Preparation of Tetrabutylammonium Octachlorodirhenate:
A Compound With A Metal-Metal Quadruple Bond

This experiment involves the preparation of the first known stable compound with a quadruple bond. The existence of a quadruple bond in inorganic systems was first recognized in 1964 when the compound \([\text{Re}_2\text{Cl}_8]^{2–}\) was isolated. The complex was actually discovered ten years prior to this in the Soviet Union, but was mistakenly characterized as a Re(II) compound, \(\text{K}_2\text{ReCl}_4\). In a now classical paper, F. Albert Cotton correctly assigned the formula and structure as being a species containing a Re–Re quadruple bond.\(^2\) The structure is shown below, Figure 1.

![Structure of \([\text{Re}_2\text{Cl}_8]^{2–}\)](image)

Figure 1

The bonding can be explained by considering the orientation of the \(d\) orbitals. Each rhenium is slightly displaced above the center of the four chloride ions square plane. The metal \(d_{x^2-y^2}\) orbital has the appropriate symmetry to bond to the four chlorides. The \(d_{e2}\) orbitals form a \(\sigma\) orbital, the \(d_{\pi}\) and the \(d_{\pi'}\) orbitals have \(\pi\) symmetry. The two \(d_{\delta}\) orbitals are parallel to each other and form a type of bond not seen in organic chemistry; a \(\delta\) (delta) bond. The molecular orbital diagram (figure 2) is constructed by forming bonding and antibonding combinations from the orbitals of each \(\text{ReCl}_4^{2–}\) fragment. The \(\sigma\) and \(\sigma^*\) are split by more than \(\pi\) and \(\pi^*\), which in turn is split more than the \(\delta\) and \(\delta^*\). Each Re(III) center is \(d^4\) resulting in a bond order of four (8 e\(^–\) in the bonding orbitals) and hence a quadruple bond.

![Molecular orbital diagram](image)

Figure 2

The quadruple bond is quite strong, short, and stable. The bond survives through a great variety of chemical transformations. In order for overlap between the two \(d_{xy}\) orbitals to be maximized, the two \(\text{ReCl}_4\) square planes must be eclipsed. Despite the fact that this maximizes interatomic
repulsions between the chlorides, formation of the quadruple bond is the overriding factor. Perhaps the most interesting feature of this compound is the $\delta$ interaction in the quadruple bond. Because the $\delta$ orbital is only weakly bonding and the $\delta^*$ is only weakly antibonding a number of interesting chemical and spectroscopic consequences result. For example, the brilliant blue color of $[\text{Re}_2\text{Cl}_8]^{2-}$ is due to a $\delta \rightarrow \delta^*$ electronic transition. Because of the weakness of the $\delta$ bond, the gain or loss of electrons has a relatively minor effect on the strength of the M–M bond. Quadruply bonded species often have interesting electron transfer chemistry.

**Hazards**

**Benzoyl chloride**  
Harmful if inhaled, ingested or absorbed through the skin, and is a possible carcinogen. It is a lachrymator and has a disagreeable odor. It should only be used in the hood. Its boiling point is 209 °C.

**Tetrabutylammonium perrhenate(VII)**  
Rhenium compounds are known to be heavy metal poisons and should be handled with care.

**Hydrochloric acid**  
This is an extremely corrosive and toxic gas. The preparation of **HCl gas** is itself highly exothermic and potentially dangerous. Follow instructions very carefully when preparing and handling this compound.

**Procedure**

Place 100 mg of tetra-$n$-butylammonium perrhenate(VII) in a 10-mL round bottom flask with a magnetic stir bar. Assemble the apparatus as illustrated below and flush the flask with nitrogen for 3 – 5 minutes.

Under a flow of nitrogen gas, add 1.0 mL of benzoyl chloride, using a syringe and needle, through the septum. Gently reflux the mixture under N$_2$ for 90 minutes, with stirring. Remove the assembly from the heat and let the solution cool to room temperature, maintaining nitrogen flow.
While the solution is cooling, dissolve 170 mg of tetra-\textit{n}-butylammonium bromide in 2.5 mL of ethanol in a small flask. You will bubble HCl gas through this solution. Prepare the HCl gas bubbler as follows: attach a Pasteur pipette and a side arm test tube to a piece of rubber tubing. Place 1 mL of concentrated HCl in the test tube and secure it with a clamp. Insert the Pasteur pipette in the flask containing the ethanol salt solution. Using dropper inserted into a one-hole stopper that fits the side arm test tube, \textbf{carefully} add drops of H$_2$SO$_4$ to the HCl solution with the stopper in the test tube. Allow the HCl gas to bubble through the solution for 5 minutes. Immediately add the HCl saturated solution to the reaction mixture with a syringe and needle through the septum under a flow of N$_2$ gas. Stop at this point by flushing the flask with nitrogen for 5 minutes and sealing with a new septum. Keep the rest of the glassware assembly intact for use next week.

Again, reflux the mixture under a positive pressure of N$_2$ for 1 hour. After the hour, remove from the heat and reduce the volume to one half by passing a stream of nitrogen over the warm solution. Collect the resulting blue-green solid by vacuum filtration with a Hirsch funnel. Rinse the reaction flask three times with small aliquots of ethanol and use the washings to rinse the product. Rinse with ether. Maintain the vacuum to dry the solid and determine the percentage yield. Obtain an IR spectrum of the product (KBr). Analyze the spectrum with respect to the tetrabutylammonium ion (only IR active portion of the molecule). Obtain a UV/Vis spectrum in acetone and assign the $\delta \rightarrow \delta^*$ transition.

\textbf{Current Research Efforts}

Since the existence of a quadruple bond was first recognized and explained, hundreds of compounds containing such bonds have been discovered. They are formed by the elements Cr, Mo, W, Tc, and Re.$^3$

\textbf{References}

1. This experiment is adapted from:
