in other joints and is traditionally measured as swelling of the injected and uninjected hind feet.[19] The effectiveness of chrysotherapy agents is measured by the reduction of swelling on day 3 (injected foot) and/or day 16 (uninjected foot) compared to untreated adjuvant controls. The trimethylphosphine analogues consistently produce lower serum gold levels and are less effective in the rat hind paw adjuvant arthritis assay.[19,24]

The facile displacement and oxidation of Me_3P observed here may reduce the absorption of $Me_3PAuSAtg$ from the gastrointestinal tract. The phosphine ligands are believed to be responsible for the uptake of orally administered auranofin analogues; the oligomeric gold(I) thiolates, which lack phosphine ligands, are not orally absorbed. Oxidation of a phosphine converts a very strong, soft Lewis base into a hard, relatively weak base that does not bind gold(I) in the biological milieu. Thus, stronger phosphine bases (e.g., Et_3P), which are less easily displaced and oxidized, may be essential for oral absorption of gold drugs.

Acknowledgment. A.A.I. thanks the Chemistry Department of the King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia, for a sabbatical leave. We thank Frank Laib for his assistance in obtaining the spectra of Figure 2.

Contribution from the Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, 91904 Jerusalem, Israel, The Technion-Israel Institute of Technology, Haifa, Israel, and Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843

Further Studies of the Monooxo-Capped Tritungsten Carboxylate Clusters

Avi Bino,*[,1a] F. Albert Cotton,*[,1b] Zvi Dori,*[,1c] Miriam Shaia-Gottlieb,[1c] and Moshe Kapon[1c]

Received March 28, 1988

An improved method for the preparation of the $[W_3O(O_2CCH_3)_6(H_2O)_3]^{2+}$ ion has been found, starting with sodium tungstate, and the compound $[W_3O(O_2CCH_3)_6(H_2O)_3]ZnCl_4{\cdot}4H_2O$ (**1**) has been shown to contain the ion in a completely ordered arrangement. The structure is thus obtained without ambiguity and with more precision than before and has the following principal dimensions (Å): W–W = 2.693 (1), 2.693 (1), 2.712 (1); W–(μ_3-O)(av) = 1.98 [1]; W–OH_2(av) = 2.17 [2]; W–O(acetate)(av) = 2.078, 2.055 on the capped and uncapped sides, respectively. Compound **1** crystallizes in space group $P2_1/n$ with a = 14.324 (2) Å, b = 17.081 (2) Å, c = 13.715 (2) Å, β = 90.87 (3)°, and Z = 4. Conversion of the cation in compound **1** to the $[W_3O(O_2CCH_3)_5(OCH_3)(H_2O)_3]^{2+}$ cation has been effected, and this has been isolated and structurally characterized as the compound $[W_3O(O_2CCH_3)_5(OCH_3)(H_2O)_3]ZnCl_4{\cdot}7H_2O$ (**2**), which crystallizes in space group $P\bar{1}$ with unit cell dimensions$a$ = 14.063 (7) Å, b = 14.216 (7) Å, c = 9.613 (5) Å, α = 103.78 (5)°, β = 100.91 (5)°, γ = 107.38 (5)°, and Z = 2. The cation in compound **2** (aqueous solution) has a proton NMR spectrum in accord with its solid-state structure, and its UV–visible spectrum shows expected similarities to that of its symmetrical parent.

Introduction

It is now well established that the elements molybdenum and tungsten have a marked tendency to form trinuclear, triangular cluster compounds in mean formal oxidation states in the range III–V. In these compounds there are bridging and capping groups that may be O, S, OR, R, Cl, and Br, and no doubt others. One of the well-characterized types of compounds has the composition $[M_3(\mu_3\text{-}X)_2(O_2CR)_6L_3]$; the essential features are an equilateral triangle of metal atoms with two capping atoms or groups (usually, but not always, the same), one above and one below, with two μ_2,η^2-O_2CR groups spanning each edge of the triangle and, finally, one monodentate ligand L (commonly H_2O) occupying a position in the M_3 plane external to each metal atom.[2]

In 1982 the surprising observation was reported that this type of cluster species could exist in an incomplete form, namely, with one capping group missing while all the other components remained roughly in the same arrangement.[3] This discovery was the result of investigating a dark blue byproduct in the preparation of the $[W_3O_2(O_2CCH_3)_6(H_2O)_3]^{2+}$ ion. It was possible to characterize this incomplete or hemicapped species, $[W_3O(O_2CCH_3)_6(H_2O)_3]^{2+}$, by an X-ray crystallographic study of its $ZnBr_4{\cdot}8H_2O$ salt. In addition, molecular orbital calculations gave a satisfactory account of the electronic structure and rationalized the deep blue color.

However, we considered this to be only the opening chapter in studying and understanding this type of system. Some of the points or questions that most obviously called for further work were as follows.

(1) Improved Preparative Procedure. The very small amounts of material, tediously accumulated from many preparations of the bicapped compound, did not provide a satisfactory basis for further chemical study.

(2) X-ray Study of an Undisordered Compound. In the bromozincate compound the cation resided on a 2-fold axis and was systematically disordered so that the upper and lower faces of the W_3 triangle were indistinguishable. Thus, the capping oxygen atom appeared as two half-oxygen atoms and it was not possible to observe whether the arrangement of the three acetate groups on the capped side was any different from the arrangement of the three on the uncapped side. Because of the way the structure was refined, it was clear that no large difference was to be expected, but nevertheless, small differences that would certainly have been anticipated were totally masked by the disorder.

(3) Could the "Missing" Cap Be Introduced? It was recognized that if the hemicapped structure could be synthesized in good yield we would then have an opportunity to obtain species with one μ_3-O and some other capping group of choice, provided we could learn to introduce the latter by design.

