Contribution from the Department of Chemistry and Molecular Structure Center,
Indiana University, Bloomington, Indiana 47405

The Tungsten-Tungsten Triple Bond. 10.[1] Ditungsten Hexapivalate

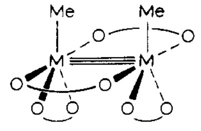
MALCOLM H. CHISHOLM,* JOSEPH A. HEPPERT, DAVID M. HOFFMAN, and JOHN C. HUFFMAN

Received January 25, 1985

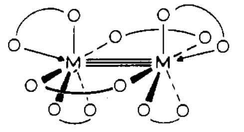
Hydrocarbon solutions of $W_2(O\text{-}t\text{-}Bu)_6$ react with pivalic acid, *t*-BuCOOH (6 equiv), to give $W_2(O_2C\text{-}t\text{-}Bu)_6$ and *t*-BuOH. $W_2(O_2C\text{-}t\text{-}Bu)_6$ crystallizes from hexane as yellow cubic crystals. (Crystal data at -156 °C: $a = 16.730$ (5) Å, $b = 10.588$ (2) Å, $c = 22.860$ (8) Å, $\beta = 107.26$ (1)°, $Z = 4$, $d_{calcd} = 1.674$ g cm^{-3}, space group = $P2_1/c$.) Each tungsten atom is coordinated to five oxygen atoms that lie roughly in a pentagonal plane, to the other tungsten atom by a W≡W bond (2.292 (1) Å), and weakly to an additional oxygen atom along an extension of the W-W axis (W-O (axial) = 2.54 Å (averaged)). The molecule has a pair of cis-bridging pivalate groups that impose a near-eclipsed geometry for the two WO_5 pentagonal units. ^1H NMR studies reveal that in toluene-d_8 solution $W_2(O_2C\text{-}t\text{-}Bu)_6$ exists as a mixture of two isomers, each having a C_2 axis of symmetry. These observations are compared with previous findings and in particular with those for $W_2(O_2CNMe_2)_6$. It is proposed that most, if not all, compounds of formula $W_2(O_2CX)_6$ will adopt a structure related to either $W_2(O_2C\text{-}t\text{-}Bu)_6$ or $W_2(O_2CNMe_2)_6$, which are closely related, differing only in the arrangement of the chelate ligands about a common $W_2O_{10}O'_2$ template.

Introduction

Molybdenum and tungsten form a series of compounds containing a central $X_nM{\equiv}MX_n$ unit, where X = a ligand atom and $n = 3\text{–}6$.[2,3] The coordination geometries for $n = 3$ and 4 are now well understood, and there are numerous structurally characterized examples of each. However, for $n = 5$ and 6, until recently the only structurally characterized examples were $W_2Me_2(O_2CNMe_2)_4$ and $W_2(O_2CNMe_2)_6$, whose structures are depicted by I and II, respectively.[4]



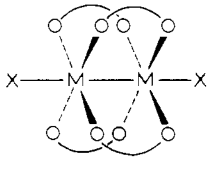
I



II

In both compounds each tungsten atom forms five bonds in a pentagonal plane to five ligand atoms, and in $W_2(O_2CNMe_2)_6$ there is an additional weak axial interaction: W-O (axial) = 2.68 Å (averaged).

Transition-metal compounds of formula $M_2(O_2CR)_4X_2$, where X represents either a neutral ligand (THF, py, PR_3) or an anionic ligand such as a halide, often, if not generally, adopt the structure depicted by III.[5] Carboxylate bridges are known to span M-M distances ranging from 2.0 to 3.3 Å corresponding in the extreme to strongly bonded and nonbonded M-M interactions, respectively.[6]



III

M.H.C. had previously argued that, in the chemistry of $(M{\equiv}M)^{6+}$-containing compounds (M = Mo, W), axial ligation is avoided because such bonding would compete for the use of the metal d_{z^2} or d_{z^2}/p_z hybrid orbital, which is used in forming the M-M σ bond.[7] For the linear M-M-X unit a trans-influence phenomenon[8] would be present so that strong axial ligation would weaken the M-M σ bond. Since for these $d^3\text{–}d^3$ dimers there are five atomic orbitals available for M-L bonding in the *xy* plane, the preference for structures of type I over type III is understood. Only when there are six ligand atoms, such as in $W_2(O_2CNMe_2)_6$, is axial ligation seen and then only in the form of weak M-O bonds, as judged by the long M-O distances, to the axial ligand atoms.

