Synthesis and Structural Characterization of Octanuclear Indium-Tungsten Mixed-metal Carboxylate Cluster, $Na_2[W_3InO_4(O_2CEt)_8]_2$

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The insoluble indium-tungsten chain cluster, $Na_2[W_3InO_4(O_2CEt)_8]_2$, has been prepared from the self-assembly reaction of $W(CO)_6$, $Na_2WO_4 \cdot 2H_2O$ and $InCl_3$ in propionic anhydride at 120°C. The octametallic dianion, $[W_3InO_4(O_2CEt)_8]_2^{2-}$, consists of the two incomplete cuboidal units $[W_3O_4(O_2CEt)_8]^{4-}$ which are centro-symmetrically bridged by two In^{3+}. The In^{3+} ions dissociate from the trinuclear units in aqueous acidic solution.

Heterometallic chemistry of $[M_3S_4]^{4+}$ (M = Mo, W) incomplete cuboidal cluster units has been well established in recent ten years especially in aspects of synthesis, structure and bonding.[1-5] Up to 16 heterometals have been incorporated into the units to form $[M_3M'S_4]$-type clusters of single, edge-linked or corner-shared double cube structures. The monooxo-substituted derivative, $[Mo_3S_3OInOS_3Mo_3]^{8+}$, was also reported recently.[6] All these clusters have been prepared directly from the adduction reactions of the $[M_3S_4]^{4+}$ units with metal elements or compounds. However, no similar reaction is established for $[M_3O_4]^{4+}$ to form the corresponding oxo-bridged $[M_3M'O_4]^{n+}$-type clusters.[7,8] Recently, we found that such species can be obtained from the self-assembly redox reaction system Na_2MO_4-$M(CO)_6$-$M'Cl_3$ in carboxylic anhydride solution. Several such clusters, $Na_2[M_3M'O_4(O_2CEt)_8]_2$ (M = Mo, W; M' = V,[9] Cr,[10,11] Mn,[12] Fe,[13,14] Mo,[13] Al[15]) have been prepared and characterized, thus opening the new heterometallic chemistry based on $[M_3O_4]^{4+}$ units. These species are of additional interest in that they may serve as precursors to modified molybdena (MoO_2) which is used as important heterogeneous catalyst support.[16]

Above self-assembly system has proven more effective in the case of M = Mo.[13] In fact, only Mo clusters were reported with M' being main group metals.[15] In this letter, it is shown that tungsten species of main group metals are also accessible from this system and the new In-W mixed-metal cluster, $Na_2[W_3InO_4(O_2CEt)_8]_2$(**1**) will be reported.

Complex **1** was prepared by the reaction of $Na_2WO_4 \cdot 2H_2O$ $W(CO)_6$ and $InCl_3$ in propionic anhydride at 120°C as well-formed black crystals. The yield (ca. 20%) is much lower than that of $Na_2[Mo_3AlO_4(O_2CEt)_8]_2$[15] as expected for poor reactivity of W. The crystals are stable in air and insoluble in water and organic solvents at ambient temperature. It is noteworthy that W(IV) ions produced by the redox reaction of $W(CO)_6$ and Na_2WO_4 in the presence of $InCl_3$ formed the $[W_3O_4]^{4+}$ incomplete cuboidal cluster unit, which was previously known to exist in the aqueous acidic solution,[20,21] rather than the soluble bioxo-capped $[W_3O_2(O_2CR)_6]^{2+}$ which dominate W(IV) in carboxylic anhydride.[9,17-19] This may due to the insolubility mentioned above which thermodynamically favors the formation of the octanuclear mixed-metal cluster.

Complex **1** has been characterized by X-ray crystallography.[22] Figure **1** shows the structure of the octanuclear dianion. The skeleton $[W_3O_4InInO_4W_3]^{14+}$ is illustrated in Figure **2**. The structure has crystallographically imposed C_i symmetry. As shown in Figure **2**, two W_3O_4 units are centro-symmetrically