In this paper we report on our efforts to date to address these three points. We have been successful with the first two. With respect to the third point, we have not yet succeeded, but in the course of trying we have made an unexpected synthetic discovery that is of interest in its own right.

Experimental Section

Synthesis of $[W_3O(O_2CCH_3)_6(H_2O)_3]ZnCl_4{\cdot}4H_2O$ (1). A mixture of $Na_2WO_4{\cdot}2H_2O$ (5.0 g) and granular (mesh 20) zinc (5.0 g) in 60 mL of acetic anhydride was refluxed for 10 h. The reaction mixture was cooled to room temperature, and a green-yellow solid that separated was isolated by filtration and washed with ethanol and ether. One gram of this solid was dissolved in water and the solution filtered. The filtrate was poured on a column of Dowex 50W-X2 cation-exchange resin, whereby a yellow solution of $[W_3O_2(OCCH_3)_9]^-$ emerged from the column, while a blue ion was retained. After the column had been washed with water, the blue ion was eluted with 0.5 M aqueous HCl and

---

(1) (a) The Hebrew University of Jerusalem. (b) Texas A&M University. (c) The Technion-Israel Institute of Technology.

(2) See for example: Cotton, F. A.; Dori, Z.; Marler, D. O.; Schwotzer, W. *Inorg. Chem.* **1984**, *23*, 4033, 4738 and earlier references cited therein.

(3) Ardon, M.; Cotton, F. A.; Dori, Z.; Fang, A.; Kapon, M.; Reisner, G. M.; Shaia, M. *J. Am. Chem. Soc.* **1982**, *104*, 5394.

0020-1669/88/1327-3592$01.50/0

Table I. Crystallographic Data for $[W_3O(O_2CCH_3)_6(H_2O)_3]ZnCl_4 \cdot 4H_2O$ and $[W_3O(O_2CCH_3)_5(OCH_3)(H_2O)_3]ZnCl_4 \cdot 7H_2O$

formula	$C_{12}H_{32}Cl_4O_{20}W_3Zn$	$C_{11}H_{38}Cl_4O_{22}W_3Zn$
fw	1255.10	1281.1
space group	$P2_1/n$	$P\bar{1}$
a, Å	14.324 (2)	14.063 (7)
b, Å	17.081 (2)	14.216 (7)
c, Å	13.715 (2)	9.613 (5)
α, deg		103.78 (5)
β, deg	90.87 (3)	100.91 (5)
γ, deg		107.38 (5)
V, Å^3	3355 (1)	1709 (1)
Z	4	2
d_{calcd}, g/cm^3	2.484	2.488
d_{measd}, g/cm^3	...	2.495^c
cryst size, mm	0.5 × 0.4 × 0.4	0.08 × 0.26 × 0.30
μ(Mo Kα), cm^{-1}	108.77	117.5
data collecn instrument	Philips PW 1100	
radiation (monochromated in incident beam)	Mo Kα (λ_α = 0.71073 Å)	
orientation rflns: no.; range (2θ), deg	20; 24–32	25; 24–34
temp, °C	22	
scan method	ω–2θ	
data collecn range, 2θ, deg	4–50	
total no. of rflns measd	6377	5895
no. of unique data, total	4560	4843
with $F_o^2 > 3\sigma(F_o^2)$	341	262
no. of params refined	0.051	0.076
R^a	0.058	0.076
R_w^b		

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. ^{c}By flotation in 1,1,2,2-tetrabromoethane/cyclohexane.

$ZnCl_2$ (100 mg) was added to the blue solution. After this solution had been reduced to ca. 10% of its volume by evaporation in air, a crop of deep blue crystals was obtained by filtration. They were washed with cold acetone and ether and dried in air (yield 0.18 g).

When this substance, shown by X-ray crystallography to be compound **1**, was recrystallized from methanol, a different compound was obtained, namely, $[W_3O(O_2CCH_3)_6(H_2O)_3]ZnCl_4 \cdot 8H_2O$, which has been shown to be isomorphous with the previously reported[3] $ZnBr_4^{2-}$ compound.

Preparation of $[W_3O(O_2CCH_3)_5(OCH_3)(H_2O)_3]ZnCl_4 \cdot 7H_2O$. A 100-mg portion of $[W_3O(O_2CCH_3)_6(H_2O)_3]Br_2$ (obtained by eluting the cation from the cation-exchange column with 0.5 M aqueous HBr and evaporating the eluate) was dissolved in 2 mL of methanol, to which was added 50 mL of CH_3CN. The resulting blue solution was refluxed under N_2 for 10 min. After it was cooled, the solution was hydrolyzed with 50 mL of H_2O and then passed through a Dowex 50W-X2 column. The adsorbed material was eluted with 2 M HCl. Slow evaporation of this solution, to which was added a small amount of $ZnCl_2$, gave the desired crystalline material in a yield of about 80%.

Crystallographic Procedures. Procedures for the collection of data and for the solution and refinement of the structures were straightforward, and no unusual problems were encountered. Table I provides the relevant facts concerning the collection of data and the refinement. Tables II and III give the atomic positional parameters for compounds **1** and **2**.

Physical Measurements. NMR spectra were measured on a Bruker 400-MHz spectrometer. UV–visible spectra were recorded on a HP 8452A diode array spectrophotometer.

Results and Discussion

Preparative and Reaction Chemistry. A new way to obtain the hemicapped cluster $[W_3O(O_2CCH_3)_6(H_2O)_3]^{2+}$ with greater ease and in better yield has been found. Instead of $W(CO)_6$ as the starting material, which can be used to prepare the bicapped cation in very good yield, but only minute amounts of the hemicapped cation as a byproduct, the new route begins with sodium tungstate and employs zinc as a reductant. This leads to a major improvement in the ratio of hemicapped to bicapped clusters. It is now possible to obtain in one run quantities on the order of 200 mg together with comparable amounts of the bicapped product. Fortunately, the two are easily separated by cation-exchange chromatography.