The validity of this argument was shattered with the discovery that $W_2R_2(O_2CEt)_4$ compounds, where R = CH_2Ph and CH_2CMe_3, adopt structures of type III in the solid state and have *shorter* W≡W bond distances[9] than that seen in $W_2Me_2(O_2CNMe_2)_4$. However, the NMR data obtained in toluene-d_8 suggested that the carbamate $W_2(CH_2Ph)_2(O_2CNMe_2)_4$ adopts a structure akin to I while $W_2(CH_2Ph)_2(O_2CEt)_4$ exists in solution as a mixture of isomers of types I and III, with the latter being favored.[10] The pivalate complex $W_2(CH_2Ph)_2(O_2C\text{-}t\text{-}Bu)_4$ in toluene-d_8 appears to adopt structure type III exclusively.[10]

Relatively subtle changes in steric and electronic factors are involved here. For a compound of formula $W_2R_2(O_2CX)_4$ increasing the bulkiness of R or X could increase internal steric pressure and thus favor structures of type III relative to I. The presence of only two bridging O_2CNMe_2 ligands in the $W_2Me_2(O_2CNMe_2)_4$ structure is presumably favored on steric grounds over an alternate structure having four bridging groups. The effects of O to W π bonding in these compounds are not considered very important since the metal atoms can attain a share of 18 electrons as a result of forming six M-O σ bonds. However, the σ-bonding contributions from bridging and terminal bidentate carboxylate or carbamate ligands differ, and this could influence the ultimate choice of structure.

These considerations have renewed our interest in the coordination chemistry of $X_nM{\equiv}MX_n$-containing compounds where $n = 5$ or 6. In this paper we describe the preparation, solid-state and molecular structure, and solution behavior of $W_2(O_2C\text{-}t\text{-}Bu)_6$. This we believe to be a good representative for a ditungsten hexacarboxylate where the alkyl group is bulky and consequently might provide a different structure type to that observed for $W_2(O_2CNMe_2)_6$.

Results and Discussion

Synthesis. The formation of $W_2(O_2C\text{-}t\text{-}Bu)_6$ in the reaction between $W_2(O\text{-}t\text{-}Bu)_6$ and *t*-BuCOOH was first noted by Leonelli

---

[1] Part 9: Chisholm, M. H.; Huffman, J. C.; Kelly, R. L. *Inorg. Chem.* **1979**, *18*, 3554.

[2] Chisholm, M. H.; Cotton, F. A. *Acc. Chem. Res.* **1978**, *11*, 356.

[3] Chisholm, M. H. *Faraday Symp. Chem. Soc.* **1980**, *14*, 194.

[4] Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Stults, B. R. *Inorg. Chem.* **1977**, *16*, 603.

[5] Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry. A Comprehensive Text", 4th ed.; Wiley: New York, 1980.

[6] E.g. in $Mo_2(O_2CR)_4$ ($M\overset{4}{-}M$) compounds, where M-M = ca. 2.1 Å (Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982.), and $Fe_2O(O_2CR)_2(HB(pz)_3)_2$ compounds, which act as models for the diiron centers in Hemerythrin, where Fe--Fe = 3.2 Å (Armstrong, W. H.; Spool, A.; Papaefthymiou, G. C.; Frankel, R. B.; Lippard, S. J. *J. Chem. Soc.* **1984**, *106*, 3653).

[7] Chisholm, M. H.; Haitko, D. A.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 4046.

[8] Appleton, T. G.; Clark, H. C.; Manzes, L. M. *Coord. Chem. Rev.* **1973**, *10*, 335.

[9] Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C.; Van Der Sluys, W. G.; Russo, S. *J. Am. Chem. Soc.* **1984**, *106*, 5386.

[10] Chisholm, M. H.; Van Der Sluys, W. G., to be submitted for publication.

