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The First Alkylidyne-Capped Tritungsten(IV) Cluster Compounds: Preparation, Structure, and Properties of $[W_3O(CCH_3)(O_2CCH_3)_6(H_2O)_3]Br_2\cdot 2H_2O$

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The equilateral trinuclear cluster cation $[W_3O(CCH_3)(O_2CCH_3)_6(H_2O)_3]^{2+}$ was obtained from the reaction of $[W(CO)_4(\text{piperidine})_2]$ and a mixture of acetic acid and acetic anhydride. The bromide salt crystallizes in the rhombohedral space group $R\bar{3}m$ with cell dimensions (on rhombohedral axes) of a = 11.915 (4) Å, α = 106.08 (5)°, V = 1442 (3) Å^3, and Z = 2. The compound is isomorphous with the bi-oxo-capped $[Mo_3O_2(O_2CCH_3)_6(H_2O)_3]Br_2\cdot 2H_2O$. Since the two capping sites are crystallographically symmetry related, a systematically disordered model had to be refined. The presence of inequivalent caps was confirmed by ^{1}H NMR. There is a total of five electrons available for metal–metal bonding, leading to an average bond order of $^5/_6$ and paramagnetism. The +2 ion can be chemically reduced to a six-electron +1 ion, $[W_3O(CCH_3)(O_2CCH_3)_6(H_2O)_3]^+$, which shows three resonances in the ^{1}H NMR spectrum at 2.71, 2.66, and 2.53 ppm downfield from Me_4Si with integrated intensities of 1:3:3. These are assigned to the capping methyl group and to the two inequivalent sets of acetate groups above and below the metal plane. The chemical shifts are consistent with the expected diamagnetism.

Introduction

Over the last few years it has been well established that the reactions of $Mo(CO)_6$ or $W(CO)_6$ with acetic acid or a mixture of acetic acid and acetic anhydride lead to the formation of trinuclear bicapped cluster compounds.[2] These contain an equilateral triangular arrangement of metal atoms, which are bonded to one another, and there are two carboxylato groups spanning each of the M–M edges. In addition, there is one unidentate ligand (most often H_2O) attached to each metal atom. Above and below the metal plane are μ_3-capping groups symmetrically placed to form a trigonal bipyramid with the metal atoms. For molybdenum, the nature of these caps has been found to vary with the reaction conditions, and bi-oxo-[3] and oxo–ethylidyne-[4] as well as bi-ethylidyne-capped[5] clusters have been obtained.

The caps so far found in tritungsten compounds have always been μ_3-O atoms (including one case[7] where one of them was simply missing). For this paper we report the synthesis and characterization of the first oxo–ethylidyne-capped trinuclear cluster of tungsten, $[W_3O(CCH_3)(O_2CCH_3)_6(H_2O)_3]^{2+}$. It is an electron-deficient, paramagnetic cluster with an average bond order of $^5/_6$. It can easily be reduced to the diamagnetic six-electron system $[W_3O(CCH_3)(O_2CCH_3)_6(H_2O)_3]^+$, which has been characterized by ^{1}H NMR.

Experimental Section

Preparation of $[W_3O(CCH_3)(O_2CCH_3)_6(H_2O)_3]Br_2\cdot 2H_2O$. A 1-g quantity of $W(CO)_4(pip)_2$ (pip = piperidine) (prepared by a published procedure[8]) was dissolved in a mixture of 50 mL of acetic acid and 50 mL of acetic anhydride. The solution was boiled under reflux for 17 h under an atmosphere of nitrogen. The dark brown solution thus obtained was cooled to room temperature. Hydrolysis with 100 mL of water for 2 h was performed in air. The filtered solution was passed through a Dowex 50W-X2 cation-exchange column. The yellow fraction obtained by elution with 0.1 M HCl was oxidized by slow addition of 0.1 M $KMnO_4$ until an orange solution was obtained. This solution was passed through a Dowex 50W-X2 ion-exchange column, and the column was washed with 0.1 M HBr to remove any trace of the yellow +1 cation. The orange band was then eluted with 2 M HBr, and crystals of the title compound were obtained by slow evaporation. Typical yields are ca. 100 mg of trinuclear complex, corresponding to ca. 10% based on tungsten used.

