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Preparative, Structural, and Spectroscopic Studies of Tetrakis(carboxylato)ditungsten(II) Compounds with W–W Quadruple Bonds

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Preparative procedures affording the following compounds in good yield are described: orange $W_2(O_2CC_6H_5)_4(C_4H_8O)_2$ (**1**), orange $W_2(O_2CC_6H_4\text{-}p\text{-}OCH_3)_4(C_4H_8O)_2\cdot 2C_4H_8O$ (**2**), and red $W_2[O_2CC_6H_2[2,4,6\text{-}(CH_3)_3]]_4\cdot 2CH_3C_6H_5$ (**3**). The general route is by reduction of WCl_4 in THF using Na/Hg in the presence of the appropriate sodium carboxylate. Each compound has been obtained in crystalline form and characterized by X-ray crystallography. The compounds are all quite sensitive to oxygen and moisture, especially in solution. Crystal data are as follows: (**1**) $P2_1/c$ with $a = 9.511$ (7) Å, $b = 17.716$ (7) Å, $c = 10.843$ (3) Å, $\beta = 109.52$ (4)°, and $Z = 2$; (**2**) $P\bar{1}$ with $a = 11.590$ (4) Å, $b = 14.421$ (3) Å, $c = 8.278$ (2) Å, $\alpha = 100.77$ (2)°, $\beta = 103.23$ (2)°, $\gamma = 68.55$ (2)°, and $Z = 1$; (**3**) $P2_1/c$ with $a = 8.141$ (3) Å, $b = 21.873$ (4) Å, $c = 14.244$ (3) Å, $\beta = 102.41$ (2)°, and $Z = 2$. In each case the molecule resides on an inversion center. The W–W distances in **1**–**3** are 2.196 (1), 2.203 (1), and 2.176 (1) Å, respectively. The shorter distance in **3** may be due to the absence of axial ligands. In **1** and **2** each phenyl group is nearly coplanar with its carboxyl group whereas in **3** it is nearly perpendicular. The visible spectra of **1**, **2**, **3**, and $W_2(O_2CC_6H_4(4\text{-}CN))_4$ have been studied and compared to the spectra of the molybdenum analogues. In **1** and **2** there are clearly two overlapping absorption bands in the 500–600-nm region and it is proposed that the one at lower energy is due to the $\delta \rightarrow \delta^*$ transition while the other one is due to a $\delta \rightarrow \pi^*_L$ transition. Other aspects of the spectra are discussed.

Introduction

In view of the tremendous range of isolable and readily characterizable complexes of Cr_2^{4+} and Mo_2^{4+}, it might be anticipated that W_2^{4+} derivatives would be quite common. In fact, this is not the case. The history of attempts to make stable compounds containing W–W quadruple bonds covers a period of more than 20 years.[1] It records many failures and frustrations and relatively few successes. In 1977 compounds containing the $[W_2(CH_3)_8]^{4-}$ and $[W_2Cl_n(CH_3)_{8-n}]^{4-}$ ions were characterized;[2] these were the first authenticated compounds containing W–W quadruple bonds, but they were very unstable, both chemically and thermally. The first stable, useful compound was $W_2(mhp)_4$ (mhp = 2-oxy-6-methylpyridine), reported in 1978,[3] and then in 1980 stable compounds of the class $W_2Cl_4(PR_3)_4$ were discovered and characterized.[4,5] However, continued failure, despite many attempts, to prepare a $W_2(O_2CR)_4$ compound was striking and also discouraging. W_2^{4+} compounds are very susceptible to oxidation, a property that is in accord with the usual trend within any transition group of the low oxidation states to become increasingly less stable with respect to oxidation with increase in atomic number. The reaction of $W(CO)_6$ with RCO_2H in a way analogous to the preparation of $Mo_2(O_2CCH_3)_4$ from $Mo(CO)_6$ and acetic acid is unsuitable for obtaining $W_2(O_2CR)_4$ compounds and affords either polymeric or high-oxidation-state tungsten trinuclear species.[6,7] In 1981, the first report[8] of the synthesis and characterization of such a compound, viz., $W_2(O_2CCF_3)_4$, was published. Subsequently, a second compound containing the $[W_2Cl_8]^{4-}$ ion has also been prepared and structurally characterized.[9]

It has been our belief for some time that much of the difficulty with the preparation and stability of compounds containing W–W quadrupole bonds is due to the weakness of the δ component of that bond and the consequent readiness with which oxidative addition of acid occurs.[10] In accordance with this, we reasoned that the synthesis of $W_2(O_2CR)_4$ compounds should be possible if done under strictly nonacidic conditions.

We found that reduction of $WCl_4(THF)_2$[11a] with 2 equiv of sodium amalgam in THF at −25 °C and subsequent addition of the sodium salt of a carboxylic acid yielded red or purple solutions that contained the $W_2(O_2CR)_4$ species. $W_2(O_2CC_6H_5)_4(C_4H_8O)_2$ was isolated from a deep purple THF solution in 80% yield. This substance is accessible enough that it should become a desirable intermediate in further synthesis.

The electronic spectra of complexes of quadruply bonded dimetal systems have been extensively studied. Particular attention has been paid to the lowest energy absorption band, which can be assigned to the $\delta \rightarrow \delta^*$ transition. The electronic spectrum of $W_2(O_2CC_6H_5)_4(C_4H_8O)_2$ showed several interesting features, namely surprisingly high intensities and doublet structure. In an effort to pursue this study further by obtaining another compound containing the same ditungsten quadruply bonded unit but having a small change of the inductive character of the bridging carboxylate group, we have isolated two more compounds, namely, $W_2[O_2CC_6H_4(4\text{-}OCH_3)]_4(C_4H_8O)_2$ and $W_2[O_2CC_6H_2[2,4,6\text{-}(CH_3)_3]]_4$.

A comparison of the spectra of these three compounds and other non-carboxylato-bridged, quadruply bonded ditungsten compounds should be helpful in understanding the $\delta \rightarrow \delta^*$ transition. In addition, comparison of these compounds and some of their molybdenum analogues provides new insight into the similarities and differences between molybdenum and tungsten in their capacity for the formation of multiple M–M bonds.