0020-1669/85/1324-3214$01.50/0

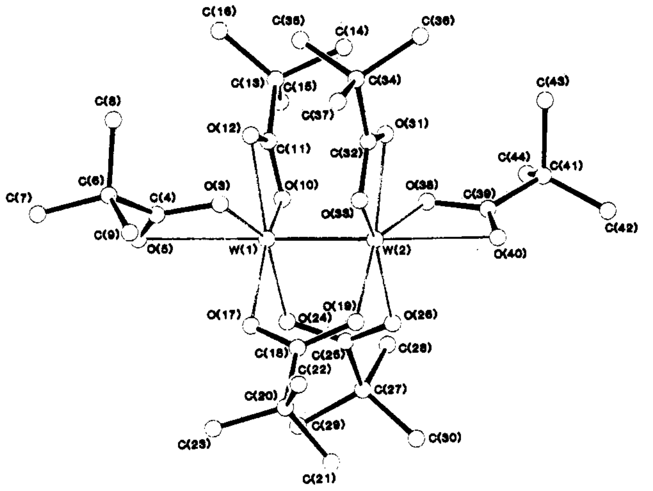


Figure 1. View of the $W_2(O\text{-}t\text{-}Bu)_6$ molecule giving number scheme for the atoms used in the tables.

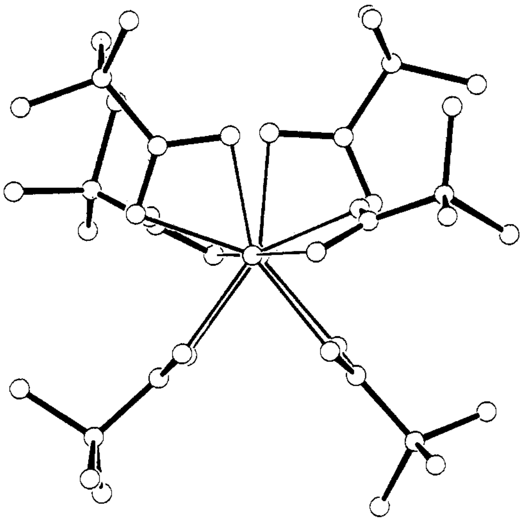


Figure 2. View of the $W_2(O_2C\text{-}t\text{-}Bu)_6$ molecule down the W–W bond emphasizing the cis-bridging pivalate ligands and the near-eclipsed geometry of the two WO_5 pentagonal units.

in this group.[11] The same preparative procedure was employed here. In the synthesis care must be taken to add only slightly greater than 6 equiv of pivalic acid. Too little acid results in only partial substitution of the t-BuO ligands by the $t\text{-}BuCO_2$ ligands (cf. $Mo_2(O_2CPh)_2(O\text{-}t\text{-}Bu)_4$)[12] while too much acid leads to oils and difficulty in crystallization of $W_2(O_2C\text{-}t\text{-}Bu)_6$ because t-BuCOOH acts as a viscous solvent, which is not easily removed in vacuo because of its low vapor pressure at ambient temperature. These problems notwithstanding, the substitution of $t\text{-}BuCO_2$ ligands for t-BuO ligands appears to be the only reaction involved, and $W_2(O_2C\text{-}t\text{-}Bu)_6$ can be isolated by crystallization as large yellow-orange cubes of jewellike quality. $W_2(O_2C\text{-}t\text{-}Bu)_6$ is oxygen and moisture sensitive and appreciably soluble in all common organic hydrocarbon solvents.

Solid-State and Molecular Structure. In the space group $P2_1/c$, there is only one crystallographically unique molecule in the unit cell. Atomic positional parameters are given in Table I, and selected bond distances and bond angles are given in Tables II and III, respectively. An ORTEP view of the molecule giving the atom number scheme is shown in Figure 1, and a view of the molecule down the W–W bond is given in Figure 2.