Table I. Pertinent Crystallographic Data about Intensity Collection and Structure Refinement

formula	$[W_3O(CCH_3)(O_3CCH_3)_6(H_2O)_3]Br_2\cdot 2H_2O$
mol wt	1198.7
lattice	rhombohedral
a_r	11.915 (4) Å
α_r	106.08 (5)°
V	1442.6 Å^3
space group	$R\bar{3}m$ (No. 166)
Z	2
d_{measd} (in s-tetrabromoethane + toluene)	2.75 g cm^{-3}
d_{calcd}	2.761 g cm^{-3}
radiation	Mo Kα (graphite monochromated)
scan mode	$\omega/2\theta$
scanning range for 2θ	$4° \le 2\theta \le 50°$
scan speed	1.5° min^{-1}
scan width in ω	1.10°
monitor reflecns for intensity control	[110, 101, 011]
no. of unique reflecns	919
no. of reflcns having $F_o \ge 1.5\sigma(F_o)$	806
weighting scheme	$1.664/(\sigma^2(F_o) + 0.0007(F_o)^2)$
no. of variables	92
$R(F)^a$	0.058
$R_w(F)^b$	0.056

$^a R(F) = (\sum||F_o| - |F_c||)/\sum|F_o|$. $^b R_w(F) = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2$.

Reduction of $[W_3O(CCH_3)(O_2CCH_3)_6(H_2O)_3]^+$. The dipositive cation is easily reduced by dithionite in acidic aqueous or ethanolic solution. In aqueous 0.1 M $HClO_4$, oxidation (even under exclusion of oxygen) is observed, whereas the unipositive cation is stable in acidified *ethanol* solution, over at least several days, and can be obtained from such solutions as a microcrystalline precipitate by cooling.

Spectroscopic Measurements. **^{1}H NMR.** Samples of the diamagnetic +1 cluster species were prepared by dissolving the +2 complex in degassed 0.1 M DCl. Sodium dithionite was added in solid form until the color of the solution had changed from orange to a clear yellow. It was then filtered, under argon, into a 5-mm sample tube. The spectrum was recorded immediately. Considerable broadening of the lines was observed over a period of 30 min. Addition of dithionite and filtration restored the diamagnetic species. The observed chemical shifts downfield relative to external Me_4Si were 2.66 and 2.53 ppm for the acetate groups and 2.71 ppm for the capping ethylidyne. The assignment is based on the relative intensities of 3:3:1 for the peaks at 2.53, 2.66, and 2.71 ppm, respectively.

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(1) (a) Texas A&M University. (b) The Technion.
(2) Müller, A.; Jostes, R.; Cotton, F. A. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 875.
(3) Ardon, M.; Bino, A.; Cotton, F. A.; Dori, Z.; Kaftory, M.; Reisner, G. M. *Inorg. Chem.* **1982**, *21*, 1912.
(4) Bino, A.; Cotton, F. A.; Dori, Z.; Kolthammer, B. W. S. *J. Am. Chem. Soc.* **1981**, *103*, 5779.
(5) Ardon, M.; Bino, A.; Cotton, F. A.; Dori, Z.; Kaftory, M.; Kolthammer, B. W. S.; Kapon, M.; Reisner, G. M. *Inorg. Chem.* **1981**, *20*, 4083.
(6) Bino, A.; Cotton, F. A.; Dori, Z.; Koch, S.; Küppers, H.; Millar, M.; Sekutowski, J. C. *Inorg. Chem.* **1978**, *17*, 3245.
(7) Ardon, M.; Cotton, F. A.; Dori, Z.; Fang, A.; Kapon, M.; Reisner, G. M.; Shaia, M. *J. Am. Chem. Soc.* **1982**, *104*, 5394.
(8) Darensbourg, D. J.; Kump, R. L. *Inorg. Chem.* **1978**, *17*, 2680.

