.8 (8)
C(1,2)	0.382 (3)	0.102 (2)	-0.044 (3)	7.2 (9)	C(6,2)	-0.312 (3)	0.078 (2)	-0.140 (4)	8.7 (11)
C(2,1)	-0.135 (3)	0.398 (2)	0.435 (3)	7.5 (9)	C(10)	0.471 (4)	0.689 (3)	0.026 (4)	9.1 (11)
C(2,2)	0.054 (4)	-0.604 (3)	0.603 (4)	9.7 (12)	C(11)	0.431 (3)	0.714 (2)	0.150 (3)	7.0 (9)
C(3,1)	0.404 (3)	0.595 (2)	0.450 (3)	5.8 (7)	C(12)	0.522 (3)	0.726 (2)	0.258 (3)	7.1 (9)
C(3,2)	0.506 (3)	0.523 (2)	0.296 (3)	6.6 (8)	C(13)	0.643 (4)	0.722 (3)	0.279 (4)	11.1 (14)
C(4,1)	0.364 (4)	0.069 (3)	0.479 (4)	8.7 (11)	C(14)	0.674 (4)	0.696 (3)	0.159 (4)	8.8 (11)
C(4,2)	0.152 (3)	0.042 (2)	0.342 (3)	8.4 (10)	C(15)	0.596 (3)	0.679 (2)	0.042 (3)	5.9 (7)
C(5,1)	0.138 (3)	0.600 (2)	0.170 (3)	5.5 (7)	C(16)	0.383 (5)	0.665 (3)	-0.102 (5)	12.5 (16)
C(5,2)	0.201 (3)	0.521 (2)	-0.013 (3)	6.4 (8)					

<sup>a</sup> Values in parentheses are the estimated standard deviation in the least significant figures. The form of the anisotropic thermal parameter is  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$ .

The only qualitative difference in the two structures has to do with the weak coordination here of additional oxygen atoms in, or near, the axial positions, namely, along the extensions of the W-W bond direction. The second oxygen atom of each of the additional carbamate ligands occupies such a position. These W-O distances are quite long,  $2.67 \pm 0.01 \text{ \AA}$ , and, moreover, there is appreciable deviation from collinearity since the W-W-O angles are 151 and 153°.

The dihedral angle between the planes of the bridging ligands is 153.1° as compared to 137.5° in compound II. This can be correlated to the fact that the W-W-O angles involving the oxygen atoms that replace the methyl groups of compound II are 98.4° rather than about 106° as in the case of the W-W-O angles. Also the average of the W-W-O angles to

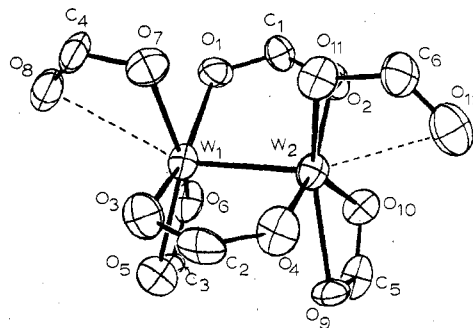


Figure 6. Central skeleton of the  $W_2(O_2CNMe_2)_6$  molecule. Dotted lines indicate the long, quasi-axial W-O bonds.

Table VII. Bond Distances<sup>a</sup> (Å) within  $W_2(O_2CNMe_2)_6 \cdot C_7H_8$ 

W(1)-W(2)	2.279 (1)	N(1)-C(1)	1.35 (2)
W(1)-O(1)	2.12 (1)	-C(1,1)	1.47 (3)
-O(3)	2.07 (1)	-C(1,2)	1.47 (3)
-O(5)	2.15 (1)	N(2)-C(2)	1.32 (2)
-O(6)	2.18 (1)	-C(2,1)	1.48 (3)
-O(7)	2.08 (1)	-C(2,2)	1.50 (3)
-O(8)	2.69 (1)	N(3)-C(3)	1.36 (3)
W(2)-O(2)	2.05 (1)	-C(3,1)	1.35 (3)
-O(4)	2.10 (1)	-C(3,2)	1.48 (3)
-O(9)	2.17 (1)	N(4)-C(4)	1.28 (3)
-O(10)	2.14 (1)	-C(4,1)	1.52 (3)
-O(11)	2.05 (1)	-C(4,2)	1.45 (3)
-O(12)	2.65 (1)	N(5)-C(5)	1.27 (3)
C(1)-O(1)	1.20 (2)	-C(5,1)	1.41 (3)
-O(2)	1.25 (2)	-C(5,2)	1.48 (3)
C(2)-O(3)	1.31 (3)	N(6)-C(6)	1.37 (3)
-O(4)	1.23 (3)	-C(6,1)	1.50 (3)
C(3)-O(5)	1.25 (2)	-C(6,2)	1.50 (3)
-O(6)	1.28 (2)	C(10)-C(11)	1.57 (4)
C(4)-O(7)	1.29 (2)	-C(15)	1.48 (4)
-O(8)	1.20 (2)	-C(16)	1.46 (4)
C(5)-O(9)	1.31 (2)	C(12)-C(11)	1.35 (3)
-O(10)	1.31 (2)	-C(13)	1.42 (4)
C(6)-O(11)	1.32 (2)	C(14)-C(13)	1.46 (4)
-O(12)	1.27 (3)	-C(15)	1.32 (3)