With the objective of introducing a sulfur atom into the vacant capping position of $[W_3O(O_2CCH_3)_6(H_2O)_3]^{2+}$, it was treated with NaHS in refluxing acetic anhydride. A black crystalline product was obtained after workup, but this was shown by X-ray crystallography (vide infra) to be another hemicapped species in which one acetate bridge has been replaced by a μ-OCH_3 group. This $[W_3O(O_2CCH_3)_5(OCH_3)(H_2O)_3]^{2+}$ ion is the first example of any $[M_3O_n(O_2CR)_5(OR)L_3]$ species, with n = 1 or 2, that has yet been observed.

Although $[W_3O(O_2CCH_3)_5(OCH_3)(H_2O)_3]^{2+}$ was first obtained accidentally in the attempt to insert an S (or SH) cap, this did not prove to be an efficient or reliable way to prepare it. After many studies of other possible procedures, the one reported in the Experimental Section has been found to be the best one we have so far. We candidly admit that our understanding of the chemistry here is still tenuous. We believe, but cannot yet prove, that the source of the μ-OCH_3 group is the methanol, but the way in which the yield depends on many conditions and reagents is still not explained.

Spectroscopic characterization of the $[W_3O(O_2CCH_3)_5(OCH_3)(H_2O)_3]^{2+}$ ion in solution confirms the structure found by X-ray crystallography (vide infra) and shows that its electronic structure is similar to that of the $[W_3O(O_2CCH_3)_6(H_2O)_3]^{2+}$ ion. The 400-MHz proton NMR spectrum consists of four signals, all singlets, with the following chemical shifts (τ) and the relative intensities give in parentheses: 3.798 (1.00), 2.466 (2.20), 2.348 (2.06), 2.289 (0.92). This pattern is consistent with the presence of one OCH_3, two equivalent O_2CCH_3 groups on one side of the

Table II. Positional Parameters and Estimated Standard Deviations for Compound **1**^{a}

atom	x	y	z	atom	x	y	z
W(1)	0.39333 (4)	0.65979 (4)	0.63253 (5)	O(31)	0.4257 (9)	0.8942 (7)	0.5678 (9)
W(2)	0.27201 (5)	0.77887 (4)	0.65364 (5)	O(32)	0.4231 (8)	0.8741 (7)	0.7821 (8)
W(3)	0.45850 (5)	0.80556 (4)	0.66436 (5)	O(33)	0.5473 (8)	0.7483 (7)	0.7626 (8)
Zn	0.1141 (2)	0.3416 (1)	0.3125 (2)	O(34)	0.5458 (7)	0.7781 (7)	0.5524 (8)
Cl(1)	0.2657 (4)	0.3448 (4)	0.3637 (4)	OL(1)	0.253 (1)	0.154 (1)	0.363 (1)
Cl(2)	0.0539 (5)	0.4626 (4)	0.3087 (6)	OL(2)	0.109 (1)	0.106 (1)	0.230 (1)
Cl(3)	0.1142 (5)	0.2806 (4)	0.1667 (5)	OL(3)	0.892 (1)	0.0091 (9)	0.913 (1)
Cl(4)	0.0374 (5)	0.2701 (4)	0.4276 (5)	OL(4)	0.934 (2)	0.038 (2)	0.315 (2)
O(1)	0.3725 (9)	0.7375 (8)	0.7384 (9)	C(1)	0.230 (1)	0.630 (1)	0.763 (1)
OW(1)	0.4235 (9)	0.5360 (7)	0.6002 (9)	C(2)	0.173 (1)	0.580 (1)	0.826 (2)
OW(2)	0.1316 (8)	0.8206 (7)	0.656 (1)	C(3)	0.231 (1)	0.665 (1)	0.491 (1)
OW(3)	0.5728 (9)	0.8875 (8)	0.6806 (9)	C(4)	0.171 (2)	0.632 (1)	0.412 (2)
O(11)	0.4886 (8)	0.6607 (6)	0.5220 (8)	C(5)	0.346 (1)	0.908 (1)	0.530 (1)
O(12)	0.4952 (8)	0.6290 (7)	0.7346 (8)	C(6)	0.339 (2)	0.968 (1)	0.451 (2)
O(13)	0.3026 (8)	0.6007 (7)	0.7241 (9)	C(7)	0.342 (1)	0.885 (1)	0.814 (1)
O(14)	0.3062 (8)	0.6308 (7)	0.5192 (9)	C(8)	0.331 (2)	0.935 (1)	0.905 (1)
O(21)	0.2030 (8)	0.6981 (7)	0.7408 (9)	C(9)	0.544 (1)	0.716 (1)	0.502 (1)
O(22)	0.2066 (8)	0.7271 (7)	0.5344 (8)	C(10)	0.611 (1)	0.707 (1)	0.419 (1)
O(23)	0.2743 (8)	0.8709 (7)	0.5578 (8)	C(11)	0.546 (1)	0.675 (1)	0.783 (1)
O(24)	0.2696 (8)	0.8558 (7)	0.7729 (8)	C(12)	0.611 (2)	0.645 (1)	0.864 (1)

^{a}Estimated standard deviations in the least significant digits are shown in parentheses.