0020-1669/85/1324-4381$01.50/0

Table II. Final Atomic Positional Parameters ($\times 10^5$ for W and $\times 10^3$ for the Light Atoms)

atom	*x*	*y*	*z*
W	29758 (7)	29758 (7)	15048 (8)
OW	359 (1)	359 (1)	19 (1)
OA(1)	135 (1)	292 (1)	18 (1)
OA(2)	493 (1)	335 (1)	218 (1)
CA(1)	33 (2)	291 (2)	33 (2)
CA(2)	−74 (2)	287 (3)	−74 (2)
CA(3)	550 (2)	292 (2)	292 (2)
CA(4)	690 (2)	332 (2)	332 (2)
CO(1)[a]	155 (3)	155 (3)	155 (3)
CO(2)[a]	333 (2)	333 (2)	333 (2)
CM(1)	42 (6)	42 (6)	42 (6)
CM(2)	450 (6)	450 (6)	450 (6)
Br(1)	785 (1)	483 (1)	97 (1)
Br(2)	596 (3)	338 (3)	−33 (2)
OWH	384 (5)	616 (5)	0 (0)

[a] These labels denote $^1/_2$ C + $^1/_2$ O atoms.

Electronic Spectra. The easy interconversion of the +1 and +2 cluster compounds can be monitored by electronic absorption spectroscopy. When one starts from either species, an equilibrium mixture will be reached. The equilibrium ratio in aqueous solution is pH dependent with the +2 species being more stable in acidic solution while the +1 species is favored at higher pH. The time-dependent spectral changes of a solution of the +2 cluster in 0.1 M HCl is shown in Figure 3.

Cyclic Voltammetry. The cyclic voltammogram was measured on a Bioanalytical Systems, Inc., Model BAS100 electrochemical analyzer instrument in connection with a Bausch and Lomb, Houston Instruments Model DMP40 digital plotter. In a three-electron system a gold-disk electrode, Model MF2014, and a platinum wire were used as working and auxiliary electrodes and a BAS MF2020 Ag–AgCl cell was used as a reference electrode. Experiments were done on aqueous solutions. Potentials were referenced to Ag–AgCl at 22 ± 2 °C and uncorrected for junction potentials.

X-ray Crystallography. Crystals of the title compound were grown as dark red prismatic needles. A prism of dimensions 0.15 × 0.15 × 0.16 mm was mounted on the Philips PW 1100/20 four-circle diffractometer, and accurate cell parameters were derived from 25 carefully centered reflections. The parameters and other pertinent details are presented in Table I. It was realized at this stage that the cell dimensions were essentially identical with those found for $[Mo_3O_2(O_2CCH_3)_6(H_3O)_3]\cdot Br_2\cdot H_2O$. However, pronounced differences between their electronic spectra suggested that they were not simply homologues and we were therefore encouraged to proceed with data collection.

Intensities were measured with graphite-monochromated Mo Kα radiation. Lorentz and polarization but not absorption corrections were applied to the intensities. With no systematic absences for *hhl* (on rhombohedral axes) the choice of space groups for the Laue class $\bar{3}m$ is restricted to $R\bar{3}m$, $R3m$, and $R32$. Refinement in either one of the noncentrosymmetric space groups ($R3m$ or $R32$) did not resolve the disorder of the capping groups but led instead to unreasonably high correlation for the remainder of the atoms. The refinement of the disorder model was therefore carried out in $R\bar{3}m$. More details about data collection and structure refinement are given in Table I.

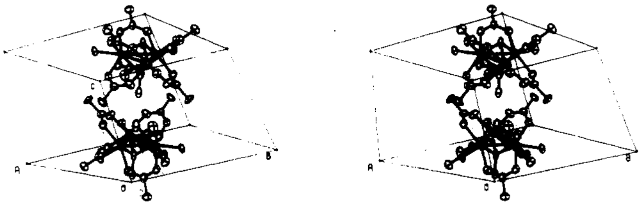

Figure 1. Two cations related by the inversion center at ($^1/_2$, $^1/_2$, $^1/_2$) showing the packing along the $\bar{3}$ axis. For clarity, the disordered CCH_3 capping group is shown at only one of its possible sites.

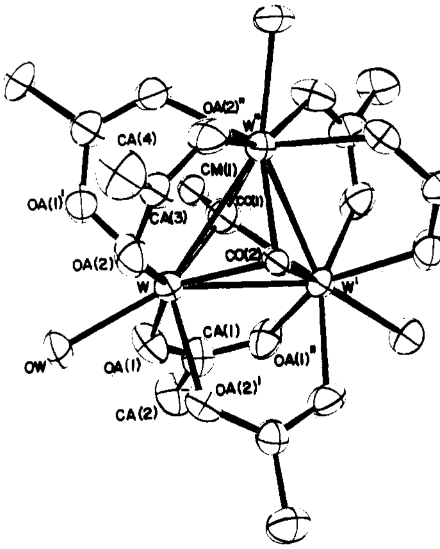

Figure 2. Perspective drawing of the $[W_3O(CCH_3)(O_2CCH_3)_6(H_2O)_3]^{2+}$ cluster unit showing the labeling scheme. Each atom is represented by thermal ellipsoids of 50% probability. For clarity, the disordered CCH_3 capping group is shown at only one of its possible sites.

Table III. Important Bond Lengths (in Å) and Angles (in deg)

	Bond Lengths		
W–W′	2.801 (1)	OA(1)–CA(1)	1.27 (2)
W–OW	2.12 (1)	OA(2)–CA(3)	1.27 (2)
W–OA(1)	2.10 (1)	CA(1)–CA(2)	1.51 (2)
W–OA(2)	2.11 (1)	CA(3)–CA(4)	1.50 (3)
W–CO(1)	2.07 (3)	CO(1)–CM(1)	1.55 (5)
W–CO(2)	1.99 (2)	CO(2)–CM(2)	1.62 (5)
	Bond Angles		
W′–W–OW	150.0 (3)	OA(1)–W–CO(2)	126.1 (6)
W′–W–OA(1)	82.2 (3)	OA(1)–W–OA(1)′	90.3 (5)
W′–W–OA(2)	125.3 (3)	CA(1)–W–OA(2)′	81.9 (6)
W′–W–CO(1)	47 (1)	OA(2)–W–CO(1)	127 (1)
W′–W–CO(2)	45.4 (9)	OA(2)–W–CO(2)	80.0 (9)
W′–W–OA(1)′	124.9 (3)	CO(1)–W–CO(2)	74 (1)
OW–W–OA(1)	74.8 (5)	W–CO(1)–W′	85 (1)
OW–W–OA(2)	75.8 (5)	W–CO(2)–W′	89 (1)
OW–W–CO(1)	140 (1)	OA(1)–CA(1)–CA(2)	119 (1)
OW–W–CO(2)	145 (1)	OA(1)–CA(1)–OA(1)″	122 (1)
OA(1)–W–OA(2)	150.6 (4)	OA(2)–CA(3)–CA(4)	118 (1)
OA(1)–W–CO(1)	78 (1)	OA(2)–CA(3)–OA(2)″	123 (1)

Structure factors were calculated by using the SHELX-77 program package with the atomic coordinates taken from the molybdenum dioxo compound, excluding the two capping oxygens and water of hydration. These gave an initial $R = 0.18$. Two cycles of least-squares isotropic refinement gave $R = 0.088$. Fourier difference maps calculated at this stage revealed two capping atoms with full occupancies above and below the metal cluster triangle; these were initially refined as oxygen atoms ($R = 0.079$). Further inspection of the difference maps showed clearly two additional peaks on the $\bar{3}$ axis with about half the electron density of a carbon atom, 1.42 and 1.51 Å away from the capping atoms. The appearance of two peaks with full occupancy and two with half-occupancy suggested a disordered model where the two types of capping groups, O and CCH_3, partially and equally occupy the two capping sites. According to this model, the peaks with "full" occupancy were introduced as 0.5 O + 0.5 C atoms and the peaks attached to these "atoms" as 0.5 C. The difference maps also revealed a water molecule of hydration located on a mirror plane at $x\bar{x}0$. This atom was refined with partial occupancy of $^1/_3$. The bromide anions were best refined when placed on two different general positions with equal occupancies of $^1/_6$. Anisotropic refinement was carried out on all the cation atoms and bromide anions but not for the water molecule of hydration, which was refined isotropically. Convergence was reached at $R = 0.058$. Unit weights were assigned throughout the initial stages of the refinement and statistical weights throughout the final stages.

