An Organoimido Derivative of the Hexatungstate Cluster: Preparation and Structure of $[W_6O_{18}(NAr)]^{2-}$ (Ar = 2,6-$(i\text{-}Pr)_2C_6H_3$)

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Polyoxotungstate systems occupy a prominent position in the constellation of polyoxometalate anions,[1] largely because of their utility in diverse applications.[2] A sampling of current research involving polyoxotungstate components includes their use as oxidation-resistant ligands,[3] the preparations of polyoxoanion-supported complexes and catalysts,[4−6] photo- and electroluminescence studies,[7] and evaluations of their efficacy as anti-HIV agents.[8] The development of synthetic methodologies for the preparation of functionalized polyoxotungstate systems seems therefore to hold the promise of enhancing their usefulness. One of the simplest polyoxotungstates is the octahedral hexatungstate, $[W_6O_{19}]^{2-}$, whose structure has been reported by Fuchs.[9] Given recent successes in the direct functionalization of the $[Mo_6O_{19}]^{2-}$ analogue to produce a variety of organoimido−hexamolybdate derivatives,[10] the preparation of corresponding imido−hexatungstate species was an appealing prospect. Despite several attempts utilizing a variety of imido delivery reagents, however, we (and others[10c]) have been unable thus far to prepare any imido−hexatungstate species by direct methods; we therefore sought an alternative route and now report the preparation and structure of the imido−hexatungstate system $[Bu_4N]_2[W_6O_{18}(NAr)]$, **1** (Ar = 2,6-$(i\text{-pr})_2C_6H_3$).

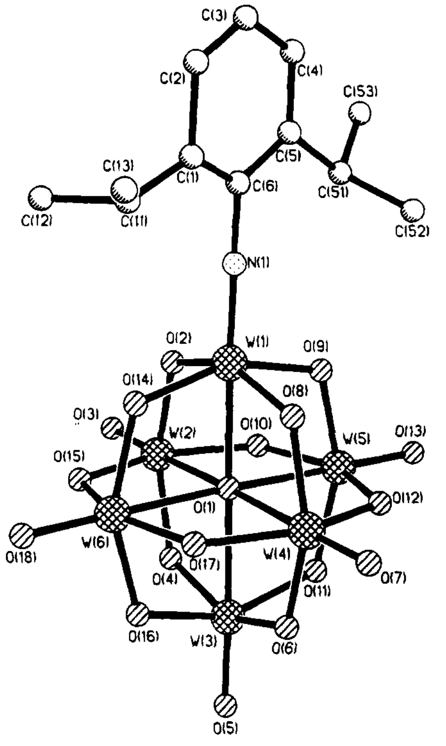
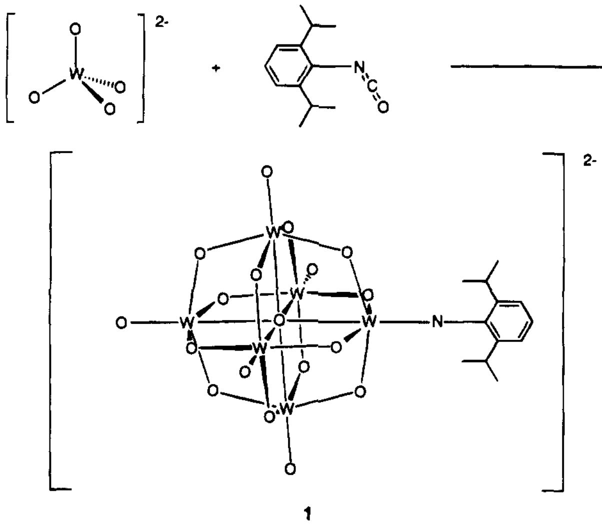


Figure 1. ORTEP representation of the anion within **1**. Selected bond lengths (Å) and angles (deg): W(1)−N(1) = 1.719(19); W(2)−O(3) = 1.681(18); W(3)−O(5) = 1.671(19); W(4)−O(7) = 1.674(19); W(5)−O(13); W(6)−O(18) = 1.723(17); W(1)−O(1) = 2.255(15); W(2)−O(1) = 2.311(15); W(3)−O(1) = 2.358(15); W(4)−O(1) = 2.342(15); W(5)−O(1) = 2.323(14); W(6)−O(1) = 2.342(14); W(1)−N(1)−C(6) = 176.7(18); N(1)−W(1)−O(1) = 177.1(7); N(1)−W(1)−O(2) = 104.4(8); N(1)−W(1)−O(8) = 102.2(8); N(1)−W(1)−O(9) = 100.0(8); N(1)−W(1)−O(14) = 105.0(8).