Table III. Final Fractional Coordinates and Equivalent Temperature Factors for Compound **2**[a]

atom	*x*	*y*	*z*	U_{eq}, Å^2
W(1)	1515 (1)	2203 (1)	3491 (1)	213 (2)
W(2)	1882 (1)	2768 (1)	1320 (1)	241 (2)
W(3)	53 (1)	2667 (1)	1858 (1)	215 (2)
O(11)	2060 (11)	1027 (9)	2763 (16)	29 (3)
O(12)	2392 (11)	1535 (10)	812 (14)	25 (3)
C(11)	2370 (16)	913 (14)	1611 (21)	25 (4)
C(12)	2793 (19)	52 (18)	1111 (26)	38 (6)
O(21)	1029 (12)	2287 (11)	−899 (15)	33 (4)
O(22)	−505 (12)	2092 (10)	−485 (15)	32 (3)
C(21)	89 (18)	2022 (17)	−1330 (26)	37 (5)
C(22)	−492 (21)	1451 (16)	−3036 (21)	41 (7)
O(31)	2049 (11)	4282 (11)	1499 (18)	36 (4)
O(32)	499 (14)	4164 (11)	1632 (15)	35 (4)
C(31)	1302 (18)	4641 (16)	1532 (23)	29 (5)
C(32)	1504 (21)	5742 (15)	1325 (29)	47 (7)
O(41)	−931 (12)	1400 (11)	2217 (16)	36 (4)
O(42)	249 (13)	1075 (10)	3686 (16)	35 (4)
C(41)	−677 (19)	848 (15)	2973 (19)	34 (6)
C(42)	−1503 (17)	−97 (17)	3056 (26)	38 (5)
O(51)	93 (12)	3573 (11)	3962 (15)	33 (4)
O(52)	1432 (12)	3319 (10)	5216 (15)	31 (3)
C(51)	673 (16)	3701 (15)	5101 (20)	24 (5)
C(52)	591 (18)	4310 (16)	6569 (22)	32 (5)
C_M	3487 (21)	4289 (15)	4343 (27)	54 (6)
O_M	2874 (11)	3235 (10)	3455 (15)	28 (3)
O_C	740 (11)	1639 (8)	1415 (12)	21 (3)
OW(1)	2368 (13)	2096 (1)	5525 (15)	36 (4)
OW(2)	3241 (13)	3399 (13)	599 (18)	42 (4)
OW(3)	−1394 (11)	2943 (11)	1553 (15)	32 (3)
Zn	3511 (2)	7832 (2)	5835 (3)	36 (1)
Cl(1)	3925 (8)	8863 (5)	8187 (7)	66 (3)
Cl(2)	4840 (6)	7290 (6)	5476 (9)	61 (2)
Cl(3)	2162 (6)	6371 (6)	5501 (8)	60 (2)
Cl(4)	3171 (8)	8664 (6)	4182 (8)	67 (3)
OW(4)	3737 (14)	1102 (13)	5698 (18)	48 (5)
OW(5)	3389 (15)	3706 (13)	7997 (18)	52 (5)
OW(6)	4806 (15)	2774 (14)	1085 (25)	65 (6)
OW(7)	3033 (15)	7711 (13)	750 (18)	52 (5)
OW(8)	4752 (19)	1302 (15)	8609 (21)	71 (6)
OW(9)	3262 (18)	5600 (16)	8178 (28)	86 (7)
OW(10)	4533 (24)	5959 (26)	1956 (32)	120 (12)

[a] Coordinates of all atoms are ×10^4. U_{eq} values for the W atoms are ×10^4 and for the light atoms ×10^3. Esds are given in parentheses. $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$.

Table IV. Important Bond Lengths (Å) for Compound **1**

W(1)–W(2)	2.6937 (9)	W(2)–O(21)	2.08 (1)
–W(3)	2.6924 (9)	–O(22)	2.07 (1)
W(2)–W(3)	2.712 (1)	–O(23)	2.05 (1)
W(1)–O(1)	1.99 (1)	–O(24)	2.10 (1)
–OW(1)	2.21 (1)	W(3)–O(1)	1.98 (1)
–O(11)	2.06 (1)	–OW(3)	2.16 (1)
–O(12)	2.07 (1)	–O(31)	2.06 (1)
–O(13)	2.08 (1)	–O(32)	2.06 (1)
–O(14)	2.04 (1)	–O(33)	2.08 (1)
W(2)–O(1)	1.97 (1)	–O(34)	2.05 (1)
–OW(2)	2.13 (1)		

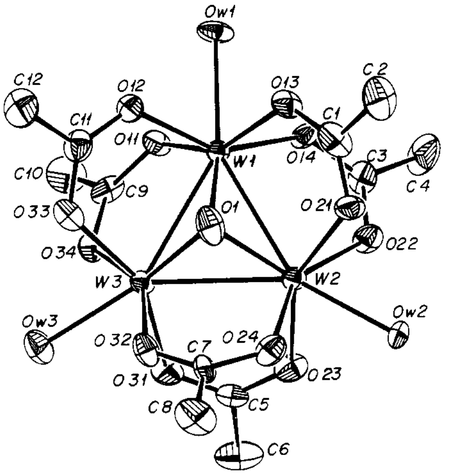


Figure 1. Structure of the cation in compound **1**. Each atom is represented by its ellipsoid of thermal displacement drawn at the 50% probability level. The atom-numbering scheme shown in Tables II, IV, and V is defined.

Table V. Important Angles (deg) for Compound **1**

W(2)–W(1)–W(3)	60.46 (3)	O(1)–W(2)–O(23)	129.5 (5)
–O(1)	46.8 (4)	–O(24)	77.6 (5)
–OW(1)	151.0 (3)	OW(2)–W(2)–O(21)	75.9 (5)
–O(11)	120.7 (3)	–O(22)	74.9 (5)
–O(12)	124.5 (3)	–O(23)	77.2 (5)
–O(13)	83.8 (3)	–O(24)	75.7 (5)
–O(14)	82.9 (3)	O(21)–W(2)–O(22)	87.6 (5)
W(3)–W(1)–O(1)	47.3 (4)	–O(23)	152.6 (5)
–OW(1)	148.3 (3)	–O(24)	87.3 (5)
–O(11)	83.1 (3)	O(22)–W(2)–O(23)	80.3 (5)
–O(12)	83.5 (3)	–O(24)	150.5 (5)
–O(13)	124.7 (3)	O(23)–W(2)–O(24)	91.2 (5)
–O(14)	123.7 (3)	W(1)–W(3)–W(2)	59.79 (2)
O(1)–W(1)–OW(1)	144.8 (5)	–O(1)	47.5 (4)
–O(11)	129.9 (5)	–OW(3)	151.0 (3)
–O(12)	77.8 (5)	–O(31)	120.0 (3)
–O(13)	77.4 (5)	–O(32)	124.2 (3)
–O(14)	128.3 (5)	–O(33)	83.0 (3)
OW(1)–W(1)–O(11)	74.0 (4)	–O(34)	83.2 (3)
–O(12)	75.8 (5)	W(2)–W(3)–O(1)	46.4 (4)
–O(13)	77.4 (5)	–OW(3)	149.1 (3)
–O(14)	74.5 (5)	–O(31)	82.7 (3)
O(11)–W(1)–O(12)	91.8 (4)	–O(32)	83.4 (3)
–O(13)	151.2 (4)	–O(33)	123.2 (3)
–O(14)	81.1 (5)	–O(34)	122.2 (3)
O(12)–W(1)–O(13)	84.8 (4)	O(1)–W(3)–OW(3)	143.2 (5)
–O(14)	150.3 (4)	–O(31)	128.4 (5)
O(13)–W(1)–O(14)	87.8 (5)	–O(32)	76.7 (5)
W(1)–W(2)–W(3)	59.75 (2)	–O(33)	76.8 (5)
–O(1)	47.5 (4)	–O(34)	129.8 (5)
–OW(2)	149.7 (3)	OW(3)–W(3)–O(31)	75.9 (5)
–O(21)	82.8 (3)	–O(32)	75.3 (5)
–O(22)	83.0 (3)	–O(33)	77.5 (5)
–O(23)	119.6 (3)	–O(34)	75.8 (5)
–O(24)	125.1 (3)	O(31)–W(3)–O(32)	91.7 (5)
W(3)–W(2)–O(1)	46.9 (4)	–O(33)	153.1 (5)
–OW(2)	150.6 (3)	–O(34)	79.8 (5)
–O(21)	123.8 (3)	O(32)–W(3)–O(33)	85.1 (4)
–O(22)	123.2 (3)	–O(34)	151.1 (4)
–O(23)	83.1 (3)	O(33)–W(3)–O(34)	90.2 (4)
–O(24)	83.1 (3)	W(1)–O(1)–W(2)	85.7 (5)
O(1)–W(2)–OW(2)	142.4 (5)	–W(3)	85.2 (5)
–O(21)	76.9 (5)	W(2)–O(1)–W(3)	86.7 (5)
–O(22)	129.2 (5)		

W_3 plane, two equivalent O_2CCH_3 groups on the other side of the W_3 plane, and one O_2CCH_3 group spanning the same W–W bond as the OCH_3 group spans, respectively. We cannot tell which signal belongs to which pair of equivalent O_2CCH_3 groups. It may also be noted that while the NMR spectrum shows that the solid-state structure persists in solution, it could not have revealed that the OCH_3 substituent is trans to the μ_3-O atom.

The UV–visible spectrum shows a marked similarity to that of the symmetrical $[W_3O(O_2CCH_3)_6(H_2O)_3]^{2+}$ ion. Most particularly, it has a moderately strong band in the red region (714 nm) and a band of about half that intensity at 500 nm. These may be compared with the following bands in the symmetrical cation: 668 nm ($\epsilon = 1250$) and 508 nm ($\epsilon = 625$). In addition, we find a strong band at 370 nm ($\epsilon \approx 1500$) whereas the more symmetrical ion had two bands in this region: 404 nm ($\epsilon = 1020$) and 340 nm ($\epsilon = 2375$). There also appears to be a band at about 274 nm in the present case.

Structure of $[W_3O(O_2CCH_3)_6(H_2O)_3]^{2+}$. Since compound **1** presents this hemicapped cation in undisordered form, it is now possible to obtain an unimpaired picture of it. It is depicted in Figure 1, and the important distances and angles are listed in Tables IV and V. The entire cation contributes to the asymmetric unit, and thus no symmetry is imposed upon it crystallographically.

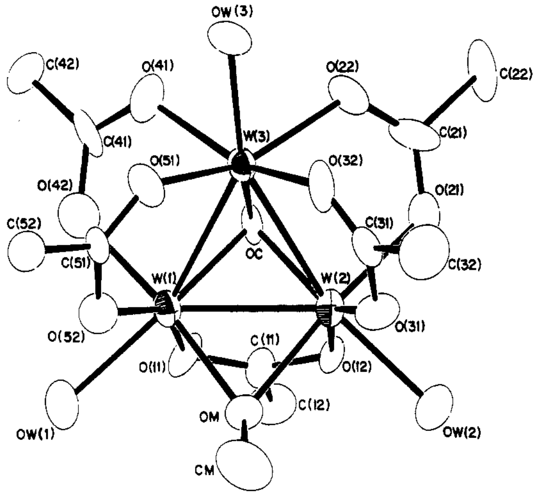


Figure 2. Structure of the cation in compound **2**. Each atom is represented by its ellipsoid of thermal displacement drawn at the 50% probability level. The atom-numbering scheme shown in Tables III, VI, and VII is defined.

