Triboluminescent Manganese Compounds
(adapted from write-up by S. Jurisson)

Introduction:

The occurrence of triboluminescence (sometimes called mechanoluminescence) has been known for centuries. Triboluminescence is the luminescence that occurs from the application of mechanical stress to crystals. Triboluminescence occurs in both organic and inorganic materials, with sucrose being a prime example of an organic material that exhibits this property.

Understanding what conditions result in triboluminescence and identifying the species that is emitting has only come to light in the last few decades. Work reported by Zink et al. in 1976 on the “Triboluminescence of Sugars” showed that the triboluminescence resulted from the excitation of trapped nitrogen gas during mechanical grinding of some sugars (D-glucose, lactose, maltose, L-rhamnose, sucrose). It is generally accepted that the excitation energy to generate the triboluminescent emission comes from very high local electric fields generated when the crystals fracture.

Cotton recently reported that the crystals that fracture must be noncentrosymmetric, so that the opposite sides of a crack can be oppositely charged. They evaluated a variety of tetrahedral manganese(II) compounds to correlate triboluminescence with their structures (centrosymmetric or noncentrosymmetric). They evaluated 11 Mn(II) compounds and found that only the six compounds that formed noncentrosymmetric crystals triboluminesce. You will be making two of the Mn(II) compounds that triboluminesce and investigating this very interesting property.

References:

Note: You will only do Parts 1 and 2.

**Part 1. Synthesis of the Triboluminescent Manganese Compounds**

[$\text{Mn(Ph}_3\text{PO)}_2\text{Cl}_2$] and [$\text{Mn(Ph}_3\text{PO)}_2\text{Br}_2$].

Half of the class will make each compound (i.e., either the chloro or the bromo analog); your TA will tell you which one you should prepare.

The triphenylphosphine oxide ($\text{Ph}_3\text{PO}$) and the manganese halide (either $\text{MnCl}_2$ or $\text{MnBr}_2$) are mixed in a 2.2:1 molar ratio in hot absolute ethanol. The triboluminescent product separates out after cooling.

**Experimental Details:**

Dissolve 0.5 grams of triphenylphosphine oxide in 5 mL of hot absolute ethanol and add this solution to the $\text{MnCl}_2 \cdot x\text{H}_2\text{O}$ or the $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$ dissolved in 5 mL of hot absolute ethanol. After about one minute, the color changes from pink to yellow. On cooling, crystals are obtained which are filtered-off, washed with cold absolute ethanol, and dried in *vacuo* (a vacuum). The compounds are slightly soluble in acetone, acetonitrile, nitrobenzene, and nitromethane. The chloro compound is pale yellow and the bromo compound is pale green.

**References:**


**Part 2. Luminescence**

The photoluminescence of the manganese compounds synthesized above can readily be observed by shining a mineral lamp or other source of UV light on them. The solid should be spread out on a watch glass or crystallizing dish and the observations made in a dimly lit or darkened room. The photoluminescence is bright green.

The triboluminescence should be observed in a darkened room for the best effect. A small amount of the solid should be placed in a dry test tube and mechanical energy be applied to the solid by using a glass rod. When the
crystals are pressed or scraped with a rod, the bright green flashes of the triboluminescence will be observed.

If the spectroscopic equipment described below is available, the student can compare the spectra of the photoluminescence and triboluminescence. (They are the same) In the absence of the equipment, the students should visually compare the colors. They will be able to observe qualitatively that the colors are the same, showing that the origin of the emitted light is the same regardless of how the material is excited. For contrast, the blue emission from Wintergreen lifesavers, which is easy to distinguish from the green of the manganese compounds, shows that different molecules (methylsalicylate) are excited.

Part 3. Spectroscopy

If any type of commercial spectroscope or spectrometer is available, the students can measure the spectra. If no commercial instrument is available, a home-built one can be constructed. A simple spectroscope that can be built by using two lenses and a prism (from the physics lab) and a microscope ocular (from the biology lab) is sketched in Figure 1. An alternative design based on a transmission diffraction grating is shown in Figure 2. The students can use the spectroscope to visually observe that the photoluminescence and triboluminescence of the manganese compounds are centered in the green region of the spectrum. For comparison purposes, day-glo orange and other dyes can be observed to show that their photoluminescence are centered in different regions of the spectrum. Many other experiments are possible. For example, the atomic line spectrum from a neon lamp or a mercury lamp can be contrasted with the broad emission spectrum from the large molecules.

References:


Reading List:

Review Articles

General Interest Article


Technical Articles


Laboratory Report:

This laboratory experiment is relatively straightforward to write-up. You are not going to perform a lot of analyses. Rather, you are going to make observations of the triboluminescent behavior of these complexes. You should look up some of the references and try to explain what triboluminescence is and what properties may make a compound exhibit triboluminescent behavior.