Table I. Fractional Coordinates and Isotropic Thermal Parameters for the $W_2(O\text{-}t\text{-}Bu)_6$ Molecule

atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
W(1)	3104.9 (2)	644.4 (4)	2814.0 (2)	12
W(2)	2088.9 (2)	2060.7 (4)	2327.1 (2)	12
O(3)	2672 (4)	183 (7)	3543 (3)	16
C(4)	3293 (7)	−420 (11)	3921 (5)	20
O(5)	3941 (5)	−615 (7)	3779 (3)	21
C(6)	3167 (7)	−855 (11)	4518 (5)	20
C(7)	3960 (9)	−1480 (17)	4919 (6)	43
C(8)	2430 (10)	−1787 (17)	4384 (7)	50
C(9)	2963 (12)	293 (16)	4845 (6)	51
O(10)	3213 (4)	−374 (7)	2029 (3)	15
C(11)	2724 (6)	−1219 (11)	2092 (5)	17
O(12)	2467 (4)	−1112 (7)	2556 (3)	18
C(13)	2424 (7)	−2280 (11)	1634 (5)	22
C(14)	1536 (8)	−1853 (13)	1238 (6)	35
C(15)	2987 (8)	−2385 (13)	1220 (6)	29
C(16)	2381 (8)	−3501 (12)	1955 (6)	26
O(17)	3586 (4)	2068 (7)	3482 (3)	15
C(18)	3216 (6)	3112 (11)	3444 (5)	18
O(19)	2567 (4)	3384 (7)	3005 (3)	14
C(20)	3537 (7)	4105 (12)	3938 (5)	25
C(21)	3766 (14)	5241 (19)	3635 (9)	71
C(22)	2847 (12)	4377 (23)	4215 (11)	88
C(23)	4262 (18)	3609 (20)	4445 (10)	110
O(24)	3982 (4)	1628 (7)	2504 (3)	13
C(25)	3746 (6)	2502 (11)	2137 (5)	16
O(26)	3018 (4)	3011 (7)	2023 (3)	14
C(27)	4335 (6)	3018 (11)	1803 (5)	17
C(28)	4106 (8)	2289 (15)	1195 (6)	35
C(29)	5248 (7)	2673 (15)	2167 (6)	34
C(30)	4225 (8)	4411 (14)	1686 (7)	36
O(31)	1028 (4)	806 (7)	2115 (3)	17
C(32)	863 (6)	1107 (11)	2610 (5)	16
O(33)	1306 (4)	1975 (7)	2929 (3)	16
C(34)	197 (7)	387 (12)	2800 (5)	22
C(35)	474 (7)	−962 (12)	2887 (6)	25
C(36)	−630 (7)	484 (12)	2281 (6)	25
C(37)	111 (8)	948 (13)	3393 (6)	30
O(38)	1850 (4)	1578 (7)	1409 (3)	16
C(39)	1332 (6)	2478 (11)	1162 (5)	20
O(40)	1190 (4)	3327 (8)	1483 (3)	21
C(41)	874 (8)	2359 (14)	480 (6)	33
C(42)	606 (13)	3640 (21)	220 (7)	75
C(43)	81 (10)	1500 (19)	452 (7)	63
C(44)	1403 (9)	1688 (15)	138 (6)	41

Table II. Selected Bond Distances (Å) for the $W_2(O_2\text{-}t\text{-}Bu)_6$ Molecule

A	B	dist	A	B	dist
W(1)	W(2)	2.2922 (8)	O(3)	C(4)	1.303 (13)
W(1)	O(3)	2.064 (7)	O(5)	C(4)	1.239 (13)
W(1)	O(10)	2.145 (7)	O(10)	C(11)	1.248 (13)
W(1)	O(12)	2.138 (7)	O(12)	C(11)	1.264 (12)
W(1)	O(17)	2.127 (7)	O(17)	C(18)	1.257 (13)
W(1)	O(24)	2.088 (6)	O(19)	C(18)	1.273 (13)
W(1)	O(5)	2.602 (7)	O(24)	C(25)	1.233 (13)
W(2)	O(19)	2.067 (7)	O(26)	C(25)	1.286 (13)
W(2)	O(26)	2.134 (6)	O(31)	C(32)	1.283 (13)
W(2)	O(31)	2.154 (7)	O(33)	C(32)	1.267 (13)
W(2)	O(33)	2.164 (7)	O(38)	C(39)	1.300 (14)
W(2)	O(38)	2.080 (7)	O(40)	C(39)	1.229 (14)
W(2)	O(40)	2.462 (7)			
C–CMe$_3$		1.52 (1) (av)	C–CH$_3$		1.53 (2) (av)