Table VI. Important Bond Lengths (Å) for the Cation in Compound **2**

W(1)–W(2)	2.495 (1)	W(2)–O(31)	2.06 (1)
W(1)–W(3)	2.684 (1)	W(2)–O_M	2.08 (1)
W(2)–W(3)	2.687 (1)	W(2)–O_C	1.94 (1)
W(1)–O(11)	2.07 (1)	W(2)–OW(2)	2.17 (1)
W(1)–O(42)	2.08 (1)	W(3)–O(22)	2.10 (1)
W(1)–O(52)	2.05 (1)	W(3)–O(32)	2.11 (1)
W(1)–O_M	2.04 (1)	W(3)–O(41)	2.07 (1)
W(1)–O_C	1.92 (1)	W(3)–O(51)	2.10 (1)
W(1)–OW(1)	2.16 (1)	W(3)–OC	1.99 (1)
W(2)–O(12)	2.07 (1)	W(3)–OW(3)	2.17 (1)
W(2)–O(21)	2.07 (1)		

In fact, it has effective C_{3v} symmetry. Two of the W–W distances are equal at 2.693 (1) Å; the third is in a statistical sense different, at 2.712 (1) Å. The average W–W distance is 2.699 [8] Å, which is essentially equal to that found previously, 2.710 [4] Å. The three W–(μ_3-O) distances are equal within their esds and have an average value of 1.98 [1] Å, which is not significantly different from the previous value of 1.96 [2] Å.

The other W–O distances are also on average the same as the ones previously found, namely, 2.17 [2] Å as compared to 2.16 [1] Å for the distances to the water oxygen atoms and 2.07 [1] Å in both studies for the W–O(acetate) distances. However, for the latter, the gross comparison of average values misses the important point that the present work makes clear, namely, that there are small differences between the sets of acetate ligands on the two faces of the metal triangle. On the capped face the average W–O(acetate) distances (each with an esd of 0.01 Å) range from 2.06 to 2.10 Å with an average of 2.078 Å, while on the uncapped face the range is 2.04–2.07 Å and the average is 2.055 Å. Statistically, these two sets are only marginally different, but the distinction is probably real. A much more convincing difference is found in the tilt of the two kinds of acetate groups. This is most easily seen in the data of Table V by comparing the two sets of O–W–O angles. On the capped side these have an average value of 85.7 ± 1° while on the uncapped side the average value is only 80.4 ± 0.5°. In summary, the acetate ions on the uncapped side have slightly longer W–O bonds and approach each other more closely as compared to those on the capped side.

The $ZnCl_4^{2-}$ ion is an essentially regular tetrahedron with a mean Zn–Cl bond length of 2.26 [1] Å. There is an extensive series of hydrogen bonds linking the ions to the water molecules, and the latter to each other.

Structure of $[W_3O(O_2CCH_3)_5(OCH_3)(H_2O)_3]^{2+}$. The structure is displayed in Figure 2, and important bond distances and angles are listed in Table VI and VII. The unit cell contains two $[W_3O(O_2CCH_3)_5(OCH_3)(H_2O)_3]^{2+}$ cations counterbalanced by two $ZnCl_4^{2-}$ ions. In addition there are 14 water molecules of hydration involved in a rather intricate hydrogen-bonded pattern. A packing diagram showing this is available as supplementary material.

Table VII. Important Bond Angles (deg) for the Cation in Compound **2**

W(2)–W(1)–W(3)	62.38 (3)	O(12)–W(2)–O(31)	150.4 (6)
W(2)–W(1)–O(11)	87.1 (3)	O(12)–W(2)–O_M	87.3 (6)
W(2)–W(1)–O(42)	132.0 (5)	O(12)–W(2)–O_C	78.4 (5)
W(2)–W(1)–O(52)	115.5 (3)	O(12)–W(2)–OW(2)	76.8 (6)
W(2)–W(1)–O_M	53.4 (4)	O(21)–W(2)–O(31)	90.6 (7)
W(2)–W(1)–O_C	50.0 (4)	O(21)–W(2)–O_M	173.7 (5)
W(2)–W(1)–OW(1)	138.3 (4)	O(21)–W(2)–O_C	82.9 (6)
W(3)–W(1)–O(11)	126.6 (5)	O(21)–W(2)–OW(2)	86.9 (7)
W(3)–W(1)–O(42)	83.9 (4)	O(31)–W(2)–O_M	90.6 (7)
W(3)–W(1)–O(52)	83.5 (4)	O(31)–W(2)–O_C	130.9 (5)
W(3)–W(1)–O_M	103.4 (3)	O(31)–W(2)–OW(2)	73.7 (6)
W(3)–W(1)–O_C	47.7 (3)	O_M–W(2)–O_C	100.9 (6)
W(3)–W(1)–OW(1)	154.2 (4)	O_M–W(2)–OW(2)	87.5 (7)
O(11)–W(1)–O(42)	87.2 (6)	O_C–W(2)–OW(2)	153.3 (6)
O(11)–W(1)–O(52)	149.4 (6)	W(1)–W(3)–W(2)	55.35 (3)
O(11)–W(1)–O_M	88.1 (6)	W(1)–W(3)–O(22)	124.5 (3)
O(11)–W(1)–O_C	79.0 (6)	W(1)–W(3)–O(32)	117.0 (5)
O(11)–W(1)–OW(1)	76.2 (6)	W(1)–W(3)–O(41)	82.5 (4)
O(42)–W(1)–O(52)	91.5 (6)	W(1)–W(3)–O(51)	83.0 (4)
O(42)–W(1)–O_M	172.6 (5)	W(1)–W(3)–O_C	45.7 (4)
O(42)–W(1)–O_C	82.2 (6)	W(1)–W(3)–OW(3)	149.7 (3)
O(42)–W(1)–OW(1)	85.7 (7)	W(2)–W(3)–O(22)	83.0 (4)
O(52)–W(1)–O_M	89.6 (6)	W(2)–W(3)–O(32)	81.8 (4)
O(52)–W(1)–O_C	131.1 (5)	W(2)–W(3)–O(41)	123.9 (4)
O(52)–W(1)–OW(1)	73.2 (5)	W(2)–W(3)–O(51)	117.4 (5)
O_M–W(1)–O_C	102.5 (6)	W(2)–W(3)–O_C	46.0 (4)
O_M–W(1)–OW(1)	87.7 (6)	W(2)–W(3)–OW(3)	154.2 (3)
O_C–W(1)–OW(1)	152.8 (5)	O(22)–W(3)–O(32)	86.8 (6)
W(1)–W(2)–W(3)	62.27 (3)	O(22)–W(3)–O(41)	95.5 (7)
W(1)–W(2)–O(12)	85.9 (3)	O(22)–W(3)–O(51)	152.5 (5)
W(1)–W(2)–O(21)	132.3 (5)	O(22)–W(3)–O_C	79.4 (5)
W(1)–W(2)–O(31)	115.6 (4)	O(22)–W(3)–OW(3)	80.2 (6)
W(1)–W(2)–O_M	52.2 (4)	O(32)–W(3)–O(41)	154.3 (6)
W(1)–W(2)–O_C	49.5 (4)	O(32)–W(3)–O(51)	78.8 (5)
W(1)–W(2)–OW(2)	136.9 (5)	O(32)–W(3)–O_C	127.0 (6)
W(3)–W(2)–O(12)	125.9 (4)	O(32)–W(3)–OW(3)	77.8 (7)
W(3)–W(2)–O(21)	83.9 (4)	O(41)–W(3)–O(51)	88.0 (6)
W(3)–W(2)–O(31)	83.3 (4)	O(41)–W(3)–O_C	78.4 (5)
W(3)–W(2)–O_M	102.4 (3)	O(41)–W(3)–OW(3)	77.4 (6)
W(3)–W(2)–O_C	47.6 (3)	O(51)–W(3)–O_C	127.9 (5)
W(3)–W(2)–OW(2)	155.1 (4)	O(51)–W(3)–OW(3)	74.0 (6)
O(12)–W(2)–O(21)	88.6 (6)	O_C–W(3)–OW(3)	146.5 (7)

