interaction. It is thus understandable that the molecules are packed in such a way (Figure 2) that there are no intermolecular interactions except van der Waals contacts between peripheral portions of the molecules.

The $Cr_2(O_2CCH_3)_2$ unit of the molecule has dimensions entirely typical of those in a host of $Cr_2(O_2CR)_4L_2$[5a,b] except that the Cr–Cr–O angles here, 95 ± 0.5°, are much larger because of the much smaller Cr–Cr distance. This observation provides further support for the point to which we first drew attention years ago,[10] namely, that bridging RCO_2^- ligands of this type merely keep the metal atoms close enough to interact according to their own electronic requirements but allow the actual M–M distance to vary enormously, as those electronic requirements may dictate.

Acknowledgment. We thank Dr. S. A. Koch for his interest and assistance and the National Science Foundation for financial support.

Registry No. $Cr_2(o\text{-}Bu^tOC_6H_4)_2(O_2CCH_3)_2$, 66183-85-5; $Cr_2(O_2CCH_3)_4$, 15020-15-2; 2-butoxyphenyllithium, 66183-92-4.

Supplementary Material Available: A table of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

References and Notes

(1) F. A. Cotton, S. Koch, and M. Millar, *J. Am. Chem. Soc.*, **99**, 7372 (1977).
(2) F. A. Cotton and M. Millar, *Inorg. Chim. Acta*, **25**, L105 (1977).
(3) J. Krausse, G. Marx, and G. Schödl, *J. Organomet. Chem.*, **21**, 159 (1970).
(4) J. Krausse and G. Schödl, *J. Organomet. Chem.*, **27**, 59 (1971).
(5) (a) F. A. Cotton, M. W. Extine, and G. W. Rice, *Inorg. Chem.*, **17**, 176 (1978); (b) F. A. Cotton and G. W. Rice, *Inorg. Chem.*, **17**, 688 (1978); (c) F. A. Cotton and M. W. Extine, unpublished work.
(6) F. A. Cotton and S. Koch, *Inorg. Chem.*, **17**, 2021 (1978).
(7) C. Frisell and S.-O. Lawesson, "Organic Synthesis", Collect. Vol. V, Wiley, New York, N.Y., 1973, p 924.
(8) D. A. Shirley and J. P. Hendrix, *J. Organomet. Chem.*, **11**, 217 (1968).
(9) All crystallographic computing was carried out on a PDP 11/45 computer, using the Enraf-Nonius structure determination package, at the Molecular Structure Corp., College Station, Tex.
(10) F. A. Cotton, *Rev. Pure Appl. Chem.*, **17**, 25 (1967).

Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843

X-ray Crystallographic Structural Studies of the Quadruply Bonded Octamethylditungsten Anion and a Related Species Containing a Mixture of Chloro and Methyl Ligands

DOUGLAS M. COLLINS, F. ALBERT COTTON,* STEPHEN A. KOCH, MICHELLE MILLAR,
and CARLOS A. MURILLO

Received January 6, 1978

Two compounds containing tungsten-to-tungsten quadruple bonds have been studied by X-ray crystallography. These are $Li_4W_2(CH_3)_8\cdot 4Et_2O$ (**1**) and $Li_4W_2(CH_3)_xCl_{8-x}\cdot 4THF$ (**2**). In each case the $W_2X_8^{4-}$ ion of idealized D_{4h} symmetry has been found and its structure defined; in **1** all X are CH_3 while in **2** CH_3 and Cl are randomly distributed with 59% of X being CH_3 and 41% being Cl in the crystal studied. The W–W distances are 2.264 (1) and 2.263 (2) Å in **1** and **2**, respectively. For **1** the space group is $C2/c$. The unit cell dimensions are a = 19.319 (3) Å, b = 11.554 (3) Å, c = 18.679 (3) Å, and β = 104.83 (1)°; V = 4031 (2) Å^3, and with Z = 4, d_{calcd} = 1.34 g cm^{-3}. For **2** the space group is $P42_12$ and the cell dimensions are a = 11.403 (8) and c = 11.969 (5) Å; V = 1556 (2) Å^3, and with Z = 2, d_{calcd} = 1.89 g cm^{-3}.