The final positional parameters are listed in Table II. Thermal parameters and tables of observed and calculated structure factors are provided as supplementary material.

Results and Discussion

Description of the Structure. A stereoscopic view of the packing of the metal cluster cations in the unit cell and a perspective drawing of the cation including the atom labeling are shown in Figures 1 and 2, respectively. A list of important bond lengths and angles is given in Table III.

This structure has similarities to that of $[Mo_3O_2(O_2CCH_3)_6(H_2O)_3]Br_2\cdot H_2O$,[3] but there are also critical differences. The unit cell dimensions are nearly identical in the two cases, and this is because the packing of the $[M_3X_2(O_2CCH_3)_6(H_2O)_3]^{2+}$ ions is the dominant factor in determining the crystal structure. In each case these form columns extending along [111] in the rhombohedral cell (see Figure 1). This leaves interstitial positions which can be occupied by the Br^- ions and by one or more H_2O molecules in various ways. In the Mo compound there is only one H_2O per trinuclear cation whereas here there are two. Moreover, the positions occupied by one of the Br^- ions are different in the two cases. It is to be noted, however, that the position occupied by OWH in the tungsten compound is close to those occupied by Br^- ions in the molybdenum compound. The presence of two rather than only one H_2O per formula unit in this case is supported by the density. The measured value of 2.75 (±0.01) g cm^{-3} agrees well with that calculated for the dihydrate, 2.761 g cm^{-3}, but less well with that calculated for the monohydrate, 2.720 g cm^{-3}. The bromide anions and the water molecules of hydration fill the space between the columns of the cluster cations in a disordered fashion and with partial occupancies. There seem to be hydrogen bonds between Br^- and the cluster water molecules with distances of 3.21 and 3.12 Å.

Figure 1 shows a pair of cations related by the inversion center at ($^1/_2$, $^1/_2$, $^1/_2$). In the dioxo complex, cavities exist between neighboring cations along the column as indicated by the shortest interatomic distances between capping oxygens (O(1)---O(1)′ = 4.22 Å, O(2)---O(2)′ = 4.43 Å). These distances are sufficient to accommodate one and only one additional non-hydrogen atom without disturbing the overall arrangement. This arrangement is such that, due to the $\bar{3}$ operation, the acetate groups of neighboring cations along the chain are interdigitated and make van der Waals contacts.

Pairs of cluster cations are related by inversion centers at (0, 0, 0) and ($^1/_2$, $^1/_2$, $^1/_2$), and the distances are such that if both the CM and CM′ sites related by such centers were simultaneously occupied, the CM---CM′ contact distances would be too short (CM(1)---CM(1)′ = 1.16 Å and CM(2)---CM(2)′ = 1.37 Å). With CCH_3 from one cluster and O from the other directed toward the inversion centers, the following distances are obtained: CM(1)---CO(1)′ = 2.70 Å and CM(2)---CO(2)′ = 2.99 Å. It may be noted that crystallographic results alone are not able to rule out the possibility that along the [111] direction we have alternating $[W_3O_2(O_2CCH_3)_6(H_2O)_3]$ and $[W_3(CCH_3)_2(O_2CCH_3)_6(H_2O)_3]$ units; the model we have refined is crystallographically equivalent to this. However, for chemical, electrochemical, and spectroscopic reasons, we rule it out.

