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$W_3(\mu_3\text{-}Cl)(\mu\text{-}Cl)_3Cl_9^{n-}$ ($n = 2, 3$), Discrete Monocapped Tritungsten Clusters Derived from a New Binary Tungsten Chloride, W_3Cl_{10}: Effect of Electron Count on Bonding in Isostructural *triangulo* M_3X_{13} Clusters[1]

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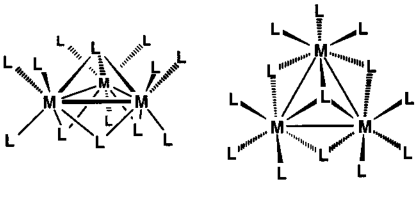
Triangular trimolybdenum and tritungsten compounds with one or two face-bridging chalcogenides are well-known.[2] Monocapped clusters, often denoted[3] M_3, with three terminal ligands L per metal and three edge-bridging ligands (e.g., μ-O), can be described as three octahedra that share edges in pairwise fashion and have a common vertex (the capping μ_3-L) or, less precisely, as an incomplete metallacubane. (μ_3-Oxo)tritungsten clusters are known with a variety of ligands, especially carboxylates. Although halides are useful ligands in polynuclear chemistry for subsequent functionalization, W_3 clusters with μ_3-halides are rare,[4] and monocapped group 6 clusters *exclusively* with halides are unknown. By contrast, perhalo trinuclear clusters are more common for the neighboring Re,[5] Nb,[6] and Ta.[7]



We recently reported convenient routes to W_6Cl_{12}[8] and to crystalline,[9] reactive[10] $(WCl_4)_x$ from reduction of WCl_6 with Hg, Sb, or Bi; therefore, we sought to apply this methodology to trivalent tungsten chlorides. Tungsten trichloride, prepared[11,12] by chlorination of W_6Cl_{12}, is believed to possess an octahedral hexatungsten structure (i.e., $W_6(\mu\text{-}Cl)_{12}Cl_6$) based on powder X-ray diffraction. Structurally uncharacterized $WCl_{2.6}$ and $WCl_{3.5}$, observed in thermochemical studies of H_2 reduction of WCl_6, have been described briefly.[13,14] Here, we report two new, isostructural, monocapped perchlorotritungstates, the first discrete group 6 trinuclear $M_3(\mu_3\text{-}L)(\mu\text{-}L)_3L_9$ clusters with identical ligands, and evidence for a new chloride, W_3Cl_{10}. Comparative structural details of the two clusters, which have differing electron counts, and MO calculations demonstrate the effect of orbital occupation on cluster bonding.

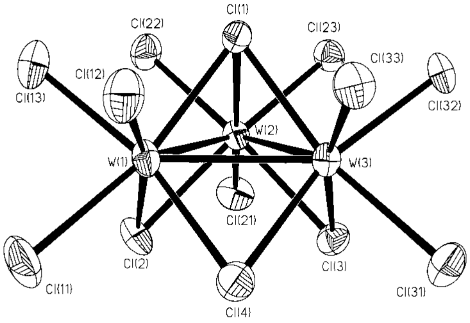


Figure 1. Thermal ellipsoid plot of the molecular structure of the trianion portion of **2**, $[W_3(\mu_3\text{-}Cl)(\mu\text{-}Cl)_3Cl_9]^{3-}$. The same atom labels apply to the isostructural dianion portion of **3**.

