Dimolybdenum tetraacetate:
Review of structure and synthesis

Advanced Inorganic Chemistry
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Compounds with multiple bonds are familiar species in organic chemistry. Carbon has three different bonding orders involving $\sigma$ and $\pi$ interactions. The multiple bonds generally represent an increase in stability and have an associated shortened bond length. A single bond with carbon accounts for interactions between two electrons, $\sigma^2$. A triple bond system has interactions between six electrons, $\sigma^2\pi^4$; likewise the quadruple bond contains interactions between eight electrons, $\sigma^2\pi^4\delta^2$.

T. A. Stevenson, E. Bannister, and G. Wilkinson report a series of molybdenum carboxylates reacting molybdenum hexacarbonyl with mono and di-acids in inert environments. He described the products as all being pale yellow and readily decomposing in moist air. Stevenson et al. describes a dimeric structure for the complexes and support the structure with percent composition and x-ray diffraction data. A great number of these compounds thought to be dimeric were recharacterized by Cotton and Wilkinson and found to contain metal-metal bonds.

Quadruple bonds were thought to be only theoretic anomalies until the synthesis of potassium octachlorodirhenate (III) and its characterization by F. A. Cotton in 1964. Cotton suggested that these quadruple bonds are not only possible, but commonplace between d-block elements isoelectronic to Rhenium. The bonds between the metal atoms are almost purely metal in character.

The molecular orbitals for metal-metal multiple bonds involve the $d_{xz}, d_{yz}$, and the $d_{xy}$ which transform into $A_{1g}, 2E_g$, and $B_{2g}$ in $D_{4h}$ symmetry respectively. The $A_{1g}$ forms the $\sigma$ bond. The two $E_g$ orbitals account for the four electrons involved in $\pi$ interactions, and the $B_{2g}$ molecular orbital forms the $\delta$ bond. Metal-ligand interaction
plays a large role in the charge density occupying the $\delta$-bond.

![MO for M-M bonding and Excited State]

The pale color in Dimolybdenum tetraacetate and other dimolybdenum compounds can be explained via excited state selection rules. The color arises from a $\delta \rightarrow \delta^*$ transition which is a Laporte allowed $g \rightarrow u$ excited state transition. The relative intensity of $\delta \rightarrow \delta^*$ Laporte allowed transition to a spin allowed transition is significantly lower which explains the paleness of the yellow color.

X-ray crystallographic studies done in 1976 by Cotton, et. al. show the Mo-Mo bond length ranges from 2.091Å to 2.093Å. The variability in this Mo-Mo bond length arises from variations in molecular twist. The twist coefficient equals zero when the $d_{x^2-y^2}$ nonbonding orbitals from the molybdenum atoms are aligned (fig. 2). The twist coefficient is one when they are staggered by 45°. This twist is caused by repulsion between the $d_{x^2-y^2}$ orbitals from the two molybdenum atoms. A twist coefficient of one is seen crystallographically in species such as Mo$_2$Cl$_8$ where there are no bridging ligands to hinder the rotation.
Another cause for variation in bond length come from the nature of the ligand bound to the metal. Two types of ligands can be found in inorganic complexes: pi-donor and pi-accepter. As seen in figure 1, dimolybdenum tetraacetate has four bridging acetyl ligands which are \( \pi \)-donors to the molybdenum atoms. Pi-donors increase the electron density on the metal which strengthens the relatively weak \( \delta-\delta \) bond. (See figure 2) Pi-accepter ligands can cause back-bonding and remove electron density from the metal, decreasing the effect of the \( \delta \)-bond.\(^4\) Quadruply bonded species display a lengthening of the M-M bond when pi-accepter ligands are attached.\(^1\) \( \pi \)-backbonding can completely negate the effects of the \( \delta-\delta \) bond.

