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The First Eight-Electron Triangular Trinuclear Cluster Compound of Tungsten without Acetate as a Bridging Ligand: $Na[W_3(\mu_3\text{-}O)(\mu\text{-}Cl)_3Cl_6(THF)_3]$

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Introduction

The chemistry of the $M_3X_4Y_9$ type of triangular M–M-bonded cluster compounds of molybdenum and tungsten has been extensively studied.

There is an enormous range of such compounds already known and even more potentially available because of the variability in the composition.[1-6] First, as already implicitly stated, the metal atoms may be either Mo or W, or even a mixed set. Second, the four intimate ligands, X, that combine with the three metal atoms to form the M_3X_4 core may be chosen from among O, S, Se, Cl, Br, and no doubt others, and they need not all be the same. Third, the ligands that occupy the nine external positions can be almost anything and Y_9 in the general formula may, of course, be a very heterogeneous group.[6] Fourth, the number of cluster electrons varies from 6 to 9 among stable compounds.[1-4] It has been shown[5] that the preferred number of electrons is affected by the nature of the intimate ligands in the M_3X_4 core. For example, with M_3O_4 the preferred number is 6, while $M_3(\mu_3\text{-}O)(\mu\text{-}Cl)_3$ favors 8 or 9. The theoretical work[5] would imply that the electronic preferences are determined solely by the set of intimate ligands, independently of the identity or character of the set of nine outer ligands.

All previous 8-electron (or 9-electron) species containing an $M_3(\mu_3\text{-}O)(\mu\text{-}Cl)_3$ core have also contained three bridging acetate ligands, one spanning each edge of the M_3 triangle. A typical and particularly relevant example is the $[W_3(\mu\text{-}O)(\mu\text{-}Cl)_3Cl_3(O_2CCH_3)_3]^-$ ion.[1] To prove experimentally that the presence of the three $\mu\text{-}O_2CCH$ ligands is not necessary for the stability of the 8-electron core, it would suffice to prepare and characterize a species of the type $[W_3(\mu_3\text{-}O)(\mu\text{-}Cl)_3Cl_6L_3]^-$. In this note, we report that this has been done, the new compound being $Na[W_3(\mu_3\text{-}O)(\mu\text{-}Cl)_3Cl_6(THF)_3]$.

Experimental Section

All manipulations were carried out under an atmosphere of dry oxygen-free argon with Schlenk techniques. Solvents were dried and deoxygenated by refluxing over appropriate reagents before use. Sodium triethylborohydride (1.0 M in toluene) was purchased from Aldrich, Inc., and used as received. WCl_4 was prepared according to published procedures.[7,8]

Preparation of $Na[W_3(\mu_3\text{-}O)(\mu_3\text{-}Cl)_3Cl_6(THF)_3]$. The first preparation occurred serendipitously. The reduction of 1.0 g of WCl_4 by 1 equiv of $NaEt_3BH$ in 20 mL of THF gave a greenish yellow solution. The solution was filtered through Celite and then kept at −15 °C for nearly 3 months. The Schlenk tube was then removed from the freezer and kept at room temperature. After several days a few dark crystals of the title compound were found on the wall of the Schlenk tube. The shape of the crystals was roughly hexagonal. One crystal was chosen to carry out the X-ray diffraction studies.

Table 1. Crystallographic Data for $Na[W_3(\mu_3\text{-}O)(\mu\text{-}Cl)_3Cl_6(THF)_3]\cdot 1.49THF$

formula	$NaC_{12}H_{24}O_4Cl_9W_3\cdot 1.49OC_4H_8$
fw	1233.01
space group	$P2_13$ (No. 198)
a	15.120(5) Å
V	3456(2) Å^3
Z	4
ρ_{calcd}	2.37 g/cm^3
μ(Mo Kα)	106.95 cm^{-1}
λ	0.710 73 Å
T	−60 °C
transm coeff: min, max	0.874, 0.998
$R_1(F_o)^{a,b}$	0.038
$R_2(F_o^2)^c$	0.092
quality-of-fit indicator[d]	1.118

[a] $I > 2\sigma(I)$. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.0216P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$. [d] $QOF = [\sum w(F_o^2 - F_c^2)^2/(N_{observns} - N_{params})]^{1/2}$.