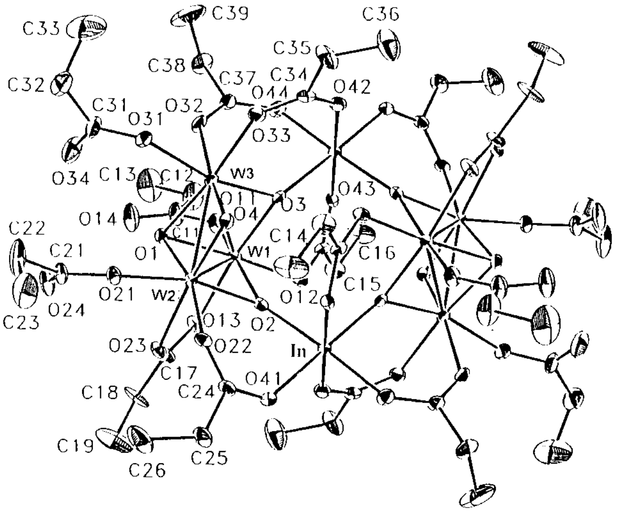

Figure 1. Structure of the octanuclear dianion$[W_3InO_4(O_2CEt)_8]_2^{2-}$. Selected bond lengths (Å) and angles (°): W1-W2, 2.5187(7), W1-W3, 2.5362(7), W2-W3, 2.5349(7), W1-O2, 1.988(8), W1-O3, 1.953(9), W2-O2, 1.973(9), W2-O4, 1.915(9), W3-O3, 1.974(10), W3-O4, 1.943(9), In-O2, 2.111(9), In-O3, 2.110(10), ∠W1-O2-W2, 79.0(3), ∠W1-O2-In, 146.3(5), ∠W2-O2-In, 131.2(4), ∠W1-O3-W3, 80.5(4), ∠W1-O3-In, 132.1(5), ∠W3-O3-In, 129.7(5), ∠W2-O4-W3, 82.1(3).

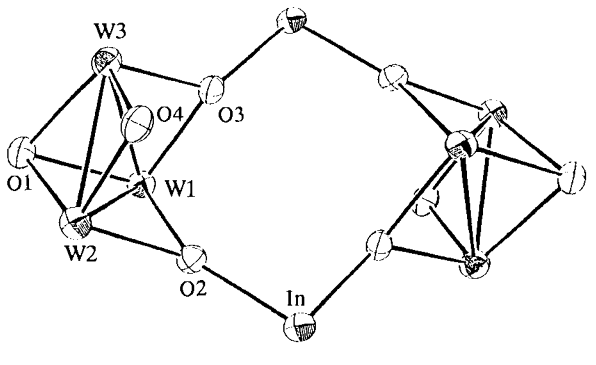

Figure 2. Structure of the skeleton, $[W_3O_4InInO_4W_3]^{14+}$.

linked by two In^{3+} ions through four In-O bonds to form a cyclic structure characteristic of $W_2In_2O_2$ eight-membered ring (deviations from the least-square plane, 0.1-0.53 Å, av. 0.3 Å). There are four near planar W_2InO triangular arrays with two types of the sum of the W-O-In angles being 359°and 346°, respectively, reminiscent of oxo-centered $M_3O(O_2CR)_6$ complexes.[23] These show that the W_3O_4 units are bound to In^{3+} by donating 2*e* of the $sp^2(p_x,p_y)$ hybridized AO's of the μ_2-O's, differing from $[M_3M'S_4]^{4+}$ cubane-type species in which M' receives 2*e* from the M-S-M 3*c*-2*e* d-p_z-d π bonds.[5] It is noteworthy that the $In(d^{10})$-μ-O bonds (av. 2.111(9) Å) are slightly shorter than the In-O (O_2CEt) (av. 2.140(10) Å), similar to the M-μ-O (M = $V(d^2)$, $Cr(d^3)$, $Mn(d^4)$, $Fe(d^5)$, $Mo(d^3)$)[9-14] but unlike the $Al(d^0)$- μ-O ones which lack d->p π interactions.[15] The W-O bonds (av. 1.972(9) Å) in the W_2InO arrays are remarkably longer than W-μ_2O bonds (av. 1.929(9) Å), as in the case of other W analogues.[9-14] The W-W bonds are not significantly different from those in $[W_3O_4]$ complexs.[20] Note that the W-In distances (ca. 3.7Å) are similar to the corresponding ones in the mixed oxo-sulfur bridged cubane-type cluster $[(H_2O)_9Mo_3S_3OInOS_3Mo_3(H_2O)_9]^{8+}$.[6] The In-O bonds are shorter than those in the latter.[6] As shown in Figure **1**, the peripheral sixteen propionato groups complete the octahedral geometry of In and W (without counting W-W bonds). As expected,[9-15] the dianion is linked by Na^+ to form an infinite chain with short Na-O bonds(av.2.30 (1) Å) which is responsible for their ready formation and insolubility as described above.

Although complex **1** is insoluble, it decomposes in aqueous acidic solution such as 2M HCl solution. Differing from solid reflectance spectrum (λ_{max} = 510 nm), the electronic spectrum of the solution shows a peak at 450nm characteristic of $[W_3O_4(H_2O)_9]^{4+}$,[20] indicating dissociation of In^{3+} from the $[W_3O_4]$ units. Similar case has also been observed for the Mo analogues.[13,15] These supports the assumption that such octanuclear dianions are formed through the combination of the trinuclear units with the heterometals. It also indicates that it is difficult or impossible to prepare such $[M_3M'O_4]$ species through the reverse reaction in aqueous acidic solution.

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References and notes

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22 Crystal Data for **1:** fw. 2675.8, $P\bar{1}$, a = 12.5747 (2), b = 12.9636(2), c = 14.1808(3) Å, α = 90.098 (1), β = 110.302 (1), γ = 117.908 (1)°, V = 1878.05 (6) $Å^3$, Z = 1, D_c = 2.37 g cm^{-3}, D_{obs} = 2.31 g cm^{-3}, R = 0.052 for 4852 reflections (I > 2 σ(I)), *Anal.* calcd. for $C_{48}H_{80}O_{40}W_6In_2Na_2$ (2675.91), C, 21.55, H, 3.01; Found, C, 21.76, H, 3.12.

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