Introduction

The first reports of compounds for which there was good evidence of the presence of quadruple W–W bonds appeared only recently.[1,2] The principal compounds described were two containing the octamethylditungsten anion, $W_2(CH_3)_8^{4-}$, and another in which the ligand set was a mixture of CH_3 and Cl in about a 5/3 ratio. Only for this last compound had it been possible to obtain crystallographic data up to the time of our earlier report,[1] and this has been reported in a preliminary note.[2] The compounds containing only methyl groups proved very difficult to crystallize in forms suitable for single-crystal X-ray structure analysis. However, we have recently succeeded in obtaining some acceptable crystals of one of them. We are, therefore, reporting fully on our structural studies of the compounds $Li_4W_2(CH_8)\cdot 4Et_2O$ (**1**) and $Li_4W_2(CH_3)_xCl_{8-x}\cdot 4THF$ (**2**).

Experimental Section

Compounds **1** and **2** were prepared by procedures previously described.[2] We also prepared, crystallized, and examined by X-ray diffraction the compound $Li_4W_2(CH_3)_8\cdot 4THF$. We never succeeded in obtaining fully satisfactory crystals of this substance. X-ray data were collected on several, and a partial structure, showing a $W_2(CH_3)_8$ unit, was obtained and refined to give imprecise but reasonable W–W and W–C distances. However, no entirely satisfactory refinement was ever obtained and we shall not discuss the crystallography of this compound further.

Crystal Mounting Procedure for Pyrophoric, Thermally Unstable Crystals. The extreme reactivity of these compounds precludes normal crystal mounting procedures. The crystals were suspended in a matrix of cold, dry, degassed mineral oil which served to protect them from attack by air or moisture. The crystals were examined and mounted while working in a cold room whose temperature was maintained at −25 to −30 °C. Potential single crystals were transferred by pipet into Nujol-filled capillaries which had already been glued to metal mounting pins. The open end of the capillary was then sealed with epoxy cement, and the crystal was transported over a pool of liquid nitrogen to a Syntex $P\bar{1}$ diffractometer equipped with a Syntex LT-1 low-temperature attachment,[3] where the capillary was placed directly into the cold nitrogen steam. The crystal was held in place by the frozen mineral oil. If the cold stream flowing over the crystal was interrupted even momentarily, the crystal decomposed.

Structure Determination[4] for $Li_4W_2(CH_3)_8\cdot 4Et_2O$ (1). The actual crystal used in data collection was chosen from a batch of crystals which was shown analytically to be free of chloride. A crystal of approximate dimensions 0.3 × 0.3 × 0.35 mm was mounted using the techniques described above. Crystal examination and data collection were done at −70 ± 2 °C. Cell constants and axial photographs showed that the crystal had monoclinic symmetry with cell parameters a = 19.319 (3) Å, b = 11.554 (3) Å, c = 18.679 (3) Å, β = 104.83 (1)°, and V = 4031 (2) Å^3. For a formula weight of 812.23 and Z = 4 the calculated density is 1.34 g cm^{-3}. Data were collected with Mo Kα radiation monochromated by a graphite crystal in the incident beam, using the θ–2θ scan technique with a variable scan rate 4.0 to 24.0°/min. In the range $\theta < 2\theta \leq 55°$, 2556 independent reflections with $I > 3\sigma(I)$ were observed, reduced to $|F_o^2|$,

0020-1669/78/1317-2017$01.00/0

and used in the structure solution and refinement. The intensities of three standard reflections recorded periodically during data collection displayed only small, random fluctuations. An absorption correction ($\mu = 61$ cm^{-1}) was not applied because it was impossible to identify the crystal faces with the crystal immersed in mineral oil.

The systematic absences were consistent with either the centric $C2/c$ or the acentric Cc space group. Initial attempts to solve the structure were made using the $C2/c$ space group. The coordinates of the unique tungsten atom were determined from a Patterson map. Subsequent Fourier difference maps revealed the positions of the methyl carbon atoms, the ether oxygen atoms, the Li cations, and most of the ether carbon atoms. Seven of the eight ether carbon atoms refined to give chemically acceptable geometries. The eighth ethyl carbon atom refined away from a chemically reasonable position. These carbon atoms, all of which have very large thermal parameters, are surrounded by numerous ghost peaks, suggestive of partial disorder. A number of attempts were made to resolve the possible disorder of these ethyl groups and to find the missing carbon atom, but no convincing results were obtained. Similar problems have been encountered in the structure determinations of other $Li_xM_2(CH_3)_8 \cdot 4$solvent. The difficulties are compounded in this case by the overwhelming contribution of the tungsten atoms to the X-ray scattering. Final refinement, with the tungsten, methyl carbon, and ether oxygen atoms treated anisotropically,[6] gave the final residuals

$$R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.069$$

and

$$R_2 = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2} = 0.091$$

with an esd for an observation of unit weight equal to 1.80.