The trinuclear cluster of W atoms is remarkable with regard to the asymmetric attachment of five acetate groups, one methoxy group, and one capping oxygen to the metal triangle. Thus, the formal oxidation number per W atom is again $^{10}/_3$. This arrangement leads to two W–W bond lengths with an average value of 2.685 (1) Å, which is similar to but slightly shorter than those found in the symmetrical tungsten cluster cation $[W_3O(O_2CCH_3)_6(H_2O)_3]^{2+}$. The third bond W(1)–W(2) of 2.495 Å opposite the methanolate oxygen is very much shorter.

The capping oxygen atom makes two almost equal bonds with W(1) and W(2), but the third bond to W(3) is significantly longer. The methanolate group and the capping oxygen atom are disposed on opposite sides of the triangle plane, which avoids short contacts with the hydrogen atoms of the methyl carbon atom. In spite of the pronounced asymmetry induced by the ligand, the cation as a whole still retains a mirror plane, which bisects the isosceles triangle of metal atoms through the bond W(1)–W(2) and through the atom W(3). The O–C bond length of 1.43 Å in the methanolate ligand is normal and can be compared with similar distances found in a trimolybdenum cluster.[4] The carbon atom, C_M, deviates from the plane defined by W(1), W(2), and O_M by 0.87 Å so that the C_M–O_M bond is directed away from the acetate group attached to the W(1)–W(2) bond; the sum of angles around O_M is 332.5°. Bridging oxygen atoms with geometry reminiscent of that in the title structure exist in the $[W_3O_4F_9]^{5-}$ ion.[5] Here,

---

(4) Birenbaum, A.; Cotton, F. A.; Dori, Z.; Kapon, M. *Inorg. Chem.* **1984**, *23*, 1617.

the W–O bond lengths are shorter by ~0.1 Å and the W–O–W bond angles are larger by ~5° than the corresponding values for the methoxy oxygen atom. Also, the W–W bond lengths of 2.514 Å opposite the bridging oxygen atoms are larger by ~0.02 Å than those in the present case. These differences indicate that the methoxy oxygen atom is bound to the metal triangle by weaker bonds than the oxo anion.

The tetrahedral $[ZnCl_4]^{2-}$ ion found in this structure has normal geometry with a mean Zn–Cl bond length of 2.259 (8) Å.

The packing forces in the unit cell between the ions and the water molecules are mainly hydrogen bonds of two types: OW-H- - -OW and OW-H- - -Cl. Bonds of the first type exist among the water molecules of hydration and also between these and the molecules of the metal cluster cation. The range of bond lengths is 2.60–2.90 Å. Bonds of the second type are formed between all four chlorine atoms of the $ZnCl_4{}^{2-}$ ions and some of the water molecules of hydration, the range of bonds being 3.15–3.35 Å.

Acknowledgment. We thank the National Science Foundation (U.S.) for support of this work.

Supplementary Material Available: Tables containing additional bond lengths, bond angles, and anisotropic thermal displacement parameters for **1** and **2** and a stereoview of the unit cell of **2** (9 pages); tables of observed and calculated structure factors (53 pages). Ordering information is given on any current masthead page.

---

(5) Mattes, R.; Mennemann, K. *Z. Anorg. Allg. Chem.* **1977**, *437*, 175.