The three carboxylato ditungsten compounds mentioned above have been synthesized and their crystal structures de-

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termined. In this paper we will give results and discussion for that work and in addition examine the electronic spectra of these compounds.

Experimental Section

Synthesis of Ditungsten(II) Compounds. All reactions and manipulations involving oxidation-sensitive solutions and compounds were carried out under atmospheres of argon or, in the case of selection and mounting of crystals for X-ray studies, under a layer of degassed mineral oil. The compounds studied are also moisture sensitive, and appropriate precautions were taken to exclude water from the reaction systems.

The tungsten(IV) chloride was prepared according to a report of King and McCarley[11b] by reaction of WCl_6 with $W(CO)_6$. A WCl_6–$W(CO)_6$ mixture with a molar ratio of 2:1 was heated to reflux in chlorobenzene. The WCl_4 precipitated and was isolated by filtration, dried under vacuum, and used without further purification.

A Cary 17 spectrophotometer was used to obtain the solution UV–visible spectra.

Preparation of $W_2(O_2CC_6H_5)_4(C_4H_8O)_2$. The reaction of 5.0 g (15.4 mmol) of WCl_4 with 2 equiv of 0.4% sodium amalgam in 300 mL of THF at −20 °C led to the greyish blue $W_2Cl_4(THF)_4$ solution.[4] Two equivalents of sodium benzoate (4.43 g, 30.7 mmol) was then added. Stirring was continued for $^1/_2$ h and the mixture then warmed to room temperature. The deep purple solution was filtered through Celite to remove sodium chloride and mercury. The filtrate was chilled to −20 °C for 3 days, and a mass of fine reddish yellow crystals formed; yield 6.12 g (80%). Suitable crystals for X-ray diffraction analysis were grown in the following way: 25 mL of the filtered reaction solution was transferred into a Schlenk tube and carefully covered with a layer (20 mL) of hexane. The tube was allowed to stand undisturbed so as to permit slow diffusion. In 3 days large orange crystals grew in the THF layer. After one week, 0.33 g (51% yield) of product was obtained. The compound is sensitive to air and moisture in the solid state and extremely sensitive to both in solution.

Preparation of $W_2[O_2CC_6H_4(4\text{-}OCH_3)]_4(C_4H_8O)_2\cdot 2C_4H_8O$. A 177.5-g amount of 0.4% sodium amalgam (30.9 mmol) and 5.35 g (30.7 mmol) of sodium *p*-methoxybenzoate were added to 5.0 g (15.4 mmol) of WCl_4 in 300 mL of THF at −20 °C. The mixture was stirred for 1 h, allowed to warm to room temperature, and filtered. The deep purple filtrate was then chilled to −20 °C for 8 h whereupon large orange crystals precipitated; yield 6.7 g (70%).

Preparation of $W_2[O_2CC_6H_4(4\text{-}CN)]_4(C_4H_8O)_2$. A 0.46-g (3-mmol) amount of lithium *p*-cyanobenzoate and 17.8 g of 0.4% sodium amalgam (3 mmol) were added to 0.5 g (1.5 mmol) of WCl_4 in 30 mL of THF at −20 °C. The mixture was stirred for 1 h, warmed to room temperature, and filtered. The solvent was then pumped out. The dark brown crystalline residue weighed 0.47 g (yield 60%). Anal. Calcd for $W_2O_{10}C_{40}H_{32}N_4$: C, 43.81; H, 2.92; N, 5.11. Found: C, 42.23; H, 2.73; N, 5.03.

Preparation of $W_2[O_2CC_6H_2[2,4,6\text{-}(CH_3)_3]]_4\cdot 2CH_3C_6H_5$. Tungsten(IV) chloride (0.50 g, 1.5 mmol) was dissolved in 30 mL of THF at −25 °C. 0.4% sodium amalgam (17.8 g, 3.1 mmol) and 0.56 g (3.0 mmol) of sodium 2,4,6-trimethylbenzoate were than added to this solution. After vigorous stirring for $^1/_2$ h, the solution was allowed to warm up to room temperature. The solvent was then stripped from this deep red solution, and the residue was redissolved in 20 mL of toluene. This bright, orange-red solution was filtered into a Schlenk tube and cooled to −20 °C. After 2 weeks, the tube contained large red single crystals (yield ca. 0.54 g, 60%).

X-ray Structure Determinations. The majority of the technical details are summarized in Table I. In each case the crystal was protected with a coating of epoxy cement and mounted either in a glass capillary or on a glass fiber. In each case absorption corrections were made by an empirical method based on ψ scans (ψ = 0–360°, every 10°) for χ values near 90°. The minimum and maximum relative transmission values are given in Table I. In each case the structure was solved by first finding the position of the tungsten atom from the Patterson function and then using a sequence of Fourier maps and least-squares refinements. Scattering factors were taken from ref 12. All atoms were refined anisotropically except for the solvent molecules in **2** and **3**, which were treated isotropically. In each compound the molecule is located on a crystallographic inversion center.

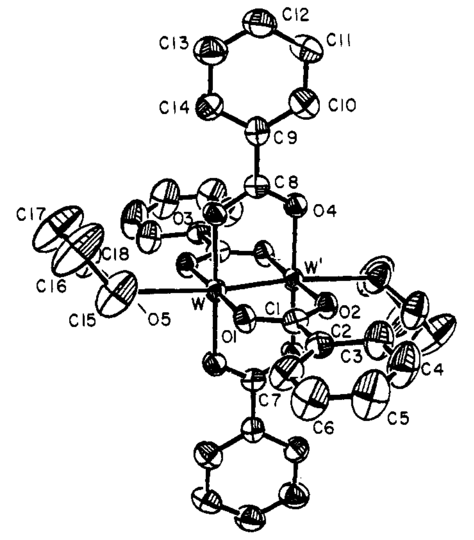

Figure 1. The $W_2(O_2CC_6H_5)_4(C_4H_8O)_2$ molecule. Thermal ellipsoids enclose 40% of the electron density for each atom.