Deformation density maps of \( \text{Mo}_2\text{Ac}_4 \) were generated by Hino, Saito, et. al. using x-ray wide angle data (fig. 3).\(^6\) The first map shows the electron density in the \( \text{MoO}_4 \) plane. Most of the electron density lies around the two metal atoms and in between the ligands. In the 3\(^{rd} \) map, the areas around the oxygen where lone p\(^\prime\)airs would be expected, there is an electron deficiency which is expected from a \( \pi \)-donor ligand. This density is largely around the Mo-Mo bond which can be seen in the 4\(^{th} \) map.\(^6\)

**Figure 3**

X-ray diffraction and neutron diffraction are very effective tools for characterization, but other method may be used as well. Nuclear magnetic resonance spectroscopy can be used to characterize the dimolybdenum compound. There are twelve equivalent methyl hydrogens, three on each of the acetate ligands. These hydrogens
should form a single peak around 2-3 δ ppm. Despite the simplicity of the NMR spectra, it can tell whether any solvents or impurities are left in the sample. Far-IR, FTIR, and UV-Vis can be used as well for characterization.

Molybdenum forms the highest number of compounds containing both homo and heteronuclear multiple metal-metal bonds.\(^1\) The number is in the thousands with hundreds of them being formally characterized.\(^1\) The first publication on Mo-Mo multiple bonds described dimolybdenum tetraacetate, and was introduced by G. Wilkinson, a graduate school colleague of F.A. Cotton.\(^2\) Wilkinson et al. described the synthesis of the molybdenum compound, dimolybdenum tetraacetate.\(^3\) The reaction scheme can be seen in figure 1. These compounds are remarkably air stable according to Cotton and Wilkinson. Despite the air stability and simplicity of the reaction, Wilkinson only reported ten to twenty percent yields when reacting molybdenum hexacarbonyl with glacial acetic acid or a mixture of glacial acetic acid and acetic anhydride. Increased yields were reported when using solvents alternative solvents such as CH\(_2\)Cl\(_2\).\(^1\)

\[\text{Glacial Acetic Acid} \quad \text{Heat} \quad \text{Mo}_2\text{Ac}_4\]

Figure 3

The synthesis of Mo\(_2\)Ac\(_4\) is proposed for use in advanced laboratories to help students learn challenging inorganic techniques.\(^7\) In the preparation proposed by Pense, Weisgerber, and Maounis, it was note that the compound is extremely air sensitive, requires a high reflux temperature and must also reflux for 20-24 hours.\(^7\) Also, the preparation calls for de-aired solvents and a close attention to maintaining an inert
atmosphere. This is contrary to Cotton’s assertion that the complex is extremely air stable.

**Experimental:**

The balanced reaction, \(2 \text{Mo(CO)}_6 + 4 \text{Acetic Acid} \rightarrow 1 \text{Mo}_2\text{Ac}_4 + 4 \text{H}^+\) was used to calculate grams of reagents needed. Acetic anhydride, glacial acetic acid and molybdenum hexacarbonyl were placed in a 10 ml round bottom flask and refluxed for five hours under nitrogen. The solution turned dark green.

<table>
<thead>
<tr>
<th>Compound</th>
<th>M.W.</th>
<th>M.P.</th>
<th>Added</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glacial acetic acid</td>
<td>60.05 g</td>
<td>118.1°C</td>
<td>2 ml</td>
</tr>
<tr>
<td>Acetic anhydride</td>
<td>102.1 g</td>
<td>139.9°C</td>
<td>4 mMol</td>
</tr>
<tr>
<td>Mo(CO)6</td>
<td>263.9 g</td>
<td></td>
<td>1 mMol</td>
</tr>
</tbody>
</table>

After the reflux was stopped, the solvents were removed by distillation. A simple distillation apparatus, hot plate, and sand-bath were used. The product was separated with the sand-bath at 175°C. The black, solid product was removed, and washed with CH\(_2\)Cl\(_2\) to remove any yellow dimolybdenum product. There was no color change in the CH\(_2\)Cl\(_2\). A TLC was run to see if there was any product present. It was negative for product.