A heated (240 °C) mixture of WCl_6, Sb, and NaCl in an evacuated, sealed ampule yields the purple, crystalline, nonhygroscopic salt $Na_3W_3Cl_{13}$ (**1**) in quantitative yield after one week and distillation of $SbCl_3$ (eq 1).[15] The synthesis is dependent on

$$9WCl_6 + 8Sb + 9NaCl \rightarrow 3Na_3W_3Cl_{13} + 8SbCl_3 \quad (1)$$

the alkali metal cation. K_2WCl_6 and small amounts of $K_2W_6Cl_{14}$ were formed with KCl, whereas $Li_3W_3Cl_{13}$ and $Li_2W_3Cl_{13}$ (vide infra) were generated with LiCl at 330−350 °C. Tetraalkylammonium derivatives $(NR_4)_3W_3Cl_{13}$ (**2**) [$R_4 = (CH_2Ph)Et_3$, $(CH_2Ph)Bu_3$, Bu_4] are isolated quantitatively after NR_4Cl metathesis of **1** in CH_3CN or CH_2Cl_2, with $N(CH_2Ph)Et_3^+$ or $N(CH_2Ph)Bu_3^+$ affording crystals. Elemental analyses and FAB mass spectrometry[16] are consistent with a trinuclear W(+3.33) formulation for **2** without μ-oxo groups. Solid $[N(CH_2Ph)Bu_3]_3W_3Cl_{13}$ is likely diamagnetic (or weakly paramagnetic) at 25 °C, with a low effective moment of 0.73−0.79 μ_B depending on the diamagnetic correction approach. The UV/vis spectrum of $[N(CH_2Ph)Bu_3]_3W_3Cl_{13}$ in CH_2Cl_2 exhibits maxima at 555 ($\epsilon = 1010$), 420 (shoulder, 1600), 350 (6630), 270 (shoulder, 25100) and 240 nm (35400). Absorptions are blue-shifted ~15 nm in 7 M HCl to values similar to that for a red-purple W(~III) species (in 6 M HCl) of unknown nuclearity that was obtained in molten salts during electrochemical reduction of $KWCl_6$ or disproportionation of $K_3W_2Cl_9$.[17]

A monocapped triangular, as opposed to linear, cluster structure for the eight-electron trianion in **2** was shown by single-crystal X-ray diffractometry.[18] Figure 1 depicts the thermal ellipsoid plot, and Table 1 lists selected bond distances and angles. The average W−W distance is 2.778[5] Å,[19] with average W−Cl_μ−W angle of 70.4[1]° and W−Cl(1) distance of 2.415[3] Å. By comparison, the W−W distance is a substantially shorter 2.602(1) Å in the

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[15] Anal. Calcd for $Cl_{13}Na_3W_3$ (**1**): W, 51.00; Cl, 42.62. Found: W, 50.9; Cl, 42.85.

[16] Data for **2**: Anal. $\{[N(CH_2Ph)Bu_3]_3W_3Cl_{13}\}$ Calcd for $C_{57}H_{102}N_3Cl_{13}W_3$: W, 29.95; Cl, 25.02; Found: W, 29.6; Cl, 25.18. MS (FAB, NPOE matrix, negative ion mode, *m/e*, base peak of isotopic grouping): 1290 $[N(CH_2Ph)Bu_3](W_3Cl_{13})$, 1253 (loss of Cl).

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[18] Crystal data for **2** ($NBnEt_3$): monoclinic, $P2_1/c$, purple, $a = 13.924(2)$ Å, $b = 12.944(3)$ Å, $c = 30.919(6)$ Å, $\beta = 99.69(2)°$, $Z = 4$, R1 = 0.0552, wR2 = 0.1086, GOF (F^2) = 1.165.

[19] The value in brackets, the standard deviation of the mean, equals $[(\Sigma_m \Delta_i^2)/m(m-1)]^{1/2}$ with Δ_i defined as the deviation from the mean of the *i*th value in a set of *m* values.