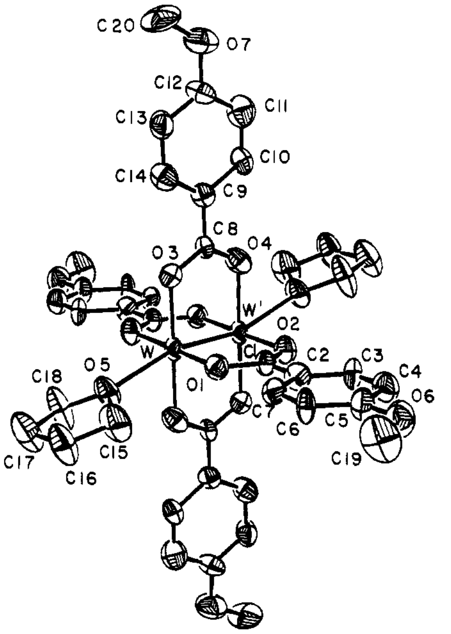

Figure 2. The $W_2[O_2CC_6H_4(4\text{-}OCH_3)]_4(C_4H_8O)_2$ molecule. Thermal ellipsoids enclose 40% of the electron density for each atom.

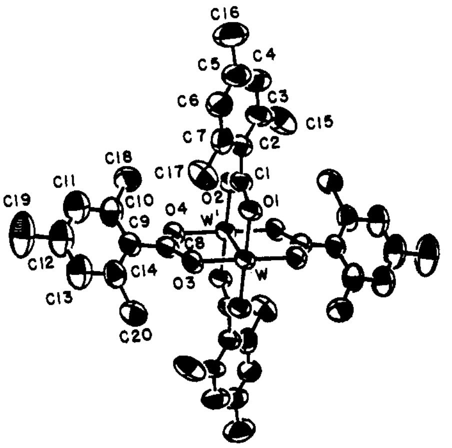

Figure 3. The $W_2[O_2CC_6H_2[2,4,6\text{-}(CH_3)_3]]_4$ molecule. Thermal ellipsoids enclose 40% of the electron density for each atom.

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Table I. Crystallographic Parameters for $W_2(O_2CC_6H_5)_4(C_4H_8O)_2$ (1), $W_2[O_2CC_6H_4(4\text{-}OCH_3)]_4(C_4H_8O)_2$ (2) and $W_2[O_2CC_6H_2[2,4,6\text{-}(CH_3)_3]]_4\cdot 2CH_3C_6H_5$ (3)

	1	2	3
fw	996.38	1260.70	1204.78
space group	$P2_1c$	$P\bar{1}$	$P2_1c$
syst abs	$h0l$, $l = 2n$; $0k0$, $k = 2n$	none	$h0l$, $l = 2n$; $0k0$, $k = 2n$
a, Å	9.511 (7)	11.590 (4)	8.141 (3)
b, Å	17.716 (7)	14.421 (3)	21.873 (4)
c, Å	10.843 (3)	8.278 (2)	14.244 (3)
α, deg	(90)	100.77 (2)	(90)
β, deg	109.52 (4)	103.23 (2)	102.41 (2)
γ, deg	(90)	68.55 (2)	(90)
V, Å^3	1722 (3)	1245 (4)	2459 (2)
Z	2	1	2
d_{calcd}, g/cm^3	1.921	1.681	1.627
cryst size, mm	0.3 × 0.3 × 0.3	0.2 × 0.2 × 0.5	0.4 × 0.4 × 0.6
μ(Mo Kα), cm^{-1}	68.742	47.792	48.265
data collection instrument	Syntex $P\bar{1}$	Syntex $P\bar{1}$	CAD-4F
radiation (monochromated in incident beam)	Mo Kα	Mo Kα	Mo Kα
orientation reflcns, no., range (2θ, deg)	15, 25–35	15, 25–35	25, 20–30
temp, °C	22 ± 2	22 ± 2	22 ± 2
scan method	θ–2θ	θ–2θ	θ–2θ
data collection range, 2θ, deg	2–50	4–50	4–50
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	3256, 2011	3819, 2486	3358, 2790
no. of parameters refined	217	273	270
transmission factors, max, min	0.814, 0.700	0.909, 0.760	0.824, 0.672
R^a	0.033	0.057	0.035
$R_w{}^b$	0.042	0.070	0.045
quality-of-fit indicator^c	0.888	1.019	1.338
largest shift/esd, final cycle	0.48	0.25	0.20
largest peak, e/Å^3	0.21	1.93	0.83

[a] $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$; $w = 1\sigma^2(|F_o|)$. [c] Quality of fit $= [\Sigma w(|F_o| - |F_c|)^2 / (N_{\text{observns}} - N_{\text{parameters}})]^{1/2}$.

Table II. Positional Parameters and Their Estimated Standard Deviations for $W_2(O_2CC_6H_5)_4(C_4H_8O)_2{}^a$

atom	x	y	z
W	0.10076 (4)	0.02482 (2)	0.07041 (3)
O(1)	0.0558 (6)	−0.0265 (4)	0.2247 (6)
O(2)	0.1499 (6)	0.0787 (4)	−0.0815 (5)
O(3)	0.2234 (6)	−0.0700 (4)	0.0543 (6)
O(4)	0.0176 (6)	−0.1186 (4)	−0.0915 (6)
O(5)	0.3675 (7)	0.0711 (5)	0.2148 (7)
C(1)	−0.0605 (9)	−0.0694 (6)	0.1976 (9)
C(2)	−0.0902 (9)	−0.1096 (6)	0.3052 (9)
C(3)	−0.198 (1)	−0.1661 (7)	0.280 (1)
C(4)	−0.225 (1)	−0.2045 (8)	0.381 (1)
C(5)	−0.140 (1)	−0.1872 (9)	0.510 (1)
C(6)	−0.032 (1)	−0.1300 (9)	0.537 (1)
C(7)	−0.005 (1)	−0.0906 (8)	0.438 (1)
C(8)	0.1556 (9)	−0.1237 (5)	−0.0251 (8)
C(9)	0.2425 (9)	−0.1900 (6)	−0.0391 (8)
C(10)	0.181 (1)	−0.2399 (6)	−0.142 (1)
C(11)	0.263 (1)	−0.3023 (6)	−0.161 (1)
C(12)	0.408 (1)	−0.3116 (7)	−0.076 (1)
C(13)	0.467 (1)	−0.2647 (7)	0.032 (1)
C(14)	0.386 (1)	−0.2014 (6)	0.050 (1)
C(15)	0.435 (1)	0.0277 (8)	0.330 (1)
C(16)	0.592 (2)	0.014 (1)	0.334 (2)
C(17)	0.612 (1)	0.052 (1)	0.226 (1)
C(18)	0.480 (1)	0.0949 (9)	0.153 (1)

[a] Estimated standard deviations in the least significant digits are shown in parentheses.

Results

Structural Results. Pertinent crystallographic data and parameters are listed in Table I. Tables II–IV give the positional parameters for the three compounds, employing the atom-numbering schemes shown in Figures 1–3. Table V gives the most important distances and angles. Complete lists are available in the supplementary material.

In each of the three compounds, the ditungsten unit is located on an inversion center, and the asymmetric unit consists of half of the molecule. The carboxylate groups are bonded in a regular fashion, imparting approximate D_{4h} symmetry to the central portion of the molecule.

Table III. Positional Parameters and Their Estimated Standard Deviations for $W_2[O_2CC_6H_4(4\text{-}OCH_3)]_4(C_4H_8O)_2\cdot 2C_4H_8O^a$

atom	x	y	z
W	0.07343 (6)	0.46476 (5)	0.10226 (9)
O(1)	−0.0167 (9)	0.5765 (7)	0.271 (1)
O(2)	−0.166 (1)	0.6499 (8)	0.067 (1)
O(3)	−0.0353 (9)	0.3820 (7)	0.131 (1)
O(4)	0.183 (1)	0.5460 (8)	0.075 (1)
O(5)	0.242 (1)	0.4356 (9)	0.368 (1)
O(6)	−0.358 (1)	0.9440 (9)	0.697 (2)
O(7)	−0.436 (1)	0.1819 (9)	0.131 (2)
C(1)	−0.121 (1)	0.646 (1)	0.222 (2)
C(2)	−0.182 (2)	0.724 (1)	0.350 (2)
C(3)	−0.295 (2)	0.803 (1)	0.294 (2)
C(4)	−0.351 (2)	0.875 (1)	0.419 (2)
C(5)	−0.296 (2)	0.868 (1)	0.589 (2)
C(6)	−0.188 (1)	0.790 (1)	0.639 (2)
C(7)	−0.131 (1)	0.717 (1)	0.518 (2)
C(8)	−0.142 (1)	0.396 (1)	0.039 (2)
C(9)	−0.217 (1)	0.339 (1)	0.063 (2)
C(10)	−0.341 (2)	0.353 (1)	−0.036 (3)
C(11)	−0.412 (2)	0.301 (1)	−0.011 (2)
C(12)	−0.363 (1)	0.232 (1)	0.109 (2)
C(13)	−0.243 (1)	0.217 (1)	0.211 (2)
C(14)	−0.172 (1)	0.272 (1)	0.182 (2)
C(15)	0.242 (2)	0.503 (2)	0.523 (2)
C(16)	0.365 (2)	0.454 (2)	0.628 (3)
C(17)	0.446 (2)	0.368 (2)	0.525 (3)
C(18)	0.374 (2)	0.372 (2)	0.349 (2)
C(19)	−0.310 (2)	0.945 (2)	0.874 (2)
C(20)	−0.393 (2)	0.116 (1)	0.256 (3)
O(8)^b	−0.021 (3)	0.866 (3)	0.217 (5)
C(21)^b	0.078 (3)	0.808 (3)	0.337 (5)
C(22)^b	0.167 (4)	0.852 (3)	0.410 (5)
C(23)^b	0.158 (4)	0.918 (3)	0.305 (6)
C(24)^b	0.037 (4)	0.952 (4)	0.198 (7)

[a] Estimated standard deviations in the least significant digits are shown in parentheses. [b] Refined isotropically.

In both $W_2(O_2CC_6H_5)_4(C_4H_8O)_2$ and $W_2[O_2CC_6H_4(4\text{-}O\text{-}CH_3)]_4(C_4H_8O)_2$, two THF molecules are present as axial

Table IV. Positional Parameters and Their Estimated Standard Deviations for $W_2[O_2CC_6H_2[2,4,6-(CH_3)_3]]_4 \cdot 2CH_3C_6H_5$[a]

atom	x	y	z
W	0.12087 (4)	0.01275 (2)	0.04538 (2)
O(1)	0.1974 (6)	0.4505 (3)	0.4273 (3)
O(2)	0.9522 (6)	0.4764 (3)	0.3348 (4)
O(3)	0.9699 (6)	0.5989 (3)	0.4336 (4)
O(4)	0.2185 (6)	0.5728 (3)	0.5259 (4)
C(1)	0.0976 (9)	0.4509 (4)	0.3467 (5)
C(2)	0.1399 (9)	0.4192 (4)	0.2627 (5)
C(3)	0.124 (1)	0.4509 (5)	0.1747 (6)
C(4)	0.156 (1)	0.4181 (6)	0.0947 (7)
C(5)	0.199 (1)	0.1427 (6)	−0.3962 (7)
C(6)	0.219 (1)	0.1729 (5)	−0.3107 (7)
C(7)	0.191 (1)	0.1418 (4)	−0.2294 (7)
C(8)	0.1219 (9)	−0.1129 (4)	−0.0242 (5)
C(9)	0.1789 (9)	−0.1776 (4)	−0.0285 (6)
C(10)	0.264 (1)	−0.2052 (5)	0.0545 (7)
C(11)	0.305 (1)	−0.2680 (5)	0.0546 (8)
C(12)	0.263 (1)	−0.3000 (5)	−0.0370 (9)
C(13)	0.182 (1)	−0.2709 (5)	−0.1196 (9)
C(14)	0.139 (1)	−0.2087 (4)	−0.1151 (7)
C(15)	0.083 (1)	−0.0188 (5)	−0.3343 (7)
C(16)	0.219 (2)	0.1784 (7)	−0.4857 (8)
C(17)	0.217 (2)	0.1766 (5)	−0.1310 (7)
C(18)	0.308 (1)	−0.1719 (6)	0.1517 (7)
C(19)	0.304 (2)	−0.3699 (5)	−0.040 (1)
C(20)	0.058 (1)	−0.1773 (5)	−0.2131 (7)
C(21)[b]	0.568 (2)	0.6302 (8)	0.301 (1)
C(22)[b]	0.600 (1)	0.6026 (5)	0.2245 (8)
C(23)[b]	0.584 (2)	0.5448 (7)	0.216 (1)
C(24)[b]	0.536 (3)	0.5044 (9)	0.288 (2)
C(25)[b]	0.509 (2)	0.5496 (8)	0.363 (1)
C(25A)[b]	0.511 (2)	0.5151 (8)	0.334 (1)
C(26)[b]	0.522 (3)	0.615 (1)	0.377 (2)
C(26A)[b]	0.506 (2)	0.5756 (8)	0.387 (1)
C(27B)[b]	0.566 (6)	0.482 (2)	0.201 (3)
C(27)[b]	0.589 (6)	0.510 (2)	0.143 (3)
C(27A)[b]	0.577 (4)	0.670 (1)	0.352 (2)