The W–W distance, 2.2922 (8) Å, is very similar to that in $W_2(O_2CNMe_2)_6$, 2.272 (1) Å, and considerably longer than those in $W_2R_2(O_2CEt)_4$ compounds where R = CH_2Ph or CH_2CMe_3 and W–W is ca. 2.19 Å.[9]

The molecular structure has virtual but not crystallographically imposed C_2 symmetry. The structure can be seen to be a variation of the structure observed for $W_2(O_2CNMe_2)_6$, which has C_{2v} symmetry, and is depicted by II. For $W_2(O_2C\text{-}t\text{-}Bu)_6$, the virtual C_2 axis of symmetry bisects the W–W bond and passes between the cis-bridging carboxylates. Each tungsten atom forms five

---

(11) Chetcutti, M. J.; Chisholm, M. H.; Huffman, J. C.; Leonelli, J. *J. Am. Chem. Soc.* **1983**, *105*, 292.

(12) Chisholm, M. H.; Huffman, J. C.; Kirkpatrick, C. C. *Inorg. Chem.* **1983**, *22*, 1704.

Table III. Selected Bond Angles (deg) for the $W_2(O_2\text{-}t\text{-}Bu)_6$ Molecule

A	B	C	angle
W(2)	W(1)	O(3)	99.20 (19)
W(2)	W(1)	O(10)	99.02 (19)
W(2)	W(1)	O(12)	101.39 (19)
W(2)	W(1)	O(17)	87.32 (19)
W(2)	W(1)	O(24)	90.21 (19)
W(2)	W(1)	O(5)	151.8 (2)
O(3)	W(1)	O(10)	133.9 (3)
O(3)	W(1)	O(12)	75.5 (3)
O(3)	W(1)	O(17)	74.7 (3)
O(3)	W(1)	O(24)	147.46 (27)
O(10)	W(1)	O(12)	59.44 (26)
O(10)	W(1)	O(17)	148.08 (26)
O(10)	W(1)	O(24)	74.03 (27)
O(12)	W(1)	O(17)	149.98 (27)
O(12)	W(1)	O(24)	133.16 (27)
O(17)	W(1)	O(24)	74.70 (27)
W(1)	W(2)	O(19)	90.76 (20)
W(1)	W(2)	O(26)	87.70 (18)
W(1)	W(2)	O(31)	98.55 (20)
W(1)	W(2)	O(33)	99.52 (19)
W(1)	W(2)	O(38)	102.81 (19)
W(1)	W(2)	O(40)	158.37 (17)
O(19)	W(2)	O(26)	76.58 (27)
O(19)	W(2)	O(31)	134.14 (27)
O(19)	W(2)	O(33)	73.96 (26)
O(19)	W(2)	O(38)	147.1 (3)
O(19)	W(2)	O(40)	103.24 (27)
O(26)	W(2)	O(31)	148.07 (27)
O(26)	W(2)	O(33)	149.71 (27)
O(26)	W(2)	O(38)	74.19 (27)
O(26)	W(2)	O(40)	79.79 (25)
O(31)	W(2)	O(33)	60.25 (27)
O(31)	W(2)	O(38)	73.89 (28)
O(31)	W(2)	O(40)	83.59 (27)
O(33)	W(2)	O(38)	131.27 (26)
O(33)	W(2)	O(40)	100.16 (25)
O(38)	W(2)	O(40)	56.89 (27)
W(1)	O(3)	C(4)	104.4 (6)
W(1)	O(10)	C(11)	92.6 (6)
W(1)	O(12)	C(11)	92.4 (6)
W(1)	O(17)	C(18)	119.9 (6)
W(2)	O(19)	C(18)	119.1 (7)
W(1)	O(24)	C(25)	119.3 (6)
W(2)	O(26)	C(25)	118.3 (7)
W(2)	O(31)	C(32)	91.5 (6)
W(2)	O(33)	C(32)	91.5 (6)
W(2)	O(38)	C(39)	99.4 (7)
W(2)	O(40)	C(39)	83.6 (6)
O(3)	C(4)	O(5)	119.7 (10)
O(3)	C(4)	C(6)	116.8 (9)
O(5)	C(4)	C(6)	123.5 (10)
O(10)	C(11)	O(12)	115.5 (10)
O(10)	C(11)	C(13)	123.1 (10)
O(12)	C(11)	C(13)	121.4 (10)
O(17)	C(18)	O(19)	122.8 (9)
O(17)	C(18)	C(20)	119.9 (10)
O(19)	C(18)	C(20)	117.3 (10)
O(24)	C(25)	O(26)	123.1 (9)
O(24)	C(25)	C(27)	119.2 (9)
O(26)	C(25)	C(27)	117.7 (10)
O(31)	C(32)	O(33)	116.4 (9)
O(31)	C(32)	C(34)	119.8 (10)
O(33)	C(32)	C(34)	123.7 (9)
O(38)	C(39)	O(40)	119.9 (10)
O(38)	C(39)	C(41)	116.9 (11)
O(40)	C(39)	C(41)	123.0 (11)

