



# Reactions of Metal-Metal Multiply Bonded Dimers with 1,4,8,11-Tetraazacyclotetradecane

Zachary T. Daniel and David Esjornson

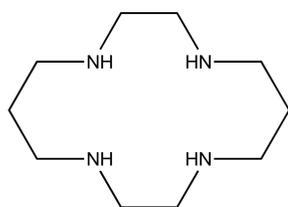
Southwestern Oklahoma State University, Weatherford, Oklahoma

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## ABSTRACT

A series of reactions between Potassium octachlorodimolybdate(II) and 1,4,8,11-Tetraazacyclotetradecane (Cyclam) and tetra-n-butyl ammonium octahalodirhenate and Cyclam were screened in order to determine the optimal conditions for the addition of Cyclam without cleavage of the dimetal unit. An extensive array of solvents have been screened in an attempt to grow crystals of sufficient quality for structural analysis. Cyclam and substituted cyclams have previously been shown to react with a variety of single metal ions. The complexes of cyclam with both the Octachlorodirhenate and the Octabromodirhenate represent the first examples of cyclam bound to metal dimers containing a metal-metal bond. These products have been characterized with Nuclear Magnetic Resonance, Electropray Mass Spectroscopy, Cyclic Voltametry, and Infrared Spectroscopy.

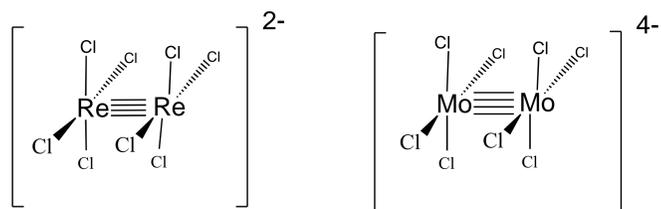
## 1,4,8,11-TETRAAZACYCLOTETRADECANE (CYCLAM)



1,4,8,11-Tetraazacyclotetradecane (Cyclam) is a macrocycle that can form coordination complexes from the four equivalent nitrogen atoms interacting with metals. (ref.1-3) Cyclam is commercially available.

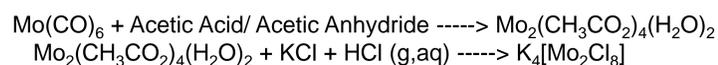
## OCTAHALODIMETALATE ANIONS

The octachloro- and octabromo- dirhenate(III,III) anions contain an  $Re_2^{6+}$  core with a  $\sigma^2\pi^4\delta^2$  electron configuration. This quadruple bond configuration leads to an eclipsed geometry from the angular dependence of the  $5d_{xy}-5d_{xy}$  interaction for the  $\delta$  component of the quadruple bond. The octachlorodimolybdate(II,II) anion has an analogous  $\sigma^2\pi^4\delta^2$  electron configuration with a  $4d_{xy}-4d_{xy}$   $\delta$  overlap (ref.4).

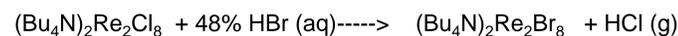
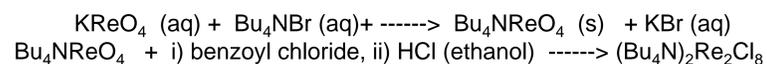


## SYNTHESIS

The Potassium octachlorodimolybdate(II,II) is prepared starting from  $Mo(CO)_6$

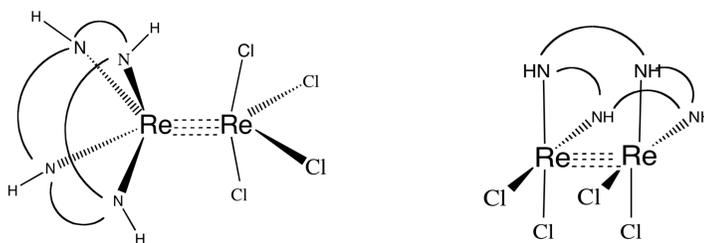


The Tetra-n-butyl ammonium octahalodirhenate(III,III) starting materials are prepared from commercially available Potassium perrhenate. (Ref.5, 6, 7)

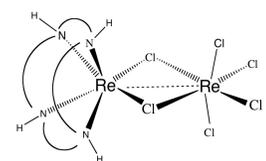


## RESULTS

The reactions between the dimetalate anions and 1,4,8,11-Tetraazacyclotetradecane (Cyclam) in acetone yields  $[Re_2(cyclam)Cl_x]$  (where  $x=4-6$ ). The retention of the dirhenium core is significant because it represents a new class of Cyclam-metal coordination complexes. Several structures are possible for Cyclam bonded to dirhenium. The Cyclam may be bound to one Rhenium, or the Cyclam may bridge the dirhenium core. (Ref. 8,9,10). The Molybdenum reactions were less successful, owing to the limited solubility of  $K_4[Mo_2Cl_8]$ .