[a] Estimated standard deviations with their least significant digits are shown in parentheses. [b] Refined isotropically.

Table V. Important Bond Distances and Angles in the Three Compounds

	1	**2**	**3**
W–W, Å	2.196 (1)	2.203 (1)	2.176 (1)
W–O(RCO_2) (av), Å	2.077 [4]	2.085 [6]	2.071 [3]
W–O(ax), Å	2.628 (8)	2.57 (1)	
W–W–O (av), deg	90.7 [2]	90.3 [2]	90.65 [6]

ligands with W–O(THF) distances 2.628 (8) and 2.569 (9) Å and ∠W′–W–O(THF) = 169.7 (2) and 163.3 (3)°, respectively. The W–W distance is 2.196 (1) Å in $W_2(O_2CC_6H_5)_4(C_4H_8O)_2$ and 2.203 (1) Å in $W_2[O_2CC_6H_4(4\text{-}OCH_3)]_4(C_4H_8O)_2$. Compared with the bond length in the molybdenum analogue,[13] $Mo_2(O_2CC_6H_5)_4(\text{diglyme})_2$, the W–W bond length is about 0.10 Å longer, while the other dimensions are practically the same.

$W_2[O_2CC_6H_2[2,4,6-(CH_3)_3]]_4$ is different from the first two. The W–W distance is 2.176 (1) Å with the axial position unoccupied; the toluene molecules are located along the axial directions but at ca. 3.2 Å away from the tungsten atoms. The toluene molecules are not coordinated to the tungsten atoms but are present simply as solvent molecules of crystallization filling voids between the ditungsten molecules. The location of these solvent molecules, which block but do not coordinate to the axial positions, leaves a totally isolated $W_2(O_2CR)_4$ unit. The W–W distance is ca. 0.02 Å shorter than those in the compounds with axial THF interactions. The M–M bond-lengthening effect of these axial ligand interactions in the tungsten case is smaller than that for chromium compounds but larger than that (ca. 0.01 Å) in the molybdenum case. This indicates that the sensitivity of the W–W quadruple bond to axial ligands is between that of chromium and molybdenum quadruple bonds.

In these three compounds, as Figures 1–3 show, the phenyl rings adopt different torsion angles about the O_2C–C(phenyl) bond. The mean dihedral angles for the phenyl rings relative to the ditungsten carboxylate units in these three compounds are 11.2 [1], 2.1 [1], and 85.8 [1]° for the phenyl, 4-methoxyphenyl, and mesityl compounds, respectively (see Table VI).

Spectroscopic Measurements. Solutions were prepared in thoroughly deoxygenated dry solvents. Since all the tungsten compounds are extremely sensitive in solution, they decomposed slowly in the quartz cell even when the cell was sealed with a rubber septum. Thus, the extinction coefficients cannot be considered accurate.

A sample of $W_2(O_2CC_6H_5)_4(C_4H_8O)_2$ pressed in a KBr pellet was examined at ca. 5 K to see if any vibrational fine structure could be determined. No structure was resolved.

Discussion

Perhaps the most important aspect of this work is that it shows that at least some $W_2(O_2CR)_4$ compounds can be prepared rather easily and prepared in excellent yield. This, along with Sattelberger's method for preparing the trifluoroacetate, is a major step forward in the field.

The W–W distances in quadruply bonded ditungsten(II) compounds span a rather large range (0.2 Å, from 2.155 (2) Å in $W_2(\text{dmhp})_4$, Hdmhp = 2,6-dimethyl-6-hydroxypyridine,[14] to 2.287 (1) Å in $W_2Cl_4(\text{dmpe})_2$,[15] dmpe = bis(dimethylphosphino)ethane). The carboxylato ditungsten compounds isolated here have W–W bonds that are longer than those in noncarboxylato-bridged compounds but shorter than those in nonbridged ditungsten compounds. The behavior of the W–W quadruple bond is consistent with the view that for the metals in the third transition series the M–M quadruple bonds owe little of their shortness to the δ component of the metal–metal bond.

The difficulties encountered with the ditungsten compounds have persistently raised the question of how much intrinsic difference there might be between Mo–Mo and W–W quadruple bonds. It is well established[10,16] that the instability of the tungsten systems resides with the metal atoms and the metal–metal interactions. The ultimate reason there is a difference in M–M bonding while the M–L bonding is essentially the same on going from Mo_2 to W_2 compounds is the presence of much larger cores (by 32 electrons) in the tungsten atoms. This has a negligible effect on the M–L bonds, but it causes the W–W bonds to be ca. 0.10 Å longer than the Mo–Mo bonds. The greater length considerably reduces the δ overlap, has a smaller but still significant adverse effect on

Table VI. Selected Dihedral Angles in $W_2(O_2CR)_4$ Compounds

compds	plane 1	plane 2	dihedral angles, deg	av, deg
$W_2(O_2CC_6H_5)_4(C_4H_8O)_2$	O(1)/C(1)/O(2)	C(3)/C(2)/C(7)	9.9 (1)	11.2 [1]
	O(3)/C(8)/O(4)	C(10)/C(9)/C(14)	12.5 (1)	
$W_2[O_2CC_6H_4(4\text{-}OCH_3)]_4(C_4H_8O)_2$	O(1)/C(1)/O(2)	C(3)/C(2)/C(7)	2.6 (1)	2.1 [1]
	O(3)/C(8)/O(4)	C(10)/C(9)/C(14)	1.6 (1)	
$W_2[O_2CC_6H_2[2,4,6-(CH_3)_3]]_4$	O(1)/C(1)/O(2)	C(3)/C(2)/C(7)	86.3 (1)	85.8 [1]
	O(3)/C(8)/O(4)	C(10)/C(9)/C(14)	85.2 (1)	

