

Experiment II.¹

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

This experiment involves the preparation of the first 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, K_2ReCl_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 and a simplified molecular orbital diagram for this compounds are shown below, Figure 1.

Figure 1.

The bonding can most easily be explained by considering the space orientation of the d orbitals. Each rhenium is slightly displaced above the center of a square planar array of four chloride ions. The metal $d_{x^2-y^2}$ orbital has the appropriate symmetry to bond to the four chlorides. The remaining d orbitals are the d_z (a σ orbital), the d_{xz} and the d_{yz} orbital (which are of π symmetry), and the d_{xy} orbitals. The two d_{xy} orbitals are parallel to each other and form a type of bond not seen in organic chemistry called a δ (delta) bond. The molecular orbital picture shown above, is constructed by forming bonding and antibonding combinations from the frontier orbitals of each ReCl_4^- fragment. We split the σ and σ^* by more than π and π^* , which in turn is split more than the δ and δ^* . Considering that each Re(III) center has a d^4 electronic configuration we see how a bond order of four and hence a quadruple bond is predicted. The quadruple bond is quite strong, short (2.23 Å), 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 ReCl_4 two square planes must be eclipsed to each other. Despite the fact that this maximizes interatomic repulsions between the chlorides, the ability to quadruple bond is the overriding factor. Perhaps the most interesting feature of this compound is the δ interaction in the quadruple bond. Because the δ orbital is only weakly bonding and the δ^* 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 δ 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 (CAS No. 16385-59-4); Benzoyl chloride is harmful if inhaled, ingested or absorbed through the skin, and is a possible carcinogen. Since the compound has a high vapor pressure it is a lachrymator and has a disagreeable odor. It should only be used in the hood.

Tetrabutylammonium perrhenate(VII) (CAS No. 16385-59-4): No toxicity data is available for this compound, however, rhenium compounds are known to be heavy metal poisons and should be handled with care.

Tetra-*n*-butylammonium bromide (CAS No. 1643-19-2): No toxicity data is available for this compound.

Hydrochloric acid (CAS No. 7647-01-0): This 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.

Ethanol (CAS No. 64-17-5): Ethanol may be fatal if inhaled, swallowed or absorbed through the skin in large amounts. It has been shown to have effects on fertility and embryo development. The vapor and liquid are flammable. ORL-HMN LDLo: 1400 mg/kg. ORL-RAT LD50:5628 mg/kg.

Experimental Procedure.

Place 50 mg of tetra-*n*-butyl ammonium perrhenate(VII) in a side arm flask with a magnetic stir bar. Attach a condenser and evacuate and purge the flask three times with nitrogen. Under a flow of nitrogen gas quickly add 0.5 mL of benzoyl chloride down the condenser. Gently reflux the mixture for ninety minutes with stirring. The boiling point of the benzoyl chloride is ~ 209 C. While the solution is refluxing, dissolve 85 mg of tetra-*n*-butylammonium bromide in 1.3 mL of ethanol.

It is necessary to bubble HCl gas through the ethanol solution you prepared. Generally this is done with a tank of HCl gas. However, to avoid the potential danger associated with large volumes of this poisonous gas, you will prepare a small amount *in situ* and use it immediately. It is therefore necessary to wait 90 minutes and allow the benzoyl chloride solution to cool before preparing the HCl gas as follows: Attach a Pasteur pipette to ~ 5 inch piece of tygon tubing and attach the other end to a 10-mL side arm test tube or side arm flask and cap it. Place 1 mL of concentrated HCl in the side arm, secure it with a three prong clamp, and re-cap it. **Carefully** (with gloves) add a few drops of H₂SO₄ to the side-arm and recap it. Invert the Pasteur pipette in the 10-mL beaker containing the ethanol salt solution. Allow the HCl gas to bubble through the solution for a few minutes. Immediately add the HCl saturated solution to the reaction mixture with a Pasteur pipette under a flow of N₂ gas. Reflux this mixture under a positive pressure of N₂ for 1 hour.

After the hour reflux, reduce the volume to one half by passing a stream of nitrogen over the warm solution. Collect the resulting blue crystals by vacuum filtration. Rinse the reaction flask with three 0.5-mL aliquots of ethanol and use the washings to rinse the product. Follow this procedure with a 0.5-mL portion of ether. Dry the crystals on a filter paper and determine the percentage yield.

Obtain an IR spectrum of the product and compare it to the published spectrum. Obtain a UV/Vis spectrum and assign the $\delta \rightarrow \delta^*$ transition.

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 Theoretical and spectroscopic studies are ongoing⁴ and have provided a more thorough description of the bonding in these fascinating compounds. However, to date these compounds have no practical value.

References

1. This experiment is adapted from: Szafran, Z.; Pike, R.M.; Singh, M.M. "Microscale Inorganic Chemistry: A Comprehensive Laboratory Experience", **1991**, John Wiley & Sons, New York, NY, pg 235.
2. a) Cotton, F.A. *Inorg. Chem.* **1965**, *4*, 334. b) Cotton, F.A.; Robinson, W.R.; Walton, R.A.; Whyman, R. *Inorg. Chem.* **1967**, *6*, 929.
3. See for example: a) Hao, S.; Gamboratta, S.; Bensimon, C. *J. Amer. Chem. Soc.* **1992**, *114*, 3556. b) Cotton, F.A.; Eglin, J.L.; Hong, B.; James, C.A. *J. Amer. Chem.*

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