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Table 1. Comparative Selected Bond Distances and Angles for $[W_3(\mu_3\text{-Cl})(\mu\text{-Cl})_3Cl_9]^{n-}$ (n = 3, 2), with Estimated Standard Deviations in Parentheses and Standard Deviations of the Mean in Brackets[a]

Bond distance or angle	$W_3(\mu_3\text{-Cl})(\mu\text{-Cl})_3Cl_9{}^{3-}$ (**2**)	$W_3(\mu_3\text{-Cl})(\mu\text{-Cl})_3Cl_9{}^{2-}$ (**3**)
W(1)−W(2)	2.788(1)	2.843(1)
W(2)−W(3)	2.777(1)	2.831(1)
W(3)−W(1)	2.770(1)	2.842(1)
W−Cl(1) avg	2.415[3]	2.432[1]
W−Cl_μ avg	2.411[3]	2.393[3]
W−Cl(a1) avg	2.452[1]	2.416[2]
W−Cl(a2,a3) avg	2.385[2]	2.335[7]
W(1)−W(2)−W(3)	59.70(3)	60.11(3)
W(2)−W(3)−W(1)	60.34(3)	60.14(3)
W(3)−W(1)−W(2)	59.96(3)	59.74(3)
W−Cl(1)−W avg	70.2[2]	71.4[1]
W−Cl_μ−W avg	70.4[1]	72.8[1]

[a] a = 1−3, with a1 labeling the Cl atoms *trans* to Cl(1); avg = average.

μ_3-oxo cluster $Na[W_3(\mu_3\text{-O})(\mu\text{-Cl})_3Cl_6(thf)_3]$,[20] which is isovalent to **2**. The difference in W−W distances for the latter cluster and isoelectronic **2** must be related to the differing ligands.

Eight-electron **2** is oxidized by $PhICl_2$ or $2,4\text{-}Cl_2C_6H_3ICl_2$ to the olive green, seven-electron $[N(CH_2Ph)R_3]_2W_3Cl_{13}$ (**3**; R = Et, Bu) in 80−90% yield. In solution, **3** is cleanly reduced back to **2** with Sb, as shown by UV/vis spectrophotometry. Solid $[N(CH_2Ph)Bu_3]_2W_3Cl_{13}$ is paramagnetic at 25 °C, with an effective moment of 1.71−1.73 μ_B. A CH_2Cl_2 solution exhibits UV/vis maxima at 705 (ϵ = 620), 450 (1980), 375 (6270), 290 (32300), and 250 nm (27700). Mass spectrometric and elemental analysis data indicated a trinuclear structure without μ-oxo ligands for the dianion in **3**,[21] and the same monocapped structure was found by X-ray diffractometry.[22] Selected comparative bond distances and angles for **2** and **3** are listed in Table 1, and Figure 1 illustrates the atom labeling scheme for **2**, which is also applicable to **3**. The key feature is the elongated average W−W distance of 2.839[4] Å in **3**, compared to **2**, which can be rationalized by partial depopulation of a bonding cluster MO and the increased Coulombic repulsions between higher oxidation state tungstens [W(+3.67)] in **3**. The average W−Cl_μ−W angle of 72.8[1]° and W−Cl(1) distance of 2.432[1] Å in **3** are greater for geometric reasons.

Published MO calculations on C_{3v} $M_3(\mu_3\text{-L})(\mu\text{-L})_3L_9$ clusters[3,23] with inequivalent ligands show that, in going from a cluster electron count of 7 to 8, the additional electron occupies a bonding orbital and this should lead to a decrease in W−W distance. We found similar results on **2** using GAMESS[24] (which utilizes SBK effective core potentials[25] for W and Cl) to optimize the structure (structural parameters were similar to that observed in the solid-state, except for typically lengthened W−Cl distances) and calculate MOs. The bonding HOMO (a_1; Figure 2)-LUMO (e) gap is 6.56 eV in **2**. The structures of **2** and **3** provide a particularly clear verification of these predictions because these isostructural compounds possess ligands of only one type and differ only in electron count.