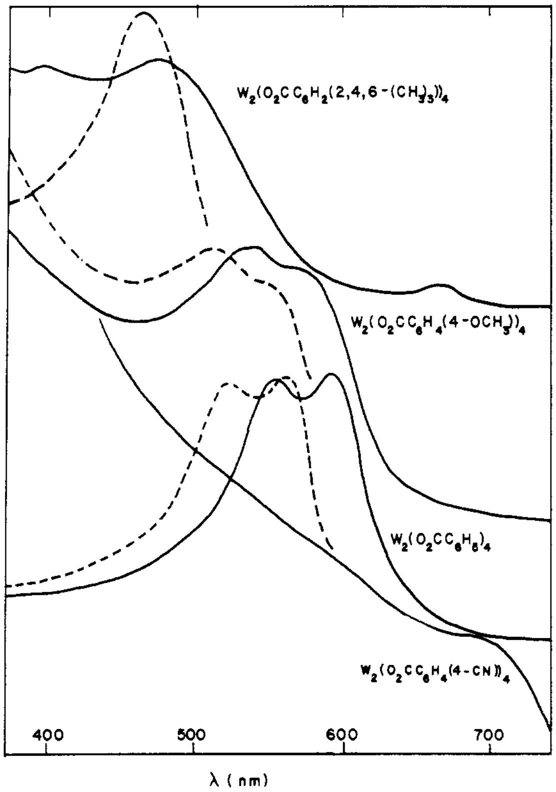

Figure 4. Electronic spectra of four carboxylate ditungsten compounds: (---) in toluene; (—) in THF. The crystal structure of $W_2[O_2CC_6H_4(4\text{-}CN)]_4$ has not been determined.

the π overlaps, and may also be responsible for reallocating d character among several orbitals with the symmetry appropriate for M–M σ bonding. Thus, the weaker W–W quadruple bond appears to be more reactive compared to the Mo–Mo quadruple bond.

For compounds with quadruple bonds the most important spectroscopic feature is the electronic transition $^1A_{1g} \rightarrow {}^1A_{2u}$ ($\delta \rightarrow \delta^*$), since this is expected to be the one of lowest energy (unless the corresponding $^1A_{1g} \rightarrow {}^3A_{2u}$ transition is observed) and it has characteristics of particular interest spectroscopically. Figure 4 shows the electronic spectra of four carboxylato ditungsten compounds, the three whose structures have been determined and the 4-cyanobenzoate, recorded in THF (solid line) and toluene (dashed line). The absorption bands shift to higher energy as the R group of the carboxylato bridging ligand changes from the strongly electron-withdrawing $(4\text{-}CN)C_6H_4CO_2^-$ to that of intermediate character, $C_6H_5CO_2^-$, and then to the electron-donating $(4\text{-}CH_3)OC_6H_4CO_2^-$. The $[2,4,6\text{-}(CH_3)_3]C_6H_2CO_2^-$ group is also electron donating relative to phenyl, but the more important factor here is that the ring is nearly perpendicular to the carboxyl group. There appears to be a relationship between the inductive effect of the bridging ligand and the M–M quadruple bond strength. This trend, which was first noted by San Filippo in the electronic spectra of the molybdenum analogues,[17] will be a major focus of our discussion.

For each compound the absorption bands recorded in the noncoordinating solvent, toluene, are at shorter wavelengths than those seen in the coordinating THF solutions with an approximately constant difference of 30 nm. This pronounced influence of solvent on the position of the bands can be attributed primarily to axial donor adduct formation in THF solution. The bonding of axial ligands weakens and lengthens the W–W bond, thus shifting the $\delta \rightarrow \delta^*$ transitions to lower energies.

Table VII. Absorption Bands for Some Dinuclear Tungsten(II) and Molybdenum(II) Carboxylates

species	medium	abs max, nm	$10^3\nu$, cm^{-1}	ref
$Mo_2[O_2CC_6H_2[2,4,6\text{-}(CH_3)_3]]_4$	acetone	366	27.3	17
$Mo_2(O_2CC_6H_5)_4$	acetone	423	23.6	17
	THF	427	23.4	17
$Mo_2[O_2CC_6H_4(4\text{-}OCH_3)]_4$	acetone	417	24.0	17
$Mo_2[O_2CC_6H_4(4\text{-}CN)]_4$	acetone	478	20.9	17
$W_2[O_2CC_6H_2[2,4,6\text{-}(CH_3)_3]]_4$	THF	664	15.1	
		477	21.0	
		400	25.0	
	toluene	466	21.5	
$W_2(O_2CC_6H_5)_4$	THF	590	16.8	
		549	18.2	
	toluene	560	17.9	
		520	19.2	
$W_2[O_2CC_6H_4(4\text{-}OCH_3)]_4$	THF	580	17.2	
		549	18.5	
	toluene	550	18.2	
		508	19.7	
$W_2[O_2CC_6H_4(4\text{-}CN)]_4$[a]	THF	700	14.3	

[a] Crystal structure not determined.

More important, in at least two cases there are clearly two maxima, rather than just one. Because of the great air and moisture sensitivity of these compounds, it is difficult to carry out experiments that might provide definitive data concerning assignments. Moreover, on examination of the spectrum of a powdered solid sample of the benzoate at ca. 5 K did not reveal any vibrational structure at all. Therefore, in attempting to account for the presence of two bands rather than only the single $\delta \rightarrow \delta^*$ peak we had expected in this region, we must necessarily speculate. With this caveat having been made, the following suggestions are proferred.