The preparation was then carried out more deliberately by introducing O_2 into the W(III) solution. Again, 1.0 g (3.07 mmol) of WCl_4 was reduced by 1 equiv of $NaEt_3BH$ in 20 mL of THF. After the solution was filtered through Celite, 12.5 mL (0.512 mmol) of O_2 (at 25 °C and 1 atm) was introduced into the Schlenk tube. The Schlenk tube was then kept at room temperature for 2 months, and dark crystals of the title compound were found on the wall of the Schlenk tube. One crystal was checked for cell parameters, and they were the same as those obtained before. The crystals were filtered off and weighed. Yield: 86 mg, 8%.

X-ray Crystallography. The basic crystallographic procedures have been fully described elsewhere.[9,10] A crystal of dimensions 0.21 × 0.21 × 0.42 mm^3 was attached to the tip of a quartz fiber with grease and immediately transferred into a cold stream of nitrogen (−60 °C) on an Enraf-Nonius CAD-4S diffractometer. Crystal quality was verified by means of a rotation photograph. The cubic cell was determined from the geometrical parameters of 25 well-centered reflections with 2θ values between 28 and 34°. Axial photographs confirmed the axial lengths and the presence of mirror planes. A photograph of the [110] direction indicated no mirror plane and that the Laue group is $m3$. The intensities of all reflections in the $+h,-k,+l$ octant of reciprocal space with 2θ values from 4 to 50° were measured by a $\omega/2\theta$ scan technique. The systematic absences are unique for space group $P2_13$ (No. 198). The positions of the W, Cl, and capping O atoms were given by direct methods. The Na and ligand THF atoms were then found in a difference Fourier map. The outer two carbon atoms of the THF ligand were later more successfully modeled as a set of two disordered pairs, the occupancy factors refining to 0.60(5)/0.40(5). At this point the Flack x parameter strongly indicated that the absolute structure should be inverted, and doing so immediately reduced the R factor by another 2 percentage points. During the final refinement stages, two highly disordered interstitial THF molecules were located and included in the least-squares model. Hydrogen atoms were used in calculated positions for the ligand THF carbon atoms for F_c^2 calculation only. Only the ordered non-hydrogen atoms of the complex were refined anisotropically. Refinement on F_o^2 was carried out with the SHELXL-93 program. A summary of crystal data is given in Table 1, and atomic positional parameters for the complex are given in Table 2.

Results and Discussion

There remains a major problem with this compound, namely, the lack of an efficient method of preparation. The method that entails deliberate introduction of oxygen is reproducible, but only with poor yields. Nevertheless, the existence and structure of this trinuclear species are worth reporting because of its place in an entire series of related structures.

The crystal structure consists of four formula units of $Na[W_3(\mu_3\text{-}O)(\mu\text{-}Cl)_3Cl_6(THF)_3]$ per unit cell. An ORTEP diagram, Figure 1, shows the structure of the tungsten trinuclear anion, in which the three tungsten atoms form an equilateral triangle. There is one capping oxygen atom above the plane of

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Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic placement Parameters (Å^2 × 10^3)[a]

	x	*y*	*z*	*U*(eq)
W	2637(1)	6163(1)	1130(1)	24(1)
Cl(1)	2584(2)	6090(3)	−453(2)	34(1)
Cl(2)	1012(2)	6037(3)	1009(3)	41(1)
Cl(3)	2320(2)	7709(3)	1145(4)	42(1)
Na	813(4)	5813(4)	−813(4)	36(3)
O(1)	3990(6)	6010(6)	1010(6)	20(3)
O(2)	4002(7)	7388(7)	−240(6)	31(2)
C(1)	4608(12)	6859(11)	−757(11)	43(4)
C(2)	4590(37)	7169(45)	−1713(26)	62(9)
C(2A)	4276(34)	6980(22)	−1725(20)	62(9)
C(3)	3661(34)	7582(45)	−1681(27)	55(8)
C(3A)	3913(29)	7937(26)	−1707(18)	55(8)
C(4)	3527(10)	8030(10)	−791(11)	49(5)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