<sup>a</sup> Figures in parentheses are the estimated standard deviations in the least significant figures.

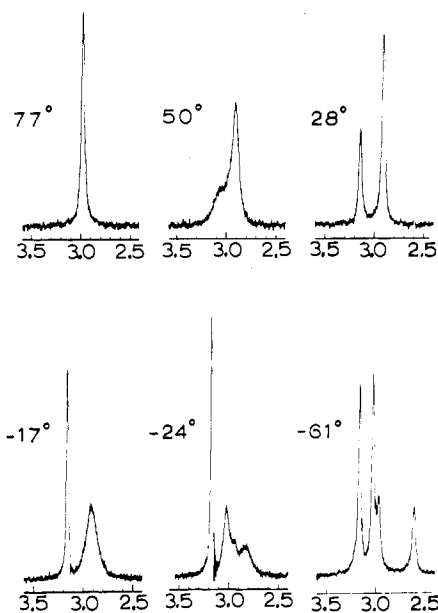


Figure 7. Proton NMR spectra of  $W_2(O_2CNMe_2)_6$ , I, at various temperatures. Chemical shifts are in parts per million downfield from hexamethyldisiloxane.

oxygen atoms of the nonbridging carbamate ligands are somewhat smaller here, viz.,  $101.7 \pm 1.2^\circ$  as compared to about  $105^\circ$  in compound II. Thus, there is greater crowding of all ligands toward a common plane and this results in a spreading of the angle between those W-O bonds from the bridging ligands. Presumably, the weak axial coordination is the principal cause of this crowding together of the other ligands.

**Remarks on Bonding.** It is interesting that the W≡W triple bond is maintained in these molecules even though the coordination number of the metal atoms is increased. In the  $W_2R_6$  and  $W_2X_2R_4$  molecules, the metal atoms make major use of only six of their nine valence-shell orbitals. Three are employed in the W≡W triple bonds and three more in the tungsten-ligand  $\sigma$  bonds. In the carbamate compounds described here the number of orbitals used by each metal atom

Table VIII. Bond Angles<sup>a</sup> (deg) within  $W_2(O_2CNMe_2)_6 \cdot C_7H_8$ 

W(2)-W(1)-O(1)	88.2 (3)	O(1)-C(1)-O(2)	124 (2)
-O(3)	89.5 (4)	O(3)-C(2)-O(4)	123 (2)
-O(5)	100.6 (4)	O(5)-C(3)-O(6)	119 (2)
-O(6)	102.9 (3)	O(7)-C(4)-O(8)	121 (2)
-O(7)	98.9 (4)	O(9)-C(5)-O(10)	111 (2)
-O(8)	150.8 (4)	O(11)-C(6)-O(12)	121 (2)
W(1)-W(2)-O(2)	88.7 (4)	N(1)-C(1)-O(1)	117 (2)
-O(4)	89.1 (4)	-O(2)	119 (2)
-O(9)	100.3 (3)	N(2)-C(2)-O(3)	117 (2)
-O(10)	102.9 (3)	-O(4)	120 (2)
-O(11)	97.8 (4)	N(3)-C(3)-O(5)	125 (2)
-O(12)	153.3 (4)	-O(6)	117 (3)
O(1)-W(1)-O(3)	152.5 (6)	N(4)-C(4)-O(7)	116 (2)
-O(5)	136.1 (5)	-O(8)	123 (2)
-O(6)	75.8 (6)	N(5)-C(5)-O(9)	122 (2)
-O(7)	76.1 (5)	-O(10)	127 (2)
O(3)-W(1)-O(5)	75.1 (6)	N(6)-C(6)-O(11)	114 (2)
-O(6)	131.2 (6)	-O(12)	126 (2)
-O(7)	77.2 (6)	C(1)-N(1)-C(1,1)	121 (2)
O(5)-W(1)-O(6)	60.3 (5)	-C(1,2)	122 (2)
-O(7)	142.4 (6)	C(2)-N(2)-C(2,1)	123 (2)
O(6)-W(1)-O(7)	143.6 (6)	-C(2,2)	121 (2)
O(2)-W(2)-O(4)	153.5 (6)	C(3)-N(3)-C(3,1)	120 (2)
-O(9)	132.3 (6)	-C(3,2)	122 (2)
-O(10)	72.1 (6)	C(4)-N(4)-C(4,1)	122 (2)
-O(11)	76.1 (5)	-C(4,2)	123 (2)
O(4)-W(2)-O(9)	74.0 (6)	C(5)-N(5)-C(5,1)	125 (2)
-O(10)	134.0 (6)	-C(5,2)	122 (2)
-O(11)	78.0 (6)	C(6)-N(6)-C(6,1)	125 (2)
O(9)-W(2)-O(10)	60.3 (5)	-C(6,2)	123 (2)
-O(11)	146.3 (5)	C(10)-C(11)-C(12)	112 (2)
O(10)-W(2)-O(11)	141.3 (6)	C(11)-C(12)-C(13)	132 (3)
W(1)-O(1)-C(1)	118 (1)	C(12)-C(13)-C(14)	113 (3)
-O(3)-C(2)	118 (1)	C(13)-C(14)-C(15)	124 (3)
W(2)-O(2)-C(1)	120 (1)	C(15)-C(10)-C(11)	118 (3)
-O(4)-C(2)	119 (1)	C(11)-C(10)-C(16)	120 (3)
W(1)-O(5)-C(3)	92 (1)	C(15)-C(10)-C(16)	122 (3)
-O(6)-C(3)	89 (1)		
W(2)-O(9)-C(5)	93 (1)		
-O(10)-C(5)	95 (1)		
W(1)-O(7)-C(4)	107 (1)		
W(2)-O(11)-C(6)	105 (1)		