Structure solutions using the acentric (Cc) space group led to similar ether disorder problems and substantially higher residuals. The initial solution with the $C2/c$ space group symmetry was considered more likely to be correct. The chemically interesting core of the structure, consisting of the tungsten atoms, the CH_3 ligands, the lithium ions, and the ether oxygen atoms, is well behaved. It is also quite reasonable when it is compared to the structures of the other $M_2(CH_3)_8$ anions, as will be shown in the Discussion.

Crystal Data and Structure Determination[7] for $Li_4W_2(CH_3)_xCl_{8-x} \cdot 4THF$ (2). A red crystal measuring about 0.2 × 0.2 × 0.2 mm was sealed in a glass capillary in mineral oil, immediately cooled to −55 °C, and examined on a Syntex $P\bar{1}$ four-circle automatic diffractometer equipped with a Syntex LT-1 low-temperature attachment. Axial photographs and ω scans of several intense reflections showed that the crystal was of good quality for X-ray diffraction studies. At small scattering angles peak widths at half-height were <0.35°. Preliminary examination indicated that the crystal belonged to the tetragonal system.

For calculation of lattice parameters, 15 of the strongest reflections in the range $17 < 2\theta < 25°$ were selected to give a variety of crystal orientations. On the basis of angular settings for these reflections, the refined lattice parameters obtained from the Syntex software package (Mo Kα, λ 0.71073 Å; −55 (3) °C) are $a = 11.403$ (8) Å, $c = 11.969$ (5) Å, and $V = 1556$ (2) Å^3. For $Z = 2$ and a molecular weight of 885.84, the calculated density is 1.89 g cm^{-3}.

Intensity data were collected at −55 (3) °C using graphite-monochromatized Mo Kα radiation and a θ–2θ scan rate varying from 3 to 24°/min, depending on the intensity of the reflection. Background measurements were made at both limits of each scan. Of the 657 integrated intensities, for which $k \geq h$, collected in the range $0 < 2\theta$(Mo Kα) $< 47°$, 436 unique observations with $I > 3\sigma(I)$ were retained as observed data and corrected for Lorentz and polarization effects. Three standard reflections remeasured after every 50 data points were stable. The linear absorption coefficient, assuming Cl/Me = 1, is 82 cm^{-1} for Mo Kα radiation. No absorption correction was applied since the mineral oil under which the crystal was mounted coupled with the low thermal stability made measurements of the crystal faces virtually impossible.

The positions of the two tungsten atoms were obtained from a three-dimensional Patterson map. Solution of the structure was first attempted in the centrosymmetric space group $P4/nmm$ which was uniquely characterized by the observed extinctions, namely, the absence of all $hk0$ for which $h + k = 2n + 1$. After several unsuccessful attempts to find a good model, refinement was attempted in the noncentric space group $P42_12$ for which the above extinctions are special for position 2c, where the tungsten atoms are located. In this space group, refinement of the metal atom coordinates followed by a difference Fourier map provided the positions of the rest of the nonhydrogen atoms. All atoms were assigned isotropic thermal parameters except for the tungsten atoms for which anisotropic temperature parameters were used. Refinement converged with R values, defined as above, of $R_1 = 0.052$ and $R_2 = 0.068$.