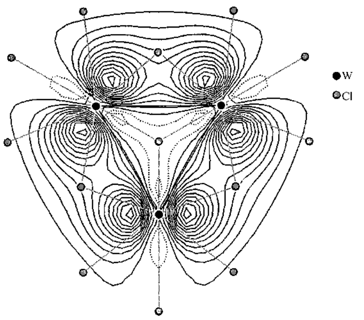
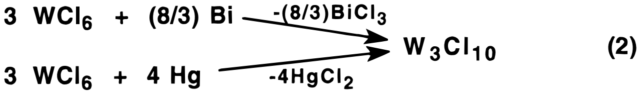


Figure 2. a_1 HOMO for $[W_3(\mu_3\text{-Cl})(\mu\text{-Cl})_3Cl_9]^{3-}$ derived from GAMESS calculations.

We postulate that **2** is derived from Cl^- addition to a new tungsten chloride, W_3Cl_{10} (**4**), under the reaction conditions. When Hg or Bi is used as reductant *in the absence of added alkali metal chloride* (eq 2), a microcrystalline, *air- and moisture-stable* solid



$$3\ WCl_6 + (8/3)\ Bi \xrightarrow{-(8/3)BiCl_3} W_3Cl_{10} \qquad (2)$$
$$3\ WCl_6 + 4\ Hg \xrightarrow[-4HgCl_2]{} W_3Cl_{10}$$

is obtained after $BiCl_3/HgCl_2$ sublimation. The product, which analyzes[26] as W_3Cl_{10}, is surprisingly inert, insoluble in common solvents, and does not react with concentrated HCl or HNO_3 (facilitating its separation from WCl_4 and W_6Cl_{12}). Single crystals suitable for X-ray diffraction have not yet been obtained, although the compound is crystalline by powder X-ray diffraction. We observed a similar phase by powder X-ray diffractometry during thermal disproportionation of $(WCl_4)_x$ at ~500 °C, under conditions where the volatile and nonvolatile chlorides were in equilibrium. W_3Cl_{10} is converted into $Na_3W_3Cl_{13}$ when heated with NaCl and $SbCl_3$ (which acts as solvent) at 350°. We postulate a structure for W_3Cl_{10} analogous to that for Nb_3Cl_8[9a,b] and $Na_2Ti_3Cl_8$,[27] with an extended structural net of nondiscrete $W_3(\mu_3\text{-Cl})(\mu\text{-Cl})_3Cl_9$ units that share chlorines. The W_3Cl_{10} formulation is further supported by the isolations of **1** and **2**.

Although structural studies on the anions in **2** and **3** are complete for the $NR_4{}^+$ cations, further work is needed to understand the cation dependence in the synthesis of **1**, to measure the temperature dependence of magnetic properties, and to determine the structure of **4**. Both **1** and **2** react with THF, AgOTf, C_5H_5N, and PPh_3 to give products that are being characterized.

Compounds **1**, **2**, **3**, and **4** constitute new synthons, readily accessed from WCl_6, for the development of tritungsten chemistry and have potential use in the synthesis of heterotetrametallacubanes and higher nuclearity[28] clusters.

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Supporting Information Available: Preparative details for **1**−**4**, UV/vis spectra (**2**, **3**), thermal ellipsoid plots, tables of crystallographic details, coordinates, distances and angles, and thermal parameters for **2** and **3** (34 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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[21] Data for **3**: Anal. $\{[N(CH_2Ph)Bu_3]_2W_3Cl_{13}(CH_2Cl_2)\}$ Calcd for $C_{39}H_{70}N_2Cl_{13}W_3$: W, 33.42; Cl, 27.92 (W-complexed Cl only). Found: W, 33.3; Cl, 28.30. MS (FAB, negative ion mode, m/e, base peak): 1288 $[N(CH_2Ph)Bu_3](W_3Cl_{13})$, 1255 (loss of Cl), 1014 (W_3Cl_{13}).

[22] Crystal data for **3** ($NBnBu_3$): triclinic, $P\bar{1}$, dark green, a = 13.725(3) Å, b = 18.548(4) Å, c = 12.361(2) Å, α = 90.48(2)°, β = 110.15(2)°, γ = 74.59(2)°, Z = 2, R1 = 0.0575, wR2 = 0.1077, GOF (F^2) = 1.117.

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