<sup>a</sup> Figures in parentheses are the estimated standard deviations in the least significant figures.

increases to 8 in the case of  $W_2Me_2(O_2CNEt_2)_4$  and nine in  $W_2(O_2CNMe_2)_6$ .

A simple analysis of the symmetry types of orbitals required to form the bonds and a consideration of the symmetry properties of the metal valence-shell orbitals lead to the following qualitative formulation of the electronic structures of these molecules. We assume that the W≡W bond is formed primarily by overlap of metal  $d_{z^2}$  orbitals to give the  $\sigma$  component and metal  $d_{xz}$  and  $d_{yz}$  orbitals to give the  $\pi$  components. This is in accord with the assumption originally made<sup>17</sup> and subsequently supported by SCF  $X\alpha$  calculations<sup>18,19</sup> for the quadruple bonds in  $Re_2Cl_8^{2-}$  and  $Mo_2Cl_8^{4-}$ . For the five quasi-coplanar bonds to the ligands we may then use the  $s$ ,  $p_x$ ,  $p_y$ ,  $d_{xy}$ , and  $d_{x^2-y^2}$  orbitals. In the case of  $W_2(O_2CNMe_2)_6$ , the  $p_z$  orbitals may be employed to help form the weak axial W-O bonds.

**NMR Studies.**  $W_2(O_2CNMe_2)_6$ . This compound is only sparingly soluble in toluene but is appreciably soluble in methylene chloride and apparently quite stable in this solvent,<sup>20</sup> allowing its use as a spectroscopic solvent. <sup>1</sup>H NMR spectra for  $W_2(O_2CNMe_2)_6$  in  $CH_2Cl_2$  at various temperatures are shown in Figure 7. The low-temperature limiting spectrum is attained at  $-60^\circ C$  and consists of four sharp signals of relative intensities 4:4:2:2 assignable to the methyl groups of the  $O_2CNMe_2$  ligands. This is entirely consistent with the freezing out of the ground-state structure (Figures 4-6) which has approximate  $C_{2v}$  symmetry. As the temperature is in-

Table IX. Unit-Weighted Mean Planes<sup>a</sup> for  $W_2(O_2CNMe_2)_6C_7H_8$ 

Plane	Atoms in plane	Equation of mean plane			
		A	B	C	D
I	O(1)–O(2)–C(1)–N(1)–C(1,1)–C(1,2)	0.4580	0.8863	–0.0681	3.8116
II	O(3)–O(4)–C(2)–N(2)–C(2,1)–C(2,2)	–0.2763	–0.9471	–0.1636	–4.3421
III	O(5)–O(6)–C(3)–N(3)–C(3,1)–C(3,2)	–0.5282	0.4471	–0.7219	–1.4775
IV	O(7)–O(8)–C(4)–N(4)–C(4,1)–C(4,2)	0.5691	–0.2690	–0.7770	–2.1022
V	O(9)–O(10)–C(5)–N(5)–C(5,1)–C(5,2)	–0.7436	0.1710	–0.6464	–0.1849
VI	O(11)–O(12)–C(6)–N(6)–C(6,1)–C(6,2)	0.6750	–0.1772	–0.7163	–1.4805
VII	W(1)–W(2)–O(1)–O(2)	0.5227	0.8459	–0.1056	3.8176
VIII	W(1)–W(2)–O(3)–O(4)	–0.2201	–0.9472	–0.2333	–4.5997