Synthesis and Reactions. The assembly of relatively complex cluster compounds from simple starting materials such as $M(CO)_6$ (M = Mo, W) and a mixture of carboxylic acid with the corresponding anhydride obviously involves a series of reaction steps which cannot at this time be specified. It has been found that additional reagents, e.g. halogen ions or base, will alter the product distribution significantly.[9]

Without any additives and under an inert atmosphere, $Mo(CO)_6$ and acetic acid/anhydride yields predominantly the biethylidyne-capped cluster together with small amounts of the mixed oxo–ethylidyne-capped cluster. Addition of base, such as diethylamine or pyridine, to the reaction mixture improves the yield of mixed oxo–alkylidyne-capped cluster. The bi-oxo-capped species is obtained only by allowing air into the reaction mixture, during or after the reaction. In the presence of an excess of halogen ions, e.g. Br^-, the type of cluster isolated is altogether different in that an ethylidyne-capped, bromide-bridged cluster of the M_3X_{13} type is obtained.[9]

With $W(CO)_6$ the type of product obtained seems to be much less influenced by the conditions used in the preparative procedure. Regardless of whether base is added or not, and also, regardless of whether atmospheric oxygen is excluded or not, the only previously obtained bicapped products contained two capping oxygen atoms.[6] Prior to this work, no way had been found to obtain a product with two ethylidyne caps, or even one. We have now found a way to prepare the oxo–ethylidyne-capped W_3 cluster. This is done by incorporating molecules of base right into the tungsten-containing reactant, namely, by employing $W(CO)_4(pip)_2$ rather than $W(CO)_6$ plus base.

In view of the great difficulty experienced in finding a way to prepare the ethylidyne-capped tritungsten cluster, it is not surprising that its properties differ considerably from those of its molybdenum analogue, $[Mo_3O(CCH_3)(O_2CCH_3)_6(H_2O)_3]^+$. The trimolybdenum species is very stable and shows no tendency to be oxidized in neutral or acid solution. The tungsten compound, which gives a reversible +1/2+ redox couple at 0.2 V (vs. Ag/AgCl),[10] is more similar to the $[Mo_2(CCH_3)_2(O_2CCH_3)_6(H_2O)]^{n+}$ system, which is most stable in the +1 and +2 states, where it has only 5 and 4 cluster electrons, respectively.

The easy +1/+2 interconversion of the $[W_3O(CCH_3)(O_2CCH_3)_6(H_2O)_3]^{n+}$ system was a source of considerable experimental difficulties, especially in recording the NMR spectrum. The procedures for circumventing these difficulties are explained in detail in the Experimental Section.

The orbital nature of the +1/+2 redox process can be discussed in terms of the molecular orbitals of this type of cluster system.[11] The +1 cluster has a full complement of six electrons for metal–metal bonding, and thus the mean W–W bond order in that case is 1.0. In the +2 ion one of these electrons has been removed; the bond order should be $^5/_6$, and there should be one unpaired electron. This difference of one bonding electron should affect the W–W distance, but we cannot verify this directly since we have structural data only for the +2 species. However, we can estimate the W–W distance in the +1 ion by the following argument.

For bi-oxo-capped trimolybdenum compounds,[12] we have Mo–Mo distances ranging from 2.752 [2] to 2.766 (2) Å, with an average value of 2.759 Å. For the $[Mo_3O(CCH_3)(O_2CCH_3)_6(H_2O)_3]^+$ ion in several different crystals, Mo–Mo distances range from 2.750 [2] to 2.752 (1) Å, with the average being 2.751 Å. Thus, the change from the bi-oxo-capped species to the oxo–ethylidyne-capped species causes the mean Mo–Mo distance to change by −0.007 Å. If we assume that the same size change would occur for tritungsten species, and take 2.746 Å, the average of the values found in two $[W_3O_2(O_2CR)_6(H_2O)]^{2+}$ compounds,[6] we can estimate a W–W distance of 2.739 Å in the $[W_3O(CCH_3)(O_2CCH_3)_6(H_2O)_3]^+$ ion.