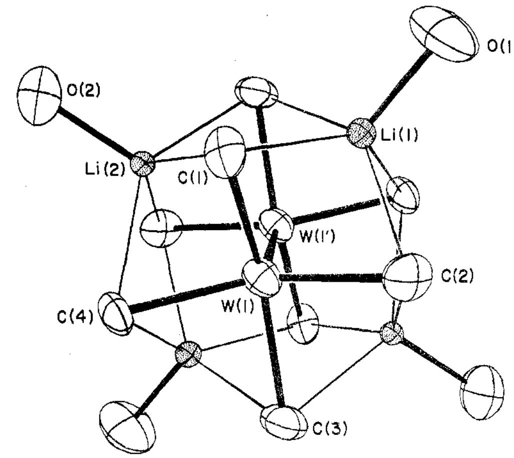

Figure 1. A drawing of the $Li_4W_2(CH_3)_8O_4$ core in $Li_4[W_2(CH_3)_8] \cdot 4(C_2H_5)_2O$, **1**. The Li atoms (stippled) are represented by ellipsoids of thermal vibration drawn to enclose 20% of their electron density while all other atoms are represented by 50% ellipsoids. Unlabeled atoms are related to labeled ones by the inversion center.

At this point of the refinement it was noticed that the atoms bonded to the tungsten atoms, all of which had so far been called carbon atoms, had surprisingly low temperature parameters (~1.3 Å^2); consequently, it was suspected that some of them might be chlorine atoms. Refinement was therefore resumed, assigning to each "carbon" position a fractional ($0 < \rho < 1$) carbon atom and a fractional ($1 - \rho$) chlorine atom. Each of the fractional C and Cl atoms was given its own positional and thermal parameters. This led to final R factors of 0.041 and 0.045 and an error in an observation of unit weight of 1.38. No attempt was made to locate the positions of the hydrogen atoms. Since $P42_12$ is a noncentrosymmetric space group, there are two enantiomeric forms. The absolute configuration was checked via the transformation of all atomic coordinates from (x, y, z) to $(-x, -y, -z)$ and refinement of parameters as before. The least-squares refinement led to convergence with similar residuals but an analysis of the bond lengths and angles around the THF molecule suggested that the first refinement $(+x, +y, +z)$ corresponds to the correct enantiomorph, although this is not conclusive. The successful refinement of the structure as well as the reasonable values of the bond lengths and angles in the molecule leaves little if any doubt that the space group $P42_12$ is correct. Also, a calculation of all structure factors shows that even though the condition for extinction ($hk0$: $h + k = 2n + 1$) is not a general space group requirement, all such reflections are calculated to be very weak. The function minimized was $\sum w(|F_o| - |F_c|)^2$ in which uniform weights were used and the scattering factors were from ref 5. Correction for anomalous scattering by tungsten was taken from Cromer and Liberman.[6] A final difference map[7] was judged to be free of significant features.

Results

Tables I and II list the positional and thermal vibration parameters for compounds **1** and **2**, respectively. Bond distances and angles are given in Tables III and IV. Figure 1 shows the $W_2(CH_3)_8{}^{4-}$ ion in **1** together with the four surrounding Li^+ ions and the oxygen atoms of the ether molecules which are coordinated to the lithium ions. The arrangement in **2** is very similar.

In **1** the $W_2(CH_3)_8{}^{4-}$ ion residues on a crystallographic center of inversion. However, the full symmetry of the anion is, to a very good approximation, D_{4h}. The four crystallographically independent W–C distances, as well as the four W–W–C and C–W–C (cis) angles are all equal within experimental error, as required by D_{4h} symmetry, and the ro-

Table I. Positional and Thermal Parameters for $Li_4[W_2(CH_3)_8]\cdot 4(C_2H_5)_2O$[a,b]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
W(1)	0.24385 (4)	0.19056 (6)	0.45059 (4)	0.00261 (2)	0.00441 (4)	0.00223 (1)	0.00049 (8)	0.00166 (2)	−0.00037 (8)
O(1)	0.2567 (9)	0.551 (2)	0.3566 (9)	0.0075 (7)	0.010 (1)	0.0056 (5)	0.000 (2)	0.0066 (9)	0.006 (2)
O(2)	0.0137 (8)	0.288 (1)	0.4498 (9)	0.0032 (4)	0.012 (2)	0.0061 (7)	0.004 (1)	0.0018 (9)	0.001 (2)
C(1)	0.1603 (10)	0.276 (2)	0.3542 (9)	0.0031 (6)	0.009 (2)	0.0019 (5)	−0.002 (2)	0.0004 (9)	−0.000 (2)
C(2)	0.3313 (9)	0.250 (2)	0.3933 (8)	0.0027 (5)	0.007 (1)	0.0021 (4)	0.003 (1)	0.0027 (7)	0.001 (1)
C(3)	0.3195 (9)	0.036 (1)	0.4893 (9)	0.0028 (5)	0.004 (1)	0.0031 (5)	0.002 (1)	0.0021 (8)	0.000 (1)
C(4)	0.1522 (9)	0.064 (2)	0.4567 (11)	0.0030 (5)	0.005 (1)	0.0049 (7)	−0.001 (2)	0.0034 (9)	0.001 (2)