bonds roughly in a pentagonal plane, and in addition there is weak axial interaction: W(1)–O(5) = 2.602 (7) Å; W(2)–O(40) = 2.462 (7) Å.

Within the pentagonal plane at each tungsten atom the O–W–O angles deviate little from the idealized 72°, with the most significant deviation arising from the small bite, 60°, of the bidentate carboxylate ligand. The presence of the cis-bridging $t\text{-}BuCO_2$ ligands appears to cause no significant mutual repulsion since the O–W–O angles are ca. 75°. An examination of the W–W–O angles reveals that for the bridging carboxylate ligands these are close to 90° but for the other carboxylates the angles are 100 ± 2°. This bending back, enlargement of the W–W–O angles from 90°, is understandable in terms of steric repulsions of the ligands across the W–W bond. These O–W–O and W–W–O angles are very similar to those observed for $W_2(O_2CNMe_2)_6$. Of note is the fact that the W–W–O angles involving the weak axial carboxylate ligands are not significantly greater than those associated with the bidentate ligands. The metal's choice is clear: tungsten forms five strong bonds in a pentagonal plane and a weak axial bond. The latter is made at no expense to the former and with little or no effect on the W≡W bond as judged by W–W distance.

^1H NMR Studies. ^1H NMR spectra were recorded on hand-picked yellow crystals of $W_2(O_2C\text{-}t\text{-}Bu)_6$ dissolved in toluene-d_8 in the temperature range −60 to +85 °C. These studies suggest that in solution the compound exists as an equilibrium mixture of two isomers, each having a C_2 axis of symmetry. At −60 °C the major isomer shows three signals (singlets) of equal intensity as does the minor isomer with the ratio of major to minor being roughly 3:1.

Upon warming, the two upfield resonances of the major isomer start to broaden and coalesce at around −20 °C. At this temperature the downfield resonance of the major isomer starts to broaden, but the three resonances of the minor isomer remain sharp. When the temperature is raised from −20 to +10 °C, the resonances of the major isomer merge as they approach coalescence while the two upfield signals of the minor isomer start to broaden. The low-field resonance of the minor isomer remains sharp until the temperature is raised above 40 °C, whereupon it too starts to broaden. Upon raising the temperature from +40 to +85 °C, a broad resonance centered at 1.38 ppm starts to sharpen corresponding to the approach toward the fast-exchange-limiting spectrum anticipated for the major isomer while the resonance of the minor isomer appear as one broad downfield resonance, ca. 1.50 ppm, with the other two upfield resonances being lost in the base line.

We believe the most reasonable interpretation of the dynamic ^1H NMR behavior is the following:

1. $W_2(O_2C\text{-}t\text{-}Bu)_6$ exists in toluene as a mixture of isomers, each having at least C_2 symmetry. The most likely candidates for the two isomers are the structures found in the solid state for $W_2(O_2C\text{-}t\text{-}Bu)_6$ and $W_2(O_2CNMe_2)_6$. These can be viewed as cis and trans bis-bridged structures having, respectively, anti and syn carboxylate ligands that are involved in the weak axial bonding.