Following the examples of Klemperer[11] and Zubieta,[12] in which their groups demonstrated the construction of $[(L_nM)W_5O_{18}]^{x-}$ clusters in condensation reactions involving $[Bu_4N]_2[WO_4]$ and an appropriate $[L_nMX_y]$ system, we investigated the reaction of ArNCO with $[WO_4]^{2-}$. As shown in eq 1, the reaction proceeds to afford the desired product, **1**, albeit in low yield (≈10% based on $[WO_4]^{2-}$).[13] The reaction can be performed in either 1,2-dichloroethane or pyridine solvent, and **1** is obtained as yellow crystals upon recrystallization from dichloroethane/diethyl ether. The assembly of **1** clearly requires



1

(1)

a $[WO_4]^{2-}$:ArNCO ratio of 6:1, but carrying out the reaction using this stoichiometry did not improve the yield of **1** over

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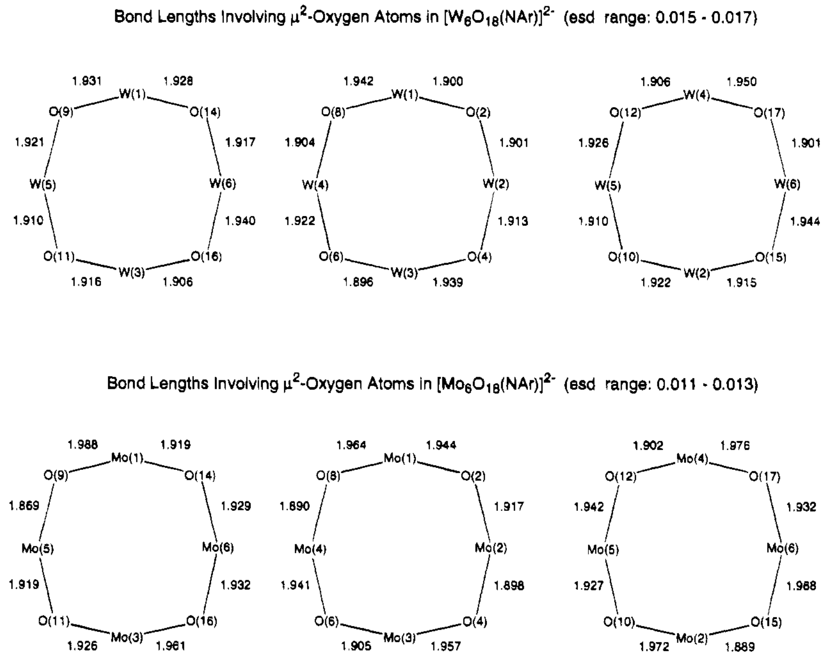
Bond Lengths Involving μ^2-Oxygen Atoms in $[W_6O_{18}(NAr)]^{2-}$ (esd range: 0.015 - 0.017)

Bond Lengths Involving μ^2-Oxygen Atoms in $[Mo_6O_{18}(NAr)]^{2-}$ (esd range: 0.011 - 0.013)

Figure 2. Comparison of bond lengths (Å) in the three equatorial belts in the structures of $[W_6O_{18}(NAr)]^{2-}$ and $[Mo_6O_{18}(NAr)]^{2-}$. The imido-bearing metal atom in each structure is M(1).

that resulting from an equimolar mixture. Likewise, the deliberate addition of H_2O to the reaction mixture did not exert a noticeable effect on the yield of **1**.[14] Although we have not detected any intermediates in the reaction sequence leading to **1**, a plausible mechanism involves the initial formation of the imido–tungstate species $[WO_3(NAr)]^{2-}$, which then aggregates with additional $[WO_4]^{2-}$ (probably with the involvement of H_2O) to yield the hexanuclear product.

The absorption spectrum of **1** in acetonitrile in the 200–600 nm region contains bands at 229 ($\epsilon = 2.91 \times 10^4$) and 292 nm ($\epsilon = 2.23 \times 10^4$), while the spectrum of $[W_6O_{19}]^{2-}$ displays bands at 209 nm ($\epsilon = 1.95 \times 10^4$) and 280 nm ($\epsilon = 1.10 \times 10^4$). For a ligand-to-metal charge transfer process, the bathochromic shift of the spectrum of **1** is the expected result of replacing an oxo ligand with the less electronegative NAr ligand.