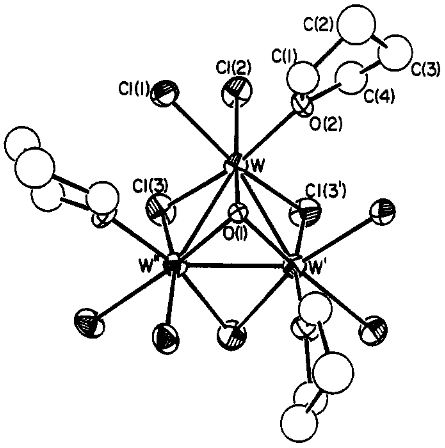

Figure 1. ORTEP diagram of the $[W_3(\mu_3\text{-}O)(\mu\text{-}Cl)_3Cl_6(THF)_3]^-$ anion showing 50% probability ellipsoids. Atoms C(2) and C(3) represent the major orientation of the disordered pair.

the triangle, and three bridging chloride atoms are below the plane. Each tungsten atom is further coordinated by two terminal chlorides and one THF ligand, providing it with a distorted octahedral coordination environment. The $[W_3OCl_9(THF)_3]^-$ ion has crystallographic (i.e., rigorous) $C_3(3)$ symmetry. The bond distances between the tungsten atoms are 2.602(1) Å. Selected bond distances and bond angles are given in Table 3. The average W–W bond distance in the related M_3X_{13} compound $[Et_4N][W_3(\mu_3\text{-}O)(\mu\text{-}Cl)_3(\mu\text{-}OAc)_3Cl_3]\cdot Me_2CO$ is 2.567(1) Å;[1] the shorter W–W distances may be attributable to three bridging acetate groups.

It is pertinent to compare the present compound, having a $W_3(\mu_3\text{-}O)(\mu\text{-}Cl)_3$ core, with a previously reported compound[11] having what might be loosely described as the "reverse" set of intimate ligands, namely a $W_3(\mu_3\text{-}Cl)(\mu\text{-}O)_3$ core. This is the only well-characterized compound with such a core. It has a 6-electron cluster count. While there has not been any theoretical study of how an $M_3(\mu_3\text{-}Cl)(\mu\text{-}O)_3$ core should behave, the comparison of this compound and the present one is in accord with the view that it is particularly the $M_3(\mu_3\text{-}O)(\mu\text{-}Cl)_3$ type of core that favors the stability of the 8-electron count.

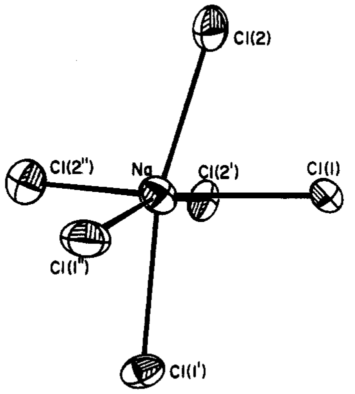

Figure 2. ORTEP diagram of the coordination environment of the Na^+ion.

Table 3. Selected Bond Distances and Angles

	Distances (Å)		
W–W	2.602(1)	W–Cl(3)	2.386(4)
W–O(1)	2.07(1)	W–Cl(3)′	2.401(4)
W–O(2)	2.132(9)	Na–Cl(1)	2.764(7)
W–Cl(1)	2.398(4)	Na–Cl(2)	2.793(6)
W–Cl(2)	2.471(4)		
	Angles (deg)		
W–O(1)–W′	78.0(5)	Cl(1)–W–Cl(3)′	165.2(1)
O(1)–W–O(2)	84.1(4)	Cl(2)–W–Cl(3)	82.9(2)
O(1)–W–Cl(3)	108.0(2)	Cl(2)–W–Cl(3)′	81.6(1)
O(1)–W′–Cl(3)	107.5(3)	Cl(3)–W–Cl(3)′	87.6(3)
O(1)–W–Cl(1)	86.5(3)	O(2)–W–Cl(1)	82.0(3)
O(1)–W–Cl(2)	165.7(3)	O(2)–W–Cl(2)	84.2(3)
W–Cl(3)–W′	65.8(1)	O(2)–W–Cl(3)	166.5(3)
Cl(1)–W–Cl(2)	83.7(1)	O(2)–W–Cl(3)′	94.4(3)
Cl(1)–W–Cl(3)	92.7(2)		

The distorted octahedral geometry about the Na^+ ion is shown in Figure 2. It is unusual to find that such a small cation packs satisfactorily with a large anion rather than with the additional solvent molecules.

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Supplementary Material Available: Tables of additional crystal and refinement data, atomic coordinates, coordinates for calculated hydrogen atoms, complete bond distances and angles, and anisotropic displacement parameters (7 pages). Ordering information is given on any current masthead page.

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