2. For each isomer there are two fluxional processes. The lowest energy process involves a site exchange of terminal-bonded carboxylate ligands, i.e. an exchange between the bidentate carboxylate that forms both W–O bonds in the pentagonal plane and the carboxylate ligand that forms one bond in the pentagonal plane and has its other oxygen atom coordinated weakly in the axial position. A higher energy process scrambles bridging and terminal-bonded carboxylates. This dynamic behavior parallels exactly that reported for $W_2(O_2CNMe_2)_6$, which exists in solution in only one NMR-detectable isomer. In the present work we see that the energies of activation for the fluxional processes are different within each isomer, and at +85 °C isomerization is not rapid on the NMR time scale, despite the fact that bridge ⇌ terminal carboxylate exchange is rapid in the major isomer.

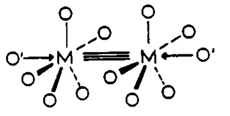
These dynamic processes parallel the solution behavior of anti and gauche $M_2R_2(NMe_2)_4$ compounds where rotations about M–N bonds have different energies of activation between the two isomers and for the gauche rotamer different activation energies for the two types of $M\text{–}NMe_2$ ligands are present within that rotamer.[2,7] Despite the fact that rotations about M–N bonds can lead to rapid proximal ⇌ methyl exchange on the NMR time scale, E_a for M–N rotations fall in the range 11–15 kcal mol^{-1}, anti ⇌ gauche isomerization is not so facile, where E_a is in the range 20–25 kcal mol^{-1}.[13] In the present work an interconversion

---

(13) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Miller, M.; Stults, B. R. *Inorg. Chem.* **1976**, *15*, 2244.

of isomers, one having a structure akin to that depicted by II with the others having the structure found in the solid state for $W_2(O_2C\text{-}t\text{-}Bu)_6$, would involve a correlated motion among the carboxylate groups just as rotation about the M≡M bond in $M_2R_2(NMe_2)_4$ compound requires a correlated motion of the propeller NC_2 blades. Thus, the threshold mechanism for bridge $\rightleftharpoons$ terminal carboxylate exchange does not lead to isomerization between the cis- and trans-bridged structures.

Concluding Remarks. The structural characterization of $W_2(O_2C\text{-}t\text{-}Bu)_6$ provides the second example of a molecule containing a central $W_2(O_2C)_6$ core that adopts a geometry based on the metal atoms being coordinated to five O atoms within a pentagonal plane and having weak ligation in the axial positions. In both $W_2(O_2C\text{-}t\text{-}Bu)_6$ and $W_2(O_2CNMe_2)_6$ there are two bridging and two bidentate ligands, and the two $W_2(O_2C)_6$ skeletons differ only with respect to the disposition of the O_2C units about a common $W_2O_{10}O'_2$ template, IV. It seems likely that most if not all other



IV

compounds of formula $W_2(O_2CX)_6$, where X = alkyl, aryl, OR, or NR_2, will adopt one of these structures.

The ^{1}H NMR studies indicate the presence of two isomers in solution, each having at least a C_2 axis of symmetry, which again is most reconcilable with an equilibrium mixture of compounds having $W_2(O_2C)_6$ skeletons of the type found for $W_2(O_2CNMe_2)_6$ and $W_2(O_2C\text{-}t\text{-}Bu)_6$ in the solid state. Though the possibility of all other isomers having a C_2 axis of symmetry (e.g., for a template of type IV one could propose a tetrabridged structure and a nonbridged structure) cannot be excluded, the NMR data do exclude a structure of type III, involving four bridging carboxylates and two axially coordinated monodentate pivalate ligands.

Experimental Section

The preparation of $W_2(O\text{-}t\text{-}Bu)_6$ has been described.[14] All manipulations were carried out under vacuum or inert atmosphere. Dry and oxygen-free solvents were used in all preparations.

^{1}H NMR spectra were recorded on a Nicolet NT-360 360-MHz spectrometer in toluene-d_8. Chemical shifts are reported relative to the CHD_2 quintet of the toluene-d_8 solvent set at δ 2.090. IR spectra were recorded on a Perkin-Elmer 283 spectrophotometer as Nujol mulls between CsI plates.

$W_2(O_2C\text{-}t\text{-}Bu)_6$. The X-ray crystal structure and IR and NMR data reported were obtained for crystals isolated by the procedure given below.