The structure of the anionic portion of **1** is shown in Figure 1.[15] The anion features the arylimido ligand occupying a terminal site on the hexatungstate cage. The short W–N bond length (1.719(19) Å) and nearly linear W–N–C angle (176.7(18)°) are typical of W≡NR interactions in W(VI) organoimido complexes. No significant variations are discerned in the terminal W–O bond lengths, which range from 1.671(19) to 1.723(17) Å. In agreement with previous observations in related $[Mo_5O_{18}(Mo{\equiv}NR)]^{2-}$ systems ($R = p\text{-}C_6H_4CH_3$;[10a] $R = t\text{-Bu}$;[10c] $R = NMePh$[12]), the bond length from the imido-bearing W(1) atom to the central O(1) atom is somewhat shorter (2.255(15) Å) than the remaining W–O(1) interactions (2.335 Å average).

Figure 2 compares the bond lengths involving the μ_2-oxygen atoms in **1** and in its Mo homologue.[10b] Patterns of distinct irregularities are evident for $[Mo_6O_{18}(NAr)]^{2-}$; corresponding variations of smaller magnitude are perhaps suggested by the data for **1**, but the differences are within 3σ. In his comparison of the parent $[Mo_6O_{19}]^{2-}$ and $[W_6O_{19}]^{2-}$ structures, Fuchs[9] noted similar relationships.

Complex **1** can be reduced to the corresponding $[W_6O_{18}(NAr)]^{3-}$ trianion. Cyclic voltammetry in acetonitrile solution reveals a quasi-reversible wave centered at −1.30 V under conditions at which the $[Cp_2Fe]/[Cp_2Fe]^+$ couple appears at 0.238 V (vs Ag/Ag^+). The parent $[W_6O_{19}]^{2-}$ system in acetonitrile displays a corresponding reduction at −1.09 V.[16] The shift of −0.21 V in reduction potential induced by oxo/NAr susbstitution in the hexatungstate system is similar to the −0.25 V effect observed in the analogous hexamolybdate species[10b] ($E_{1/2}$ values: $[Mo_6O_{19}]^{2-}$, −0.707 V; $[Mo_6O_{18}(NAr)]^{2-}$, −0.958 V) and underscores the premise that an NAr ligand is superior to the oxo ligand as an electron donor.[17]

1 possesses good hydrolytic stability: a sample of **1** in CD_3CN treated with H_2O (1 equiv) showed no detectable decomposition as monitored by ^1H NMR spectroscopy after being maintained at 56 °C for 26 days; further addition of H_2O (10 equiv total) likewise caused no decomposition after 5 additional days at 56 °C.

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Supplementary Material Available: Text giving synthetic details and tables giving a structure determination summary, atomic coordinates, bond distances, bond angles, anisotropic thermal parameters, and hydrogen atom coordinates (12 pages). Ordering information is given on any current masthead page.

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(13) Anal. Calcd (found) for $C_{44}H_{89}N_3O_{18}W_6$: C, 25.76 (26.22); H, 4.37 (4.50); N, 2.05 (1.99). ^1H NMR (CD_3CN, 298 K, 400 MHz): δ 7.23 (d, 2 H, $C_6H_3(m)$), 6.89 (t, 1 H, $C_6H_3(p)$), 3.80 (septet, 2 H, $CH(CH_3)_2$), 3.09 (m, 16 H, NCH_2), 1.60 (m, 16 H, CH_2), 1.35 (m, 16 H, CH_2), 1.27 (d, 12 H, $CH(CH_3)_2$), 0.95 (t, 24 H, CH_3). IR (Nujol, cm^{-1}): 998 (w, sh), 976 (s), 808 (br, s).

(14) These reactions were undertaken with the consideration that a likely stoichiometry for the reaction is

$$6[Bu_4N]_2[WO_4] + ArNCO + 5H_2O \rightarrow [Bu_4N]_2[W_6O_{18}(NAr)] + CO_2 + 10[Bu_4N][OH]$$

(15) Crystal data (217 K) for **1**: orthorhombic, *Pbca*, $a = 18.429(3)$ Å, $b = 20.600(6)$ Å, $c = 31.428(6)$ Å, $V = 11931(5)$ Å^3, $Z = 8$, $\lambda = 0.710\,73$ Å, $\mu = 11.587$ mm^{-1}. A total of 9366 independent reflections were collected ($4° \le 2\theta \le 48°$), of which 4866 with $F_o > 5\sigma(F_o)$ were used in the refinement, leading to final discrepancy indices of $R = 5.65\%$ and $R_w = 7.61\%$.

(16) $[W_6O_{19}]^{2-}$ in acetonitrile was reported to display two successive one-electron reductions at −1.24 and −2.33 V vs Ag/Ag^+, but the value for the $[Cp_2Fe]/[Cp_2Fe]^+$ couple was not mentioned: Dabbabi, M.; Boyer, M.; Launay, J. P.; Jeannin, Y. *J. Electroanal. Chem. Interfacial Electrochem.* **1977**, *76*, 153.

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