Displacement of Atoms from Mean Plane, Å					
Plane I	O(1)	–0.015	Plane II	O(3)	0.038
	O(2)	0.037		O(4)	–0.020
	C(1)	–0.008		C(2)	–0.019
	N(1)	–0.055		N(2)	–0.010
	C(1,1)	–0.002		C(2,1)	0.032
	C(1,2)	0.043		C(2,2)	–0.021
	W(1)	0.142		W(1)	–0.174
	W(2)	0.215		W(2)	–0.177
Plane III	O(5)	–0.012	Plane IV	O(7)	0.075
	O(6)	0.022		O(8)	–0.070
	C(3)	–0.002		C(4)	0.002
	N(4)	–0.033		N(4)	–0.014
	C(3,1)	0.028		C(4,1)	0.066
	C(3,2)	–0.004		C(4,2)	–0.059
	W(1)	0.140		W(2)	–0.100
Plane V	O(9)	0.040	Plane VI	O(11)	–0.027
	O(10)	–0.042		O(12)	0.009
	C(5)	0.000		C(6)	0.017
	N(5)	0.011		N(6)	0.012
	C(5,1)	–0.041		C(6,1)	0.011
	C(5,2)	0.033		C(6,2)	–0.022
	W(2)	–0.122		W(2)	0.046
Plane VII	W(1)	–0.006	Plane VIII	W(1)	–0.014
	W(2)	0.006		W(2)	0.014
	O(1)	0.006		O(3)	0.015
	O(2)	–0.006		O(4)	–0.015

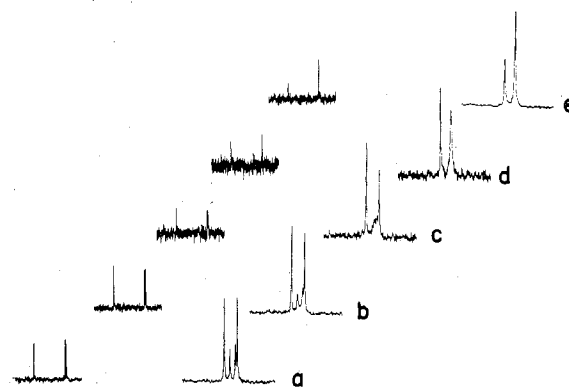
  

Dihedral Angles between Planes, Deg			
I–II	162.7	I–VI	78.4
I–IV	85.7	II–VI	84.3
II–IV	77.0	VII–VIII	153.1
I–VII	4.9	II–VIII	5.1

<sup>a</sup> The equation for the plane is of the form  $Ax + By + Cz - D = 0$ .

creased from  $-60^\circ\text{C}$ , the high-field resonances, assignable to proximal and distal methyl groups of the unsymmetrically bonded nonbridging  $O_2CNMe_2$  ligand, broaden, as does the resonance assignable to the methyl groups of the other nonbridging  $O_2CNMe_2$  ligand. At ca.  $-17^\circ\text{C}$  these resonances coalesce to a single broad resonance which sharpens with increasing the temperature to ca.  $28^\circ$ . At this temperature the spectrum consists of two sharp resonances in the integral ratio 4:8 assignable to the methyl groups of bridging and nonbridging  $O_2CNMe_2$  ligands, respectively. With a further increase in temperature both resonances broaden, coalesce, and finally yield a sharp singlet at  $77^\circ\text{C}$ . At this temperature exchange between bridging and nonbridging carbamate ligands is fast on the NMR time scale.

Since the  $O_2CNC_2$  moiety of the carbamate ligand is essentially planar and since the free energy of activation for rotation about the  $O_2C-NC_2$  bond can be assumed<sup>21</sup> to be at least  $16\text{ kcal mol}^{-1}$ , the exchange of proximal and distal methyl groups observed at low temperatures corresponds to a site exchange of the oxygen atoms of the unsymmetrically bonded terminal carbamate ligand. However, what is not readily apparent from the variable-temperature  $^1\text{H}$  NMR spectra is whether  $W-O$  axial-equatorial site exchange occurs preferentially for the unsymmetrically bonded carbamate ligand or whether  $W-O$  axial-equatorial exchange is mechanistically correlated with a simultaneous exchange between the non-



**Figure 8.** Carbon-13 NMR spectra of  $W_2(O_2CNMe_2)_6$  showing the carboxylate carbons, left, and the methyl carbons, right, recorded simultaneously at various temperatures: a,  $-60^\circ\text{C}$ ; b,  $-45^\circ\text{C}$ ; c,  $-30^\circ\text{C}$ ; d,  $0^\circ\text{C}$ ; e,  $+38^\circ\text{C}$ . The width shown for both the ketonic and methyl carbons is 500 Hz. Chemical shifts relative to TMS are given in the text.

bridging carbamate ligands. This question is resolved by a consideration of the variable-temperature  $^{13}\text{C}$  NMR spectra shown in Figure 8.