To $W_2(O\text{-}t\text{-}Bu)_6$ (0.40 g, 0.50 mmol) in hexanes (6 mL) was added excess solid $t\text{-}BuCO_2H$ (6 mmol). The reaction mixture was stirred for 18 h. The volume of the dark solution was reduced, and the solution was then warmed (40–50 °C) to redissolve some yellow precipitate. Standing at room temperature for 5–6 h produced yellow crystals. Cooling at 5 C, then −20 °C, produced more crystals. The crystalline solid was isolated by filtration and dried in vacuo (yield 0.16 g, 33%).

^{1}H NMR (−65 °C, toluene-d_8): $\delta(O_2C\text{-}t\text{-}Bu)$ 1.37, 1.38, 1.43 (equally intense singlets). Three other singlets of equal intensity but of one-third the intensity of these resonances are also observed: δ 1.05, 1.34, 1.47.

IR (cm^{-1}): 1601 m, 1589 m, 1566 m, 1519 s, 1505 s, 1425 s, 1400 s, 1349 s, 1230 s, 1212 s, 1031 w, 939 w, 930 s, 908 w, 899 m, 822 w, 812 m, 806 w, 788 w, 782 w, 778 w, 632 s, 554 w, 471 m, 455 m, 385 w, 356 w, 332 w, 316 w, 228 w.

Table IV. Summary of Crystal Data

empirical formula	$W_2C_{30}H_{54}O_{12}$
color of cryst	yellow
cryst dimens, mm	0.25 × 0.25 × 0.28
space group	$P2_1/c$
temp, °C	−156
cell dimens	
a, Å	16.730 (5)
b, Å	10.588 (12)
c, Å	22.860 (8)
β, deg	107.26 (1)
Z, molecules/cell	4
vol, Å^3	3866.84
calcd density, g/cm^3	1.674
wavelength, Å	0.71069
mol wt	974.45
linear abs coeff, cm^{-1}	61.228
detector to sample dist, cm	22.5
sample to source dist, cm	23.5
av ω scan width at half-height	0.25
scan speed, deg/min	4.0
scan width, deg + dispersion	2.0
individual bkgd, s	6
aperture size, mm	3.0 × 4.0
2θ range, deg	5–45
total no. of reflcns collcd	6031
no. of unique intensities	5081
no. of $F > 2.33\sigma(F)$	4555
$R(F)$	0.0458
$R_w(F)$	0.0464
goodness of fit for the last cycle	1.271
max Δ/σ for last cycle	0.05

Crystallographic Studies. General operating procedures and a listing of programs have been given.[15] Crystal data for $W_2(O_2C\text{-}t\text{-}Bu)_6$ are summarized in Table IV. A large yellow crystal was carefully cleaved to form a nearly equidimensional cube approximately $^1/_4$ mm in thickness. The crystal was affixed to a glass fiber and transferred to the goniostat by using inert-atmosphere handling techniques. Once transferred, the crystal was cooled to −156 °C for characterization and data collection.

Examination of a limited region of reciprocal space revealed a set of diffraction maxima that could be indexed as monoclinic with extinctions corresponding to the unique space group $P2_1/c$.

Data were collected in the usual manner, and the structure was solved by a combination of direct methods and Fourier techniques. Hydrogen atoms were clearly visible in a difference Fourier phased on the nonhydrogen atoms and were included in final refinement (isotropic thermal parameters for H; anisotropic for W, C, and O).

A final difference Fourier was essentially featureless, the largest peak (other than a W satellite) was 0.34 e/Å^3. An attempt to correct the data for absorption failed to improve the refinement and in fact caused an atom to go nonpositve definite, indicating that the correction was invalid. For this reason, the final cycles used uncorrected data.

Acknowledgment. We thank the National Science Foundation and the Wrubel Computing Center for support.

Registry No. *cis*-$W_2(O_2C\text{-}t\text{-}Bu)_6$, 97689-86-6; *trans*-$W_2(O_2C\text{-}t\text{-}Bu)_6$, 97747-16-5; W, 7440-33-7.

Supplementary Material Available: Listings of anisotropic thermal parameters, complete bond distances and angles, and F_o and F_c (37 pages). Ordering information is given on any current masthead page.

---

(14) Akiyama, M.; Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Haitko, D. A.; Little, D.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 2266.

(15) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C. *Inorg. Chem.* **1984**, *23*, 1021.