Atom	x	y	z	B_{iso}, Å^2	Atom	x	y	z	B_{iso}, Å^2
C(11)	0.302 (2)	0.545 (4)	0.295 (2)	13.0 (13)	C(23)	−0.027 (3)	0.375 (6)	0.411 (4)	20.6 (24)
C(12)	0.266 (2)	0.489 (3)	0.233 (2)	8.4 (8)	C(24)	−0.055 (3)	0.386 (6)	0.329 (4)	20.5 (24)
C(13)	0.186 (3)	0.662 (5)	0.338 (3)	16.0 (17)	Li(1)	0.256 (2)	0.418 (5)	0.419 (3)	6.9 (10)
C(14)	0.232 (2)	0.738 (4)	0.393 (2)	10.5 (11)	Li(2)	0.116 (2)	0.270 (3)	0.470 (2)	5.1 (8)
C(21)	−0.032 (2)	0.202 (3)	0.491 (2)	10.0 (10)					

[a] The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [b] Numbers in parentheses are esd's occurring in the least significant digit of the preceding number.

Table II. Positional and Thermal Parameters for $Li_4W_2(CH_3)_xCl_{8-x}\cdot 4THF$[a,b]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
W(1)	$^1/_2$	0	0.1418 (1)	0.0091 (2)	β_{11}	0.0036 (1)	0	0	0
W(2)	$^1/_2$	0	0.3308 (1)	0.0103 (2)	β_{11}	0.0036 (1)	0	0	0

Atom	x	y	z	B_{iso}, Å^2	Atom	x	y	z	B_{iso}, Å^2
C(1)[b]	0.427 (10)	0.173 (10)	0.085 (9)	7 (4)	C(6)[c]	0.664 (4)	0.420 (3)	0.356 (2)	5.9 (9)
C(2)[b]	0.414 (5)	0.155 (5)	0.396 (4)	4 (1)	Cl(1)[b]	0.407 (4)	0.187 (4)	0.094 (3)	5.9 (9)
C(3)[c]	0.668 (4)	0.443 (3)	0.161 (2)	5.9 (9)	Cl(2)[b]	0.409 (3)	0.196 (3)	0.373 (3)	5.6 (7)
C(4)[c]	0.756 (4)	0.527 (7)	0.207 (3)	10.4 (15)	Li	0.571 (5)	0.206 (5)	0.230 (5)	6.7 (13)
C(5)[c]	0.745 (4)	0.487 (11)	0.331 (3)	9.2 (13)	O[c]	0.633 (2)	0.366 (2)	0.247 (1)	5.2 (4)

[a] The form of an anisotropic thermal parameter is given in Table I. [b] The occupancy of a C(1) site is given by $\rho = 0.58$ (3); thus the occupancy of a Cl(1) site is 0.42; similarly, the occupancies for C(2) and Cl(2) are 0.61 (3) and 0.39, respectively. In the molecular formula, $x = 4.8$ (2) is the corresponding value. The ligands are numbered as the tungsten atoms to which they are bonded. [c] Atom in a tetrahydrofuran ring.