At  $-60^\circ\text{C}$  three downfield resonances of equal intensity,  $\delta$  178.4, 163.7, and 163.1 ppm (relative to TMS = 0), are assignable to the carboxylic carbon atoms. Four resonances

at  $\delta$  36.8, 35.5, 34.2, and 33.7 ppm, in the intensity ratio 4:2:2:4, respectively, are assigned to the methyl carbon atoms. On raising the temperature, the signals assignable to the proximal and distal methyl carbon atoms broaden preferentially. Thus, at  $-45^\circ\text{C}$  the rate of proximal-distal methyl exchange is sufficiently fast to cause line broadening of the signals at  $\delta$  35.5 and 34.2 ppm. The carboxylic carbon signals at 163.7 and 163.1 ppm remain essentially unchanged from their appearance at  $-60^\circ\text{C}$ . At  $-30^\circ\text{C}$  the proximal-distal methyl resonances coalesce to give a broad signal. The rate of exchange between the two types of nonbridging carbamates is still quite slow as the carboxylic carbon signals at  $\delta$  163.7 and 163.1 ppm are well resolved; also, the signal at  $\delta$  33.7 ppm assignable to the methyl carbon atoms of the other nonbridging carbamate ligand is a sharp singlet. However, on raising the temperature to  $0^\circ\text{C}$  the carboxylic resonances at  $\delta$  163.7 and 163.1 ppm coalesce to a single resonance; similarly the methyl carbon signals appear as two resonances of integral intensity 1:2. The spectrum at  $+38^\circ\text{C}$  shows that exchange between nonbridging carbamate ligands is fast on the NMR time scale. We did not attempt to obtain a high-temperature limiting  $^{13}\text{C}$  NMR spectrum because of the dangers involved in heating a fragile 10-mm NMR tube containing  $\text{CD}_2\text{Cl}_2$  to temperatures above  $70^\circ\text{C}$ .

We conclude that  $\text{W}_2(\text{O}_2\text{CNMe}_2)_6$  shows three types of exchange processes which, in order of increasing energy, are (1) proximal-distal exchange of the axially bonded carbamate ligand, (2) exchange of nonbridging carbamate ligands, and (3) scrambling of bridging and nonbridging ligands.

These observations may be compared to the dynamical solution behavior of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\text{dik})_3$  compounds. The latter may also be considered to adopt a pentagonal-bipyramidal structure in which the center of the  $\text{C}_5\text{H}_5$  ring occupies an axial vertex. In solution two types of rearrangements are observed: (1) a low-energy process interchanges substituents on the diketone ligands spanning the equatorial edges while (2) a higher energy process interchanges the unique ligand spanning an axial and equatorial edge with the two equatorial ligands.<sup>22</sup>

$\text{W}_2\text{Me}_2(\text{O}_2\text{CNEt}_2)_4$ . This substance is only sparingly soluble in toluene and decomposes in methylene chloride. Consequently its dynamical behavior was not so amenable to detailed study. However,  $^1\text{H}$  NMR data are consistent with solution behavior similar to that found for  $\text{W}_2(\text{O}_2\text{CNMe}_2)_6$ . At and below  $40^\circ\text{C}$  in toluene- $d_8$   $\text{W}_2\text{Me}_2(\text{O}_2\text{CNEt}_2)_4$  shows a single resonance  $\delta$  1.60 ppm (relative to TMS) assignable to the tungsten-methyl protons. The  $\text{NEt}_2$  resonances are broad and poorly resolved. On raising the temperature to  $100^\circ\text{C}$ , the  $\text{NEt}_2$  resonances sharpen to give a quartet,  $\delta$  3.18 ppm, and a triplet,  $\delta$  0.98 ppm,  $J_{\text{HH}} = 7$  Hz. Thus, at high temperature, exchange between bridging and terminal  $\text{O}_2\text{CNEt}_2$  is rapid on the NMR time scale.

### Experimental Section

$\text{W}_2(\text{O}_2\text{CNMe}_2)_6$  and  $\text{W}_2\text{Me}_2(\text{O}_2\text{CNEt}_2)_4$  were prepared as described elsewhere<sup>15</sup> and crystallized from toluene.