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843

Further Studies of Low-Valent Alkoxide Complexes of Niobium. Synthesis and Structure of Dimeric Niobium(IV) Nonamethoxide

F. Albert Cotton,* Michael P. Diebold, and Wieslaw J. Roth

Received May 6, 1988

The synthesis and properties of the niobium(IV) nonamethoxide anion, $Nb_2(OMe)_9{}^-$, are described. This anion is most easily prepared by reaction of $Nb_2Cl_4(OMe)_4(HOMe)_2$ (made in situ from either $NbCl_5$ or $NbCl_4(THF)_2$) with an excess of methoxide in methanol. This anion is stable only in solutions containing an excess of MeO^-; in neat methanol and in the solid state decomposition occurs to give a red compound tentatively identified as $[Nb(OMe)_4]_n$. Three salts of $Nb_2(OMe)_9{}^-$ were characterized by X-ray crystallography: $[Mg(MeOH)_6]_2[Nb_2(OMe)_9]Cl_3$ (**1a**), $[Mg(MeOH)_6][Nb_2(OMe)_9]I\cdot 2CH_3OH$ (**1b**), and $[Na(MeOH)_6][Nb_2(OMe)_9]$ (**1c**). Crystallographic data: compound **1a**, space group *C*2 with $a = 16.235$ (4) Å, $b = 14.453$ (4) Å, $c = 10.209$ (3) Å, $\beta = 94.02$ (2)°, $V = 2389$ (1) Å^3, and $Z = 2$; compound **1b**, space group *Cmcm* with $a = 12.397$ (1) Å, $b = 13.068$ (6) Å, $c = 24.347$ (3) Å, $V = 3944$ (3) Å^3, and $Z = 4$; compound **1c**, space group *C*2/*c* with $a = 17.510$ (4) Å, $b = 14.126$ (4) Å, $c = 13.932$ (3) Å, $\beta = 108.75$ (2)°, $V = 3263$ (5) Å^3, and $Z = 4$. In each case the solvated cation shows disorder about a virtual 3-fold axis and an extensive network of hydrogen bonding is present. The Nb–Nb distance, 2.64 Å, is unusually short; the reason for this is discussed.

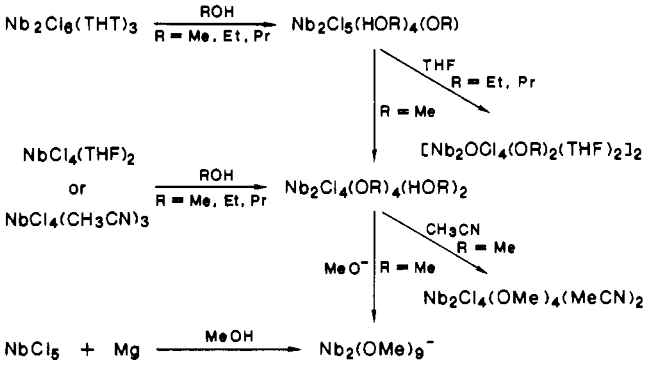
Introduction

Known complexes of niobium containing alcohol or alkoxide ligands have to date been mainly limited to those in which the metal atom is in the +5 oxidation state.[1] We have recently reported the synthesis and characterization of a number of Nb(III) and Nb(IV) alkoxide complexes, including $Nb_2Cl_5(OR)(HOR)_4$ (R = Me, Et, ^{i}Pr),[2] $[Nb_2OCl_4(OR)_2(THF)_2]_2$ (R = Et, ^{i}Pr),[2] $Nb_2Cl_4(OMe)_4(MeCN)_2$,[3] and $Nb_2Cl_4(OR)_4(HOR)_2$ (R = Me, Et, ^{i}Pr)[3] (see Scheme I). These products were obtained by using alcohols as the reactants. The reaction of $Nb_2Cl_4(OMe)_4(HOMe)_2$ with excess methoxide resulted in complete substitution of all ligating chlorides, producing an intense blue homoleptic Nb(IV) methoxide anion of the formula $Nb_2(OMe)_9{}^-$. We now wish to report the synthesis and properties of this compound as well as the crystal structures of this anion with a number of different counterions.

Experimental Section

All manipulations were carried out under an atmosphere of argon using standard vacuum line techniques. $NbCl_5$ was purchased from Johnson-Matthey, and $NbCl_4(THF)_2$ was prepared according to the literature method.[4] Solvents were distilled under nitrogen from appropriate drying agents prior to use. UV–visible spectra were recorded on a Cary 17d spectrometer.

Scheme I



Preparation of $Nb_2(OMe)_9{}^-$. (A) From $NbCl_5$. Magnesium turnings (0.88 g) and $NbCl_5$ (1.45 g, 5.36 mmol) were placed in a 100-mL round-bottomed flask and cooled with a dry-ice/acetone bath. Methanol (30 mL) was added with stirring over a period of 1 min. After 5 min the cold bath was removed and the flask allowed to warm to room temperature while the contents were rapidly stirred. Within 1 h the solution changed color to red-purple, followed by red-brown, green, and finally blue-purple. The initial red/purple complex has been identified by UV-vis spectroscopy as $Nb_2Cl_4(OMe)_4(HOMe)_2$.[2b] Should the reaction at any time become too vigorous, the solution may be cooled to −78 °C and then allowed to warm back up. After 1 h the solution was filtered from a white solid and the remaining Mg turnings. The filtrate was then placed at −20 °C overnight and, the following day, filtered from the clear crystals that had formed. When this reaction mixture was carefully layered with diethyl ether, large crystals of $[Mg(MeOH)_6]_2[Nb_2(OMe)_9]Cl_3$ (**1a**), contaminated with a white crystalline material, were

---

(1) Bradley, D. C.; Mehrotra, R. C.; Guar, G. P. *Metal Alkoxides*; Academic: New York, 1978, and references therein.

(2) (a) Cotton, F. A.; Diebold, M. P.; Roth, W. J. *Inorg. Chem.* **1985**, *24*, 3509. (b) Cotton, F. A.; Diebold, M. P.; Roth, W. J. *Inorg. Chem.* **1987**, *26*, 3319.

(3) Cotton, F. A.; Diebold, M. P.; Roth, W. J. *Inorg. Chem.* **1987**, *26*, 3323.

(4) Manzer, L. *Inorg. Chem.* **1977**, *16*, 525.

0020-1669/88/1327-3596$01.50/0 © 1988 American Chemical Society