Table III. Bond Distances (Å) and Angles (deg) for $Li_4W_2(CH_3)_8\cdot 4Et_2O$

A. For the $Li_4W_2(CH_3)_8O_4$ Core			
Distances			
W(1)-W(1′)	2.264 (1)		
W(1)-C(1)	2.31 (1)	W(1)-Li(1)	2.75 (3)
W(1)-C(2)	2.32 (1)	W(1′)-Li(1)	2.77 (3)
W(1)-C(3)	2.30 (1)	W(1)-Li(2)	2.72 (4)
W(1)-C(4)	2.32 (1)	W(1′)-Li(2)	2.74 (4)
W-C, av	2.32 (1)	W-Li, av	2.74 (4)
Li(1)-O(1)	1.93 (4)		
Li(2)-O(2)	1.92 (3)		
Li(1)-C(1)	2.53 (4)	Li(2)-C(1)	2.53 (3)
-C(2)	2.54 (4)	-C(2)	2.50 (3)
-C(3)	2.58 (4)	-C(3)	2.58 (3)
-C(4)	2.55 (4)	-C(4)	2.51 (3)
		Li-C, av	2.54 (4)
Angles			
W(1)-W(1′)-C(1)	106.4 (4)		
-C(2)	105.0 (4)	C(1)-W(1)-C(2)	87.7 (5)
-C(3)	106.7 (3)	-C(4)	85.3 (5)
-C(4)	105.4 (4)	C(2)-W(1)-C(3)	84.0 (5)
∠WWC, av	105.9 (7)	C(3)-W(1)-C(4)	85.8 (5)
C(1)-W(1)-C(3)	146.8 (5)	∠CWC, cis, av	85.7 (10)
C(2)-W(1)-C(4)	149.6 (5)		
∠CWC, trans, av	148 (1)		
B. For Diethyl Ether			
Distances			
O(1)-C(11)	1.63 (4)	O(2)-C(21)	1.64 (3)
O(1)-C(13)	1.85 (5)	O(2)-C(23)	1.36 (6)
C(11)-C(12)	1.35 (4)	C(23)-C(24)	1.50 (6)
C(13)-C(14)	1.46 (5)		
Angles			
C(11)-O(1)-C(13)	114 (2)	C(21)-O(2)-C(23)	112 (3)
O(1)-C(11)-C(12)	112 (3)	O(2)-C(23)-C(24)	128 (5)
O(1)-C(13)-C(14)	90 (3)		

Table IV. Bond Distances (Å) and Selected Angles (deg) for $Li_4W_2(CH_3)_xCl_{8-x}\cdot 4THF$[a]

Distances			
W(1)-W(2)	2.263 (2)	Li-O	1.96 (6)
W(1)-C(1)[b]	2.24 (12)	O-C(3)	1.41 (4)
W(1)-Cl(1)[b]	2.45 (5)	O-C(6)	1.49 (4)
W(2)-C(2)[b]	2.17 (6)	C(3)-C(4)	1.49 (7)
W(2)-Cl(2)[b]	2.51 (3)	C(4)-C(5)	1.56 (5)
Li-X[c]	2.55	C(5)-C(6)	1.24 (9)
Angles			
W(2)-W(1)-C(1)[b]	108 (3)	C(3)-O-C(6)	108 (2)
W(2)-W(1)-Cl(1)[b]	104 (1)	O-C(3)-C(4)	109 (3)
W(1)-W(2)-C(2)[b]	111 (1)	C(3)-C(4)-C(5)	97 (4)
W(1)-W(2)-Cl(2)[b]	102 (1)	C(4)-C(5)-C(6)	118 (4)
Li-O-C(3)	127 (3)	O-C(6)-C(5)	103 (3)
Li-O-C(6)	124 (3)		

[a] A tetrahydrofuran ring comprises O, C(3), C(4), C(5), and C(6). [b] The structure model requires each ligand site to be occupied by either a Cl or a CH_3 group. The ligands are numbered as the tungsten atoms to which they are bonded. [c] The value tabulated is an unweighted average of the eight possible short lithium–ligand distances, although a particular lithium atom could be close to only four tungsten ligands.

tational configuration is eclipsed within experimental error.

In **2** the presence of both CH_3 groups and Cl atoms at the X sites of the $W_2X_8^{4-}$ ions leads to greater uncertainties in the molecular dimensions. To begin with, there is the question of how to distribute these two entities. By trial and error we have found that each of the X sites (one for each end of the $W_2X_8^{4-}$ ion, replicated by the C_4 rotation operation) is best treated as though there is a random scrambling of CH_3 and Cl on it, as opposed to some scheme in which there is ordering within individual molecules but random scrambling of the molecules, but this is not a distinction that can be established with certainty. Moreover, the two CH_3 and two Cl groups, four ligands in all, have been refined with entirely independent positional and thermal parameters for each. The fractional occupancies were refined, subject only to the requirement that their sum, for each end of the ions independent of the other, total unity. The two separate occupancy parameters for carbon atoms refined to 0.58 (3) and 0.61 (3); thus, they are, within the errors, identical. This is not strictly required by the random model assumed, since the two sites are crystallographically distinct and need not have the same CH_3/Cl ratio.