The W–W distance we have found in $[W_3O(CCH_3)(O_2CCH_3)_6(H_2O)_3]^{2+}$ is 2.801 (1) Å, which is 0.062 Å longer than that which we have just estimated for the +1 ion. This increase, for a W–W bond order change of $^1/_6$ (from unity to $^5/_6$) is very similar to the changes of 0.062 and ca. 0.075 Å found in trimolybdenum systems[5] accompanying changes in bond order by $^1/_6$. Thus, despite the chemical differences between the trimolybdenum and tritungsten systems, their stereoelectronic properties are very similar.

Spectroscopy. ^{1}H NMR Spectra. The ^{1}H NMR spectrum of the +1 ion is consistent with the molecular symmetry and the expected diamagnetism. We note that complete reduction is essential for a successful measurement. Within ca. 30 min after preparation of the solution line broadening was observed, affecting the capping alkylidyne group more severely than the acetate groups. When a line width of ca. 5 Hz was observed for the acetate protons, the line corresponding to the cap was already undetectable. We attribute the line broadening to a fast electron-transfer process between the +1 and the +2 cluster species since the line width of the H_2O peak did not change over the time period of the

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(9) Birnbaum, A.; Cotton, F. A.; Dori, Z.; Kapon, M.; Marler, D. O.; Reisner, G. M.; Schwotzer, W. *J. Am. Chem. Soc.* **1985**, *107*, 2405.

(10) A study of the electrochemical properties of this and other trinuclear cluster compounds of Mo and W is in progress.

(11) (a) Bursten, B. E.; Cotton, F. A.; Hall, M. B.; Najjar, R. C. *Inorg. Chem.* **1982**, *21*, 302. (b) Jiang, Y.; Tang, A.; Hoffman, R.; Huang, J.; Jiaxi, L. *Organometallics* **1985**, *4*, 27.

(12) Cotton, F. A.; Dori, Z.; Marler, D. O.; Schwotzer, W. *Inorg. Chem.* **1983**, *22*, 3104.

(13) Bino, A.; Cotton, F. A.; Dori, Z.; Falvello, L. R.; Reisner, G. M. *Inorg. Chem.* **1982**, *21*, 3750.

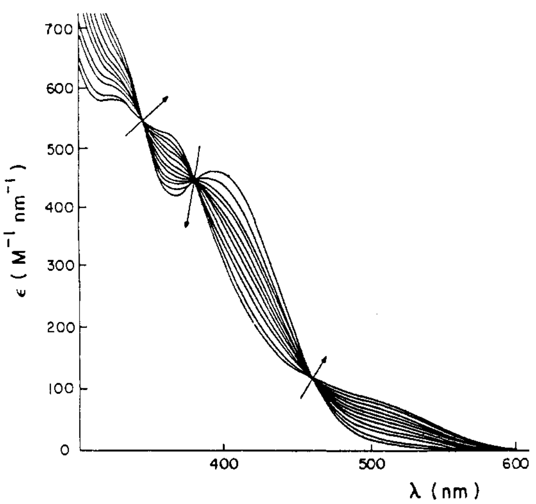

Figure 3. Time-dependent electronic spectrum of a solution of the +2 cluster in 0.1 M HCl.

experiment. The paramagnetic +2 cluster cation shows very broad lines for the acetate protons centered around 16 and 20 ppm downfield while the capping group (expected at ca. 90 ppm) was not detected. This might not be considered surprising since it is a paramagnetic species. We note, however, that in the isoelectronic $[Mo_3(CCH_3)_2(O_2CCH_3)_6(H_2O)_3]^+$ ion the ^1H NMR lines are reasonably sharp[5] because of efficient electron relaxation. It therefore seems conceivable that the broadening observed here is caused primarily by the rapid interconversion of the +1 and +2 ions.

Electronic Spectra. Figure 3 shows the time-dependent changes in the electronic spectrum of a solution of the +2 cluster cation in 0.1 M HCl. The presence of three isosbestic points corroborates our model of a simple one-electron transfer, viz., conversion of the +2 ion and the +1 ion without intermediates. The situation is not fully understood since we have not yet identified the nature of the reductant. A likely candidate is the cluster itself, viz., oxidation of W(IV) to W(VI) accompanied by disruption of the trinuclear unit. One molecule of cluster compound could thus be used to provide the electrons necessary for the reduction of six other cluster molecules, so that there would be no drastic effect on the visible spectrum.