It is believed that when two close bands are seen, one is due to the $\delta \rightarrow \delta^*$ transition and the other can be assigned to a $\delta \rightarrow \pi^*$ transition. The π^* level concerned is a suitable combination of the empty π^* levels of individual carboxyl ligands, mainly localized in the $-CO_2^-$ part of each ligand. The four antibonding π orbitals of individual carboxyl groups can be combined to make MO's of a_{2g}, b_{2g}, and e_u symmetry. Since the δ orbital is of b_{2g} symmetry, selection rules allow a $b_{2g} \rightarrow e_u$ charge-transfer transition, with xy polarization.

The question that next arises is why such transitions are not also seen in the spectra of the corresponding dimolybdenum compounds (Table VII). We believe that they do occur but at higher energies in the molybdenum compounds[18] and are a part of the strong absorption that sets in at energies above 25 000 cm^{-1}. They are found at lower energies, close to the $\delta \rightarrow \delta^*$ bands in the W_2 compounds, for two reasons. One is that the δ bonding electrons in the $W_2(O_2CR)_4$ species are less tightly held than in the $Mo_2(O_2CR)_4$ molecules, probably by about 1 eV, as was the case with the $M_2Cl_4(PR_3)_4$ molecules recently studied by SCF–Xα–SW calculations and photoelectron spectroscopy.[16] This would mean a shift of about 8000

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(18) Support for the views expressed here has recently been provided by unpublished work of A. Bino and co-workers at the Hebrew University, Jerusalem. They find that, with conjugation of the carboxyl π^* orbitals to π systems of suitable R groups, this transition can be brought into the visible region. We thank Professor Bino for informing us of these results prior to publication.

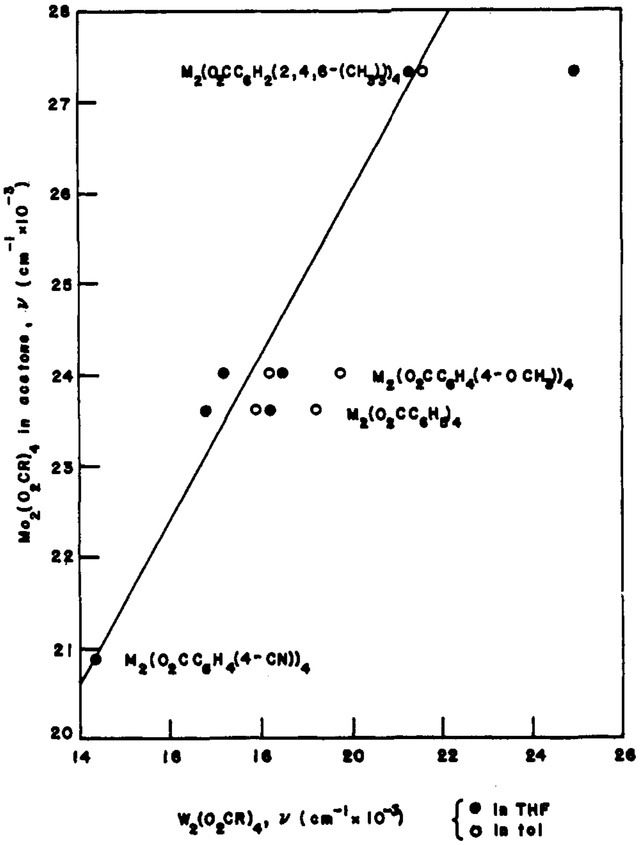

Figure 5. Plot of peak energies for the two observed bands in the $W_2(O_2CR)_4$ compounds vs. the peak energies for the $\delta \rightarrow \delta^*$ transitions in the corresponding $Mo_2(O_2CR)_4$ compounds.

cm^{-1} to lower energy in going from an $Mo_2(O_2CR)_4$ to a $W_2(O_2CR)_4$ compound.

A second factor may well be specific to the arene carboxylic acid compounds in which conjugation between the phenyl or substituted phenyl groups and the carboxyl group alters the energy and perhaps also the polarity of the π^* ligand orbital involved in the $\delta \rightarrow \pi^*$ transition. This would explain why in the compound $W_2(O_2CC_6H_2[2,4,6-(CH_3)_3])_4$, where the substituted phenyl rings are kept at angles of almost 90° to the planes of the carboxyl groups, only a single band, presumably the $\delta \rightarrow \delta^*$ band, is seen at low energy. Some light would be shed on this point if we could obtain the spectrum of a $W_2(O_2CR)_4$ compound in which R is an ordinary alkyl group, such as CH_3, C_2H_5, etc., but so far data for these compounds have not been reported.

Obviously, an experimental test of the proposed assignments, which would also show unambiguously which band is the $\delta \rightarrow \delta^*$ band and which band is the $\delta \rightarrow \pi_L^*$ band, is, in principle, possible using polarized spectroscopy of single crystals. The $\delta \rightarrow \delta^*$ band should be *z* polarized while the $\delta \rightarrow \pi^*_L$ band should be *xy* polarized. However, in view of the extreme sensitivity of these compounds to the atmosphere and the intensity of the bands, such an experiment is probably not feasible.

In the absence of any rigorous experimental test of proposed assignments, we can at least look for internal consistency in the available data. One correlation that might be expected is that the energies of the $\delta \rightarrow \delta^*$ transitions for analogous $Mo_2(O_2CR)_4$ and $W_2(O_2CR)_4$ compounds would be linearly related. This possibility is examined in Figure 5, where the peak positions for $\delta \rightarrow \delta^*$ transitions in acetone or THF in the four $Mo_2(O_2CR)_4$ compounds with R = $4\text{-}CNC_6H_4$, C_6H_5, $4\text{-}CH_3OC_6H_4$, and $2,4,6\text{-}(CH_3)_3C_6H_2$ are plotted against the peak positions for all observed bands for the ditungsten analogues in both THF and toluene solutions. These data seem to correlate best on the assumption that the lower energy peaks in the tungsten compounds are the $\delta \rightarrow \delta^*$ transitions.

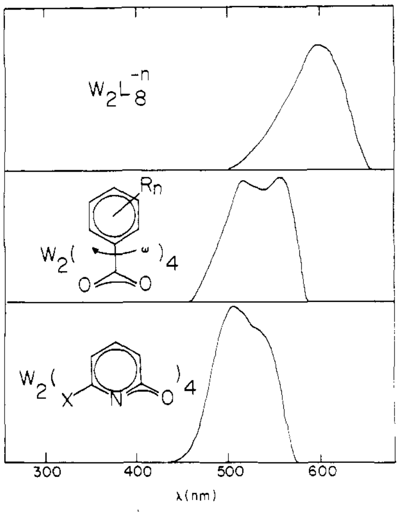

Figure 6. Typical visible spectra for three types of quadruply bonded ditungsten compounds.