Even if the model upon which refinement was based is physically perfect, the results of refining such a disordered structure are bound to be less accurate than those obtained for a comparable conventional, ordered structure, as in **1**. A pertinent point of comparison between **1** and **2** is provided by the W–C bond lengths. The mean value in **1** is 2.32 (1) Å while in **2** the independent values, 2.24 (12) and 2.17 (6) Å, give an average of 2.20 (12) Å, where we use the larger of the individual esd's as an uncertainty estimate. The distances in the two structures are not significantly different from a statistical point of view. The best W–C distance, which may be taken to be 2.32 (1) Å, is slightly larger than that in the $Mo_2(CH_3)_8^{4-}$ ion, 2.29 (1) Å,[8] and appreciably larger than that, 2.19 (1) Å, in the $Re_2(CH_3)_8^{2-}$ ion[9] where the formal oxidation number is +3.

The W–Cl distances, 2.45 (5) and 2.51 (3) Å, also carry rather large uncertainties; their average value, 2.48 (5) Å, is slightly larger than the Mo–Cl distances, 2.45 (2) Å, found in various compounds[10] containing the $Mo_2Cl_8^{4-}$ ion and considerably larger than the Re–Cl distances, 2.33 (2) Å, found in several compounds[11] containing the $Re_2Cl_8^{2-}$ ion. Clearly, the pattern of Mo–X, W–X, and Re–X distances is essentially the same for both X = CH_3 and X = Cl.

The W–W distances in the two compounds are identical, within the limits of any criterion of statistical or chemical significance, with a value of 2.264 (1) Å.

Discussion

The quantitative structural characterization of the $W_2(CH_3)_8^{4-}$ ion completes the structural work on one of the only two complete triads of homologous compounds containing metal-to-metal multiple bonds. The other triad is comprised of the $M_2(C_8H_8)_3$ (M = Cr, Mo, W) molecules which are described by Brauer and Krüger[12] and by several of us in a following paper.[13] The compounds in these two sets are quite different in many respects. In thermal and chemical stability the octamethyl anions are far inferior to the cyclooctatetraene compounds. However, the $M_2(CH_3)_8^{4-}$ anions are more closely related to the vast majority of species containing M–M quadruple bonds. Like most others (e.g., $Re_2X_8^{2-}$, $Mo_2(O_2Cr)_4$, etc.) they involve metal atoms with formal 16-electron configurations, whereas the $M_2(C_8H_8)_3$ compounds have metal atoms with formal 18-electron configurations.

It has already been shown by SCF–SW–Xα calculations that the $W_2Cl_8^{4-}$ ion (not yet prepared but approached by the $[W_2(CH_3)_{\sim5}Cl_{\sim3}]^{4-}$ ion described here) is electronically closely related to the $Mo_2Cl_8^{4-}$ and $Re_2Cl_8^{2-}$ ions, which are, in turn, quite comparable to the $Mo_2(CH_3)_4^{4-}$ and $Re_2(CH_3)_4^{4-}$ ions. It has also been shown[2,14] that the band in the visible spectrum of the $W_2(CH_3)_8^{4-}$ ion, for which the $\delta \rightarrow \delta^*$ assignment seems very likely, is related in a systematic way to the analogous bands found in the other $M_2(CH_3)_8^{n-}$ species with M = Cr, Mo, and Re.