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Registry No. $[W_3O(CCH_3)(O_2CCH_3)_6(H_2O)_3]Br_2 \cdot 2H_2O$, 98990-69-3; $[W_3O(CCH_3)(O_2CCH_3)_6(H_2O)_3]^{2+}$, 98990-71-7; $[W_3O(CCH_3)(O_2CCH_3)_6(H_2O)_3]^+$, 98990-70-6; $W(CO)_4(pip)_2$, 14515-95-8.

Supplementary Material Available: Tables of observed and calculated structure factors and anisotropic displacement parameters (6 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding,
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Steric and Electronic Factors Influencing the Structures of Bridged (β-Type) $M_2Cl_4(LL)_2$ (M = Mo, Re) Compounds: A Refined Correlation of Bond Length with Torsion Angle

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Two compounds of the type β-$M_2Cl_4(LL)_2$ have been prepared, where M = Mo (**1**) and Re (**2**) and LL is the diphosphine ligand depe (1,2-bis(diethylphosphino)ethane, $Et_2PCH_2CH_2PEt_2$). The two compounds are isomorphous, and there is an elegant form of systematic disordering due to the fact that the molecules reside on positions where the crystallographic symmetry is higher than the symmetry of an individual molecule. This has made it impossible to refine the Cl and P atoms independently. Important dimensions of the molecules are as follows: for **1**, Mo–Mo = 2.173 (2) Å, Mo–Cl(P) = 2.460 (5) Å, ∠Mo–Mo–Cl(P) = 104.1°, torsion angle Cl(P)–Mo–Mo–Cl(P) = 42.7 (2)°; for **2**, Re–Re = 2.211 (1) Å, Re–Cl(P) = 2.395 (7) Å, ∠Re–Re–Cl(P) = 105.2 (2)°, torsion angle Cl(P)–Re–Re–Cl(P) = 43.7 (3)°. Compounds **1** and **2** form tetragonal crystals in space group *I*4/*mmm* with *Z* = 2 and *a* = 9.494 (4) Å, *c* = 18.097 (1) Å for **1** and *a* = 9.423 (6) Å, *c* = 18.073 (4) Å for **2**. With use of data for these compounds as a guide to the magnitude of steric and inductive effects on the structures of $Mo_2X_4(LL)_2$ compounds generally, the correlation between Mo–Mo bond length and cos 2χ has been revised to yield an inverse linear function with a correlation coefficient of 0.9547. According to this new relationship, the complete loss of the δ bond is associated with an increase of 0.097 Å in the bond length.

Introduction

It is well-known that compounds containing a metal–metal quadruple bond have a preference for an eclipsed rotational conformation about the M–M bond because of the angular dependence of the δ bond. In simple, unbridged compounds of the type $X_4M{-}MX_4$, this tendency dominates the repulsive forces between opposed ligand atoms and fully eclipsed structures are always observed.[1] However, in compounds of the β-$Mo_2X_4(LL)_2$ type, in which the LL ligands are 1,2-bis(diphosphino)ethanes that bridge from one metal atom to the other, there is always a rotational twist (by an angle χ) away from the fully eclipsed conformation ($\chi = 0°$) owing to the conformational demands of the fused six-membered rings that are present in these β-$Mo_2X_4(LL)_2$ molecules.

It has also been recognized[2] that the strength of the δ component of a quadruple metal–metal bond depends inversely on the angle of rotation away from the eclipsed conformation; the δ bond strength varies according to cos 2χ. Thus, for $\chi = 0°$ the δ bond has its maximum strength and as χ increases the δ bond strength decreases as a linear function of cos 2χ until at $\chi = 45°$ it becomes zero. From this it would follow that the Mo–Mo bond lengths in a series of $Mo_2X_4L_4$ type compounds might be expected to vary

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[1] Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982.

[2] Cotton, F. A.; Fanwick, P. E.; Fitch, J. W.; Glicksman, H. D.; Walton, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 1752.

0020-1669/85/1324-4384$01.50/0