$^1\text{H}$  NMR spectra were obtained from a Varian A-60 spectrometer equipped with a variable-temperature probe. Temperatures were calibrated with methanol (low temperatures) and ethylene glycol (high temperatures).  $^1\text{H}$  chemical shifts are shown in Figure 7 as ppm downfield from HMDS (hexamethyldisiloxane) which was used as an internal reference.

Variable-temperature  $^{13}\text{C}$  NMR spectra were recorded in the Fourier mode on a Varian XL 100 spectrometer. The temperature was regulated by a copper-constantan thermocouple located directly beneath the NMR tube. Temperatures were calibrated with methanol or ethylene glycol.

**Crystal Selection and Data Collection for  $\text{W}_2(\text{O}_2\text{CNEt}_2)_4\text{Me}_2$ .** In a nitrogen-filled glovebag a crystalline sample was transferred from an evacuated sealed tube to a petri dish and immersed in heavy mineral oil. From this sample a well-formed, yellow crystal measuring  $0.304 \times 0.298 \times 0.274$  mm was selected for use in data collection and sealed

in a thin-walled glass capillary. The crystal was found to be monoclinic and to belong to the uniquely determined, centrosymmetric space group,<sup>23</sup>  $P2_1/c$ , and it was judged to be of acceptable quality for data collection, having peak widths at half-height  $\leq 0.22^\circ$  in  $\omega$  scans of several intense reflections.

The final lattice constants and an orientation matrix used to calculate setting angles for data collection were determined by the least-squares refinement of the setting angles for 15 high-angle reflections ( $18.0^\circ \leq 2\theta(\text{Mo K}\alpha) \leq 35.0^\circ$ ) chosen to give a good sampling of Miller indices and diffractometer settings. Final lattice parameters are  $a = 16.014$  (4) Å,  $b = 10.433$  (4) Å,  $c = 18.983$  (5) Å,  $\beta = 107.51$  (2)°, and  $V = 3024$  (1) Å<sup>3</sup>. The volume of 3024 (1) Å<sup>3</sup> is consistent with that anticipated for  $Z = 4$  and indicates that all atoms might be expected to occupy positions of general crystallographic symmetry in space group  $P2_1/c$  with no symmetry restrictions imposed on the molecule.

A syntax  $P1$  autodiffractometer equipped with a graphite-crystal monochromator utilizing Mo  $K\alpha$  radiation was used to measure intensity data. Symmetric  $\theta$ - $2\theta$  scans ranging  $1.0^\circ$  above and below the calculated Mo  $K\alpha_1$ -Mo  $K\alpha_2$  doublet were used to record integrated intensities; scan rates varied from  $4.0$  to  $24.0^\circ/\text{min}$ , depending upon the intensity of the reflection. The ratio of total background time to scan time was 0.50 for all scans. A total of 4042 unique data having  $0^\circ < 2\theta(\text{Mo K}\alpha) < 45.0^\circ$  were recorded. Three standard reflections were measured every 100 reflections and showed no significant fluctuations during data collection. Corrections for absorption effects,  $\mu = 81.03$  cm<sup>-1</sup>, were applied to all data. The minimum, maximum, and average transmission coefficients are 0.101, 0.287, and 0.169, respectively. The data were reduced to a set of relative  $|F_o|^2$  values after corrections for Lorentz and polarization effects and the 2671 data having  $I > 3\sigma(I)$  were used in the subsequent structural solution and refinement.<sup>24</sup>

**Structural Solution and Refinement for  $\text{W}_2(\text{O}_2\text{CNEt}_2)_4\text{Me}_2$ .** Atomic coordinates for the two unique tungsten atoms were derived from a three-dimensional Patterson map. The positional parameters for the tungsten atoms were refined in three cycles of full-matrix least-squares refinement to give discrepancy indices

$$R_1 = \sum | |F_o| - |F_c| | / \sum |F_o| = 0.177$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.243$$