A second preparation was attempted using CH\(_2\)Cl\(_2\) as a co-solvent. The reagents were doubled and 4ml of the methylene chloride were added as well. The mixture was refluxed overnight under nitrogen, 20 hours. During this time, the flow of nitrogen stopped when the tank went empty. The reaction mixture was a very dark brown color. After the reflux was stopped, the solvents were removed by distillation under vacuum using an aspirator. The separation went considerably faster under vacuum, and the temperature in the sand-bath was kept much lower than the first separation, 90°C. A water pressure problem caused the aspirator to flash back into reaction flask and flood the product which was known to be air and water sensitive. The project was abandoned.
Discussion:

Finding a preparation for this material proved to be a challenge in itself. Cotton described the preparation and the compound as being “remarkably air stable”\(^1\). Stevenson describes the same preparation but describes a different, dimerized product and makes note on the importance of an inert atmosphere.\(^3\) Pence, \textit{et. al.} describe the synthesis using de-aired solvents and a dry, inert atmosphere for the reaction.\(^7\) It is unfortunate that there is a lack of consistency in the peer reviewed texts. The last version of the preparation that was found, \textit{Synthesis of Molybdenum- Molybdenum Quadruple Bonds: A Multistep Advanced Synthesis Laboratory Experiment}, appears to be an effective synthesis. It was, unfortunately, found very late and not able to be attempted. In situ preparations were used and proved not to be effective.

The first attempt went fairly smoothly with the exception of the distillation. During the first solvent distillation, the sand-bath was left unwatched for a while, allowing the temperature to get very high, 220\(^\circ\)C. As a result, any product that was present was thermally decomposed and lost. There was only a black, crystalline mass remaining. Isolating a product would have been impossible as the product is insoluble in all solvents.\(^3\)

Several problems presented themselves in the second synthesis. A faulty primary regulator gauge gave a false reading for the N\(_2\) gas pressure at the beginning of reflux. The N\(_2\) supply ran out during the night and allowed the refluxing mixture to be exposed to oxygen and water vapor. The sand-bath temperature in the second attempt was kept low by using a vacuum to lower the vapor pressures of the solvents. The separation went well until a sudden drop in water pressure caused the aspirator to backwash into the product.
In the future, the synthesis will be attempted again using the preparation found in “Synthesis of Molybdenum-Molybdenum Quadruple Bonds: A Multistep Advanced Synthesis Laboratory Experiment”

Conclusions:

By refluxing Mo(Co)_6 under inert condition with acetic anhydride and glacial acetic acid, I came close to the published preparation. Unfortunately, I did not de-air my solvents nor was I able to maintain an inert atmosphere for the duration of the reflux. Knowing the extent of the air and moisture sensitivity would have been a tremendous help. Unfortunately, Cotton gave a false hope that the synthesis was relatively air stable and great care was not taken in removing air or moisture. I believe that the assertion that this compound is “remarkably air stable” is a geographically sensitive statement. Professor Dr. Julia Metzker, Ph. D. claimed to have no problems synthesizing dimolybdenum(II) tetraacetate in New Mexico which is an analogous environment to Cotton’s home in southern Texas where humidity is scarce.

Water and air sensitive products require skill and devotion to produce especially in the warm, humid climate of central Georgia. Several problems involving both oxygen and water were encountered while attempting to produce quadruply bonded compounds, granted one instance was not dependant on ambient conditions. Rather, it was a plumbing issue. It is crucial to ensure enough inert gas is available to carry through the long, twenty hour reflux. Running out of nitrogen was surely part of my problem during the second attempt. Also, it is important to ensure that the reagents used are, if not new, in the same condition that they were packaged. The glacial acetic acid used was, in fact, quite old and most likely had an elevated concentration of water above the .5% listed. A lack of attention on my part to reaction conditions, reagent quality, and nitrogen gas quantity are why this preparation failed.
References:


3) E.W. Abel, A. Singh and G. Wilkinson, JACS, 1959, 3097