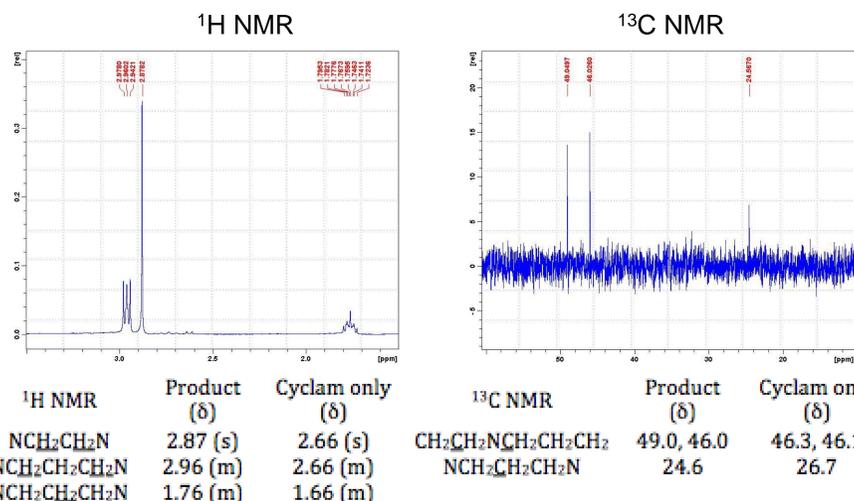
The structures above show one of the possible oxidation states for the product, namely the  $Re_2^{4+}$  core. The  $Re_2^{4+}$  complexes would have a  $\sigma^2\pi^4\delta^2$   $\delta^2$  electron configuration. The metal-metal triple bond is free to adopt either a staggered or eclipsed conformation.



Other structures and oxidation states are possible. For example, a  $Re_2^{6+}$  core with one or two bridging halides is also possible. These structures lead to a lengthening of the metal-metal bond. (Ref.8).

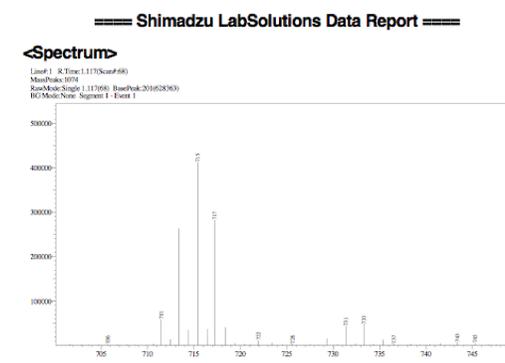
## NUCLEAR MAGNETIC RESONANCE

The  $^1H$  and  $^{13}C$  NMR (in  $D_2O$ ) of the product from  $Re_2Cl_8^{2-} + \text{Cyclam} + KPF_6$  (reflux  $CH_2Cl_2$  / 30 hours)



## MASS SPECTROMETRY

A portion of the electropray mass spectrum of the product from  $Re_2Cl_8^{2-} + \text{Cyclam} + KPF_6$  (reflux  $CH_2Cl_2$  / 30 hours)



The peaks centered around 715 M/Z are consistent with the isotope pattern for  $[Re_2Cl_4(Cyclam)]^+$ .

The lower count peaks at 733 M/Z are consistent with  $[Re_2Cl_4(Cyclam)H_2O]^+$

## CONCLUSIONS

The reactions of  $Re_2X_8^{2-}$  and Cyclam lead to new types of metal-Cyclam complexes. NMR and mass spectroscopy have identified reliable routes to these compounds and narrowed the range of possible structures. The complexes have resisted attempts to grow X-ray quality crystals. Attempts to prepare similar dimolybdenum complexes to solve these crystallization problems have run into solubility issues. Currently, work is underway to prepare more soluble salts of Octachlorodimolybdate(II,II). Cyclam is representative of a large class of nitrogen macrocycles (Ref.11), and other related macrocycles are being explored.

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