All least-squares refinements minimized the function  $\sum w(|F_o| - |F_c|)^2$ , where the weighting factor,  $w$ , equals  $4|F_o|^2/\sigma^2(|F_o|^2)$  and  $\sigma$  is the esd of  $|F_o|^2$ . A value of 0.070 was used for  $p$  in the calculation of  $\sigma$ . The atomic scattering factors used in all least-squares refinements were those of Cromer and Waber.<sup>25</sup> Anomalous dispersion effects<sup>26</sup> were included in the calculated scattering factors for tungsten. Two difference Fourier maps, each following least-squares refinement of the atoms located up to that point, resulted in location of an additional 30 atoms. At this point no satisfactory positions had been obtained for two of the ethyl groups, one of them bonded to N(3) and the other to N(4) (see Figure 1). Two cycles of least-squares refinement of the 32 atoms, employing isotropic thermal parameters for all atoms, gave  $R_1 = 0.103$  and  $R_2 = 0.132$ . A difference Fourier map at this point indicated that the two remaining ethyl groups were disordered. Two distinct orientations were observed for each group and a 50:50 disorder was assumed. The structure was refined to convergence in five cycles of full-matrix least-squares refinement employing isotropic thermal parameters for the carbon atoms of the ethyl groups and anisotropic thermal parameters for all remaining atoms. The final residuals are  $R_1 = 0.040$  and  $R_2 = 0.054$  for the 2671 reflections having  $I > 3\sigma(I)$ . During the final cycle of least-squares refinement, no parameter shifted by more than  $0.06\sigma$ , where  $\sigma$  is the estimated standard deviation of that parameter. A final difference Fourier map showed no features of structural significance other than possible positions for some of the hydrogen atoms. No effort was made to locate and refine the hydrogen atoms. An examination of the final observed and calculated structure factors showed no unusual trends as a function of reflection number, Miller indices, or  $(\sin \theta)/\lambda$ .

**Crystal Selection and Data Collection for  $\text{W}_2(\text{O}_2\text{CNMe}_2)_6\cdot\text{C}_7\text{H}_8$ .** Procedures used for this compound were essentially identical with those for  $\text{W}_2(\text{O}_2\text{CNEt}_2)_4\text{Me}_2$ . A yellow crystal measuring  $0.086 \times 0.266 \times 0.290$  mm was sealed in a glass capillary under mineral oil. The space group was found to be  $P1$ . Accurate lattice constants, determined from 15 reflections in the range  $20.0^\circ \leq 2\theta(\text{Mo K}\alpha) \leq 35.0^\circ$ , are  $a = 12.018$  (2) Å,  $b = 16.516$  (4) Å,  $c = 11.630$  (3) Å,  $\alpha = 111.09$



(2)°,  $\beta = 107.26$  (2)°,  $\gamma = 91.00$  (2)°, and  $V = 2036.5$  (8) Å<sup>3</sup>. From results of elemental analysis and proton NMR the crystals were believed to contain toluene solvent molecules and the observed volume of 2036.5 Å<sup>3</sup> corresponded to that expected for  $Z = 2$  with the asymmetric unit being composed of one  $W_2(O_2CNMe_2)_6$  molecule and one toluene molecule. The crystal used for intensity measurements had peak widths at half-height for  $\omega$  scans of less than 0.20°.

The data were measured using Mo  $K\alpha$  radiation and  $\theta$ - $2\theta$  scans. Variable scan rates from 4.0 to 24.0°/min and symmetric scan ranges from 0.9° above to 0.9° below the calculated Mo  $K\alpha_1$ -Mo  $K\alpha_2$  doublet were used. A total of 5281 data having  $2\theta \leq 45.0^\circ$  were recorded. Three standard reflections, measured every 100 reflections, showed an average decrease of 17% during data collection. The crystal decay was essentially linear and a correction for the linear decay was applied to all data. Corrections for absorption effects,  $\mu = 60.38$  cm<sup>-1</sup>, were also applied to all data. The minimum, maximum, and average transmission coefficient were 0.244, 0.650, and 0.470, respectively. Those 1964 data having  $I < 3\sigma(I)$  were rejected and the 3317 remaining data were used in the structural solution and refinement.

**Structural Solution and Refinement for  $W_2(O_2CNMe_2)_6 \cdot C_7H_8$ .** The coordinates for the two tungsten atoms were derived from a three-dimensional Patterson function and refined in three cycles of least-squares refinement to give  $R_1 = 0.237$  and  $R_2 = 0.299$ . A difference Fourier map at this point clearly revealed the positions for twelve oxygen atoms, six nitrogen atoms, and the six carboxylate carbon atoms of the six carbamate ligands. These 24 atoms and the two tungsten atoms were refined to give  $R_1 = 0.132$  and  $R_2 = 0.183$ . The remaining atoms, twelve methyl carbon atoms and the seven carbon atoms of the toluene, were easily located from a second difference Fourier map. All 45 atoms were refined in two cycles of least-squares refinement employing isotropic thermal parameters for all atoms to give  $R_1 = 0.104$  and  $R_2 = 0.138$ . The structure was refined to convergence in four cycles of full-matrix least-squares refinement employing isotropic temperature parameters for all methyl carbon atoms and the seven toluene carbon atoms and anisotropic temperature parameters for all other atoms to yield final residuals of  $R_1 = 0.073$  and  $R_2 = 0.103$ . No parameters shifted by more than 0.12 $\sigma$  during the final refinement cycle and a final difference Fourier map was devoid of any peaks of structural significance.