We note with interest that in a broad survey of quadruply bonded ditungsten compounds the spectral region in which the $\delta \rightarrow \delta^*$ transition is found shows features specific to the type of ligands coordinated to the dimetal center. Though the spectra show some variations even for compounds of the same type, nevertheless, trends can be seen that are in good agreement with the chemistry involved. Figure 6 shows three representative spectra for given types of ditungsten compounds. The $\delta \rightarrow \delta^*$ transitions are assigned,[15,19,20] and in the last two, metal to metal π^* transitions are also observed.

For ditungsten compounds of type M_2L_8, where L is a nonbridging ligand, the $\delta \rightarrow \delta^*$ transition is seen as a single peak. This is not unexpected since the dimetal unit is unsupported, is free from ligand π systems, and is therefore free from such interactions. Spectra such as this are seen in $W_2(CH_3)_8^{4-}$ and $W_2Cl_4[P(CH_3)_3]_4$.[15,19]

For compounds of the second type, which contain bridging arene carboxylato ligands, the spectra characteristically take on the shape of a doublet when the aryl ring is essentially coplanar with the five-membered ring formed by the tungstens and the carboxylato unit. As already suggested, the peak at lower energy is considered to be the $\delta \rightarrow \delta^*$ transition and the one at higher energy may be assigned to an M → L, $\delta \rightarrow \pi^*$ charge-transfer transition. This is due to the presence of the aryl group π system, which now interacts with the metal δ orbitals when arranged in favorable orientations, i.e., coplanar. In the molybdenum analogues, only one peak is seen and this may be attributed to the stronger δ bonding in these compounds, which effectively places the δ orbitals at lower energy, thereby increasing the energy difference between the δ bonding orbital and ligand π^* orbitals and perhaps also reducing the δ to π^* overlap.

The spectra of compounds of the third type, M_2(6-X-2-hydroxypyridine)$_4$, X = CH_3, F, have the shape of a large peak with a pronounced shoulder. We believe that the shoulder may be assigned to the $\delta \rightarrow \delta^*$ transition and the large peak is $\delta \rightarrow \pi_L^*$.[20] This greater overlap of the two peaks is due to the close proximity of the aromatic π system in the ligand to the dimetal center. This results in a large overlap of metal δ and ligand π orbitals and brings those transitions involved closer in energy. However, the molybdenum analogues show a

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Table VIII. Electronic Spectra of $M_2(6\text{-}X\text{-}2\text{-}(O)\text{-}C_5H_3N)_4$ Type Compounds

species	media	abs max, nm	$10^3\nu$, cm^{-1}	ref
$Mo_2[6\text{-}CH_3\text{-}2\text{-}(O)C_5H_3N]_4$	THF	400	25.0	
		495	20.2	
$Mo_2[6\text{-}F\text{-}2\text{-}(O)C_5H_3N]_4(C_4H_8O)$	THF	400	25.0	20
		498	20.1	
$W_2[6\text{-}CH_3\text{-}2\text{-}(O)C_5H_3N]_4$	THF	505	19.8	
		535	18.7	
$W_2[6\text{-}F\text{-}2\text{-}(O)C_5H_3N]_4(C_4H_8O)$	THF	475	21.1	20
		501	20.0	

greater separation of those two peaks with distinct $\delta \rightarrow \delta^*$ and $\delta \rightarrow \pi^*_L$ bands (see Table VIII). In each of the two molybdenum compounds the $\delta \rightarrow \pi^*_L$ peaks appear at the same wavelength, and this indicates a much lesser degree of δ^*_M–π^*_L interaction. This is not true for the tungsten compounds because, as implied previously, there is now a weaker δ bond and the δ orbitals lie at higher energy, closer to the ligand π^* orbital, and interact more strongly.[21]

A final point to be noted here is that for two compounds the region of the $\delta \rightarrow \delta^*$ transition in ditungsten compounds has been examined at liquid-helium temperature with use of powdered crystalline samples. This work was done with the help of Dr. P. E. Fanwick. The compounds used were $W_2(O_2CC_6H_5)_4$ and $W_2(mhp)_4$. In neither case was any vibrational structure resolved, contrary to the behavior of dimolydenum compounds, which nearly always display a progression in ν_{M-M} for the excited state. There are perhaps several factors that might lead to this result. First, the value of ν_{W-W} is likely to be only 250 ± 30 cm^{-1}, thus making even a single progression more difficult to resolve. In addition, however, if W–W δ bonding is weaker while W–O π bonding is stronger, the "$\delta \rightarrow \delta^*$ excitation" may no longer be so accurately described in this simple way. The electronic transition in question may thus also excite totally symmetric vibrations roughly describable as W–O stretching and W–W–O bending. If progressions in these frequencies as well as one in the ν_{W-W} vibration were all present, they would doubtless overlap in such a way as to make resolution of any individual vibrational components impossible.

Acknowledgment. We thank the National Science Foundation for support. Dr. Dennis Lay carried out some early attempts to prepare $W_2(O_2CR)_4$ compounds which, though unsuccessful, were helpful in guiding our own work. Dr. Graham N. Mott provided encouragement and advice. We thank Dr. Philip Fanwick for helpful discussions and for providing information on unpublished studies.

Registry No. **1**, 82752-90-7; **2**, 89637-11-6; **3**, 89637-13-8; $W_2[O_2CC_6H_4(4\text{-}CN)]_4(C_4H_8O)_2$, 89637-14-9; WCl_4, 13470-13-8; W, 7440-33-7.

Supplementary Material Available: Tables of thermal parameters, complete lists of bond distances and angles, and tables of observed and calculated structure factors for all three compounds (44 pages). Ordering information is given on any current masthead page.

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[21] A recent study of the spectra of the $M_2(mhp)_4$ compounds with M = Cr, Mo by Fanwick, Bursten, and Kaufmann (to be submitted for publication) is in harmony with the suggestions made here.