In the series $Cr_2(CH_3)_8^{4-}$, $Mo_2(CH_3)_8^{4-}$, $W_2(CH_3)_8^{4-}$ there is a trend to greater reactivity (toward air and moisture, for example) and to lower thermal stability as the group is descended, but these changes are particularly marked in passing from the Mo to the W compound. To some extent the structures seem to be consistent with this. The increase in the M–M bond lengths, from 1.980 (5) Å in $Cr_2(CH_3)_8^{4-}$[15] to 2.148 (2) Å in $Mo_2(CH_3)_8^{4-}$[8] to 2.264 (1) Å in $W_2(CH_3)_8^{4-}$, are 0.168 and 0.116 Å at the two stages. The increase from the Cr_2 to the Mo_2 compound is not surprising; for example, the Pauling metallic radii[16] for Cr and Mo differ by 0.11 Å. However, for Mo and W atoms these radii differ by only 0.008 Å (a result of the lanthanide contraction) so that, on this basis, only a slight increase in the M–M distance on going from the Mo_2 to the W_2 species might have been anticipated. The very substantial increase that is observed surely implies that the W–W bond is substantially weaker than the Mo–Mo bond. The ultimate cause of this relative weakness in the W–W quadruple bond must be the presence of the filled 4f shell in the case of the tungsten atom while, at the same time, the other orbitals of the W atoms are very similar in size and shape to those of the Mo atom. Hence, under otherwise similar circumstances, it is impossible for two tungsten atoms to achieve the same strength of σ, π, and, especially, δ bonding as can two molybdenum atoms, because inner-shell repulsion, at the pertinent distances, is very much greater for the tungsten atoms.

Acknowledgment. We thank the National Science Foundation for financial support and Drs. John Kolb and L. W. Shive for assistance in the early phases of the work.

Registry No. **1**, 65406-19-1; **2** (x = 8), 65339-28-8; **2** (x = 0), 66373-92-0.

Supplementary Material Available: Tables of observed and calculated structure factors for both compounds (21 pages). Ordering information is available on any current masthead page.

References and Notes

(1) D. M. Collins, F. A. Cotton, S. Koch, M. Millar, and C. A. Murillo, *J. Am. Chem. Soc.*, **99**, 1259 (1977).
(2) F. A. Cotton, S. Koch, K. Mertis, M. Millar, and G. Wilkinson, *J. Am. Chem. Soc.*, **99**, 4989 (1977).
(3) A detailed account of how this device is used in this laboratory will be found in the Ph.D. Dissertation of A. G. Stanislowski, Texas A&M University, 1976, pp 173–175.
(4) For this compound the processing of data, solution of structure, and refinement were carried out on the PDP 11/45 computer at the Molecular Structure Corp., College Station, Tex., using the Enraf-Nonius structure determination package.
(5) "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974.
(6) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
(7) The calculations were carried out using the following programs: DATARED, a data reduction program by Frenz; FOURIER, a Fourier summation program (based on Zalkin's FORDAP) by Dellaca and Robinson, modified by Hodgson; FAME, a program for calculating normalized structure factors by Dewar; HYDROGEN, a program for calculating atom positions in certain arrangements by Frenz and Stanislowski; NUCLS, a full-matrix least-squares program by Ibers and Doedens, similar to Busing and Levy's ORFLS; SADIAN, a distances and angles program by Baur, rewritten by Frenz; ORFFE, a function and error program by Busing, Martin, and Levy as modified by Brown, Johnson, and Theissen; ORTEP, a plotting program by Johnson; LIST, a program for listing the data by Snyder.
(8) F. A. Cotton, J. M. Troup, T. R. Webb, D. H. Williams, and G. Wilkinson, *J. Am. Chem. Soc.*, **96**, 3824 (1974).
(9) F. A. Cotton, L. D. Gage, K. Mertis, L. W. Shive, and G. Wilkinson, *J. Am. Chem. Soc.*, **98**, 6922 (1976).
(10) J. V. Brencic and F. A. Cotton, *Inorg. Chem.*, **9**, 346 (1970).
(11) F. A. Cotton and W. T. Hall, *Inorg. Chem.*, **16**, 1867 (1977).
(12) D. J. Brauer and C. Krüger, *Inorg. Chem.*, **15**, 2511 (1976).
(13) F. A. Cotton, S. A. Koch, A. J. Schultz, and J. M. Williams, *Inorg. Chem.*, in press.
(14) A. P. Sattelberger and J. P. Fackler, Jr., *J. Am. Chem. Soc.*, **99**, 1258 (1977).
(15) J. Krausse, G. Marx, and G. Schödl, *J. Organomet. Chem.*, **21**, 159 (1970).
(16) L. Pauling, "The Nature of the Chemical Bond", 3rd ed, Cornell University Press, Ithaca, N.Y., 1960, p 403.