Tables of observed and calculated structure factors for the data used in the final refinement for both compounds are available elsewhere.<sup>27</sup>

**Acknowledgment.** We thank the Research Corp., the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation at Princeton University (Grant No. MPS-73-05016) and at Texas A&M University (Grant No. CHE75-05509) for support of this work.

Registry No. I, 61091-29-0; II, 60673-99-6.

**Supplementary Material Available:** Tables of structure factor amplitudes (27 pages). For ordering information see any current masthead page.

## References and Notes

- (1) (a) Princeton University. (b) Texas A&M University.
- (2) (a) F. A. Cotton, *Chem. Soc. Rev.*, **4**, 27 (1975); (b) It seems that compounds of the types  $W_2(O_2CR)_4$  do exist in a noncrystalline form: F. A. Cotton and M. Jeremic, *Synth. Inorg. Met.-Org. Chem.*, **1**, 265 (1971).
- (3) M. H. Chisholm, F. A. Cotton, M. W. Extine, and B. R. Stults, *J. Am. Chem. Soc.*, **98**, 4477 (1976).
- (4) M. H. Chisholm, F. A. Cotton, M. W. Extine, M. Millar, and B. R. Stults, *J. Am. Chem. Soc.*, **98**, 4486 (1976).
- (5) M. H. Chisholm, F. A. Cotton, M. W. Extine, M. Millar, and B. R. Stults, *Inorg. Chem.*, **16**, 320 (1977).
- (6) M. H. Chisholm, F. A. Cotton, M. W. Extine, M. Millar, and B. R. Stults, *Inorg. Chem.*, **15**, 2244 (1976).
- (7) W. Mowat, A. J. Shortland, G. Yagupsky, M. Yagupsky, N. J. Hill, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 533 (1972).
- (8) M. H. Chisholm, F. A. Cotton, M. Extine, and B. R. Stults, *Inorg. Chem.*, **15**, 2252 (1976).
- (9) M. H. Chisholm and M. W. Extine, *J. Am. Chem. Soc.*, **97**, 5625 (1975).
- (10) F. Huq, W. Mowat, A. Shortland, A. C. Skapski, and G. Wilkinson, *Chem. Commun.*, 1079 (1971).
- (11) M. H. Chisholm, F. A. Cotton, B. A. Frenz, W. W. Reichert, L. W. Shive, and B. R. Stults, *J. Am. Chem. Soc.*, **98**, 4469 (1976).
- (12) M. H. Chisholm and W. W. Reichert, *J. Am. Chem. Soc.*, **96**, 1249 (1974).
- (13) D. C. Bradley and M. H. Chisholm, *Acc. Chem. Res.*, **9**, 273 (1976).
- (14) M. H. Chisholm, F. A. Cotton, M. W. Extine, and B. R. Stults, *J. Am. Chem. Soc.*, **98**, 4683 (1976).
- (15) M. H. Chisholm and M. W. Extine, *J. Am. Chem. Soc.*, **99**, 782 (1977).
- (16) M. H. Chisholm and M. W. Extine, *J. Am. Chem. Soc.*, **99**, 792 (1977).
- (17) F. A. Cotton, *Inorg. Chem.*, **4**, 334 (1965).
- (18) A. P. Mortola, J. W. Moskowitz, and N. Rosch, *Int. J. Quantum Chem.*, **S8**, 161 (1974).
- (19) J. G. Norman, Jr., and H. J. Kolari, *J. Am. Chem. Soc.*, **97**, 33 (1975).
- (20) This is not true for all  $M(O_2CNMe_2)_n$  compounds: see ref 15.
- (21) Simple organic carbamate esters  $Me_2NC(O)OR$  show a barrier to rotation about the N-C bond of 16 kcal mol<sup>-1</sup>: E. Lustig, W. R. Benson, and N. Duy, *J. Org. Chem.*, **32**, 851 (1967). See also discussion in ref 15.
- (22) T. J. Pinnavaia, J. J. Howe, and R. E. Teets, *Inorg. Chem.*, **13**, 1074 (1974).
- (23) "International Tables for X-Ray Crystallography", Vol. I, Kynoch Press, Birmingham, England.
- (24) The crystallographic programs used for the structural solution and refinement were those of the Enraf-Nonius Structure Determination Package. These programs were used on a PDP 11/45 computer at the Molecular Structure Corp., College Station, Texas.
- (25) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, Table 2.3.1.
- (26) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
- (27) Supplementary material.
- (28) **Note Added in Proof.** Since this paper was written conclusive proof for the existence of W-W quadruple bonds has been obtained at Texas A&M University: See D. M. Collins, F. A. Cotton, S. Koch, M. Millar, and C. A. Murillo, *J. Am. Chem. Soc.*, **99**, 1259 (1977).