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# Co(acac)<sub>3</sub>: Synthesis, Reactions, and Spectra

*An experiment for general chemistry*

What constitutes a good general chemistry experiment? A good experiment keeps the student interested; it also requires that the student apply the principles of chemistry rather than just to follow directions. The experiment should amplify concepts that are presented in lecture, and the experiment should be one that can be completed successfully by most students. The last point is extremely important, because experiments that are unsuccessful make chemistry much less interesting and the incorrect results lead many students to doubt the validity of the material that they have learned in class.

We have introduced into our laboratory program an experiment which we feel achieves a number of the aforementioned objectives. It is designed to allow students to practice common laboratory techniques while furnishing a concrete experience in spectroscopy. This area of chemistry is presented in many general textbooks (1) but is rarely used by the students. The experiment is interesting because it utilizes chemicals and equipment not normally used in first year laboratories. Most importantly, the experiment is successful for most students giving them the feeling that chemistry "works."

The experiment chosen to illustrate the use of spectroscopy is the synthesis, characterization, and nitration of tris(acetylacetonato)cobalt(III), Co(acac)<sub>3</sub>. We use this compound because it is easy to prepare, easy to nitrate, and has readily apparent spectral differences between Co(acac)<sub>3</sub> and its nitrated cogen. Not only is the experiment an introduction to spectroscopic techniques, but also it allows the students to gain experience in common laboratory practices such as vacuum filtration, recrystallization, and melting point determination. In a sense, the experiment resembles a mini research project because the students are required to show, by spectroscopic means, that nitration has occurred. They are asked also to describe the position where the nitro group has become attached to the complex. We feel that this experience enhances the students' understanding of spectroscopy and its relation to molecular structure; furthermore, it prepares the class for the extensive use they will make of spectroscopy in organic chemistry. An additional benefit is gained from the emphasis on spectroscopy: student interest. The enthusiasm many students expressed during the experiment can probably be attributed to their use of rather unusual instrumentation for a freshman laboratory. Many students may have carried out titrations in high school and therefore may find such experiments uninteresting in college; however, none of our students have used either an infrared or NMR spectrometer before and they are very enthusiastic when they learn these new techniques.

The experiment, scheduled for three 3-hr laboratory periods is not difficult to perform. Usually Co(acac)<sub>3</sub> is prepared the first week; the nitrated product is synthesized the second week; and the third week (and any free time) is used to obtain good spectra. Thirty minutes of each laboratory is devoted to a brief discussion of spectroscopy in which only fundamental ideas are presented. For infrared, Hooke's Law and the group vibration concept are discussed; the latter is demonstrated by presenting overhead projections of typical spectra. NMR is developed at its most basic level and without the complications of spin coupling. This demonstration is possible because no spin coupling is observed in these compounds. Visible

spectra are interpreted by using the Crystal Field Theory which is the model that is taught in the lecture. Salient features of each branch of spectroscopy are also presented in the laboratory handout.

During the laboratory, the instructor demonstrates the preparation of samples for spectral analysis. The instructor also discusses proper use of the spectrometers (Perkin Elmer 727 and Beckman DB) to small groups of students. General chemistry students are not allowed to operate the NMR spectrometer because of the difficulty in tuning the device. However, they do prepare their own samples and then ask an upperclass student to obtain spectra of their compounds. This system works quite well because it introduces the newer students to the juniors and seniors and also allows the experienced, upperclass students the opportunity to teach some of the chemistry they have learned.

All the students were able to prepare the complex in good yield (60–85%, mean: 76%). Melting points ranged from 206° to 214° C (literature value is 213° C), but all compounds melted in a small range of 2 or 3° C. The nitrated complex was also synthesized in good yield (40–70%, mean: 60%), and the melting points were in agreement with the literature value of 198° C.

The main purpose of the experiment is to analyze the products of the reaction using spectroscopy and therefore determine where nitration has occurred. The class was not told how to solve this problem, but all were able to do so by using

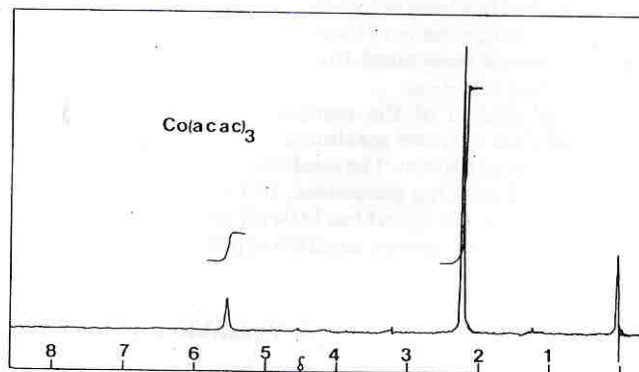


Figure 1. Student NMR of Co(acac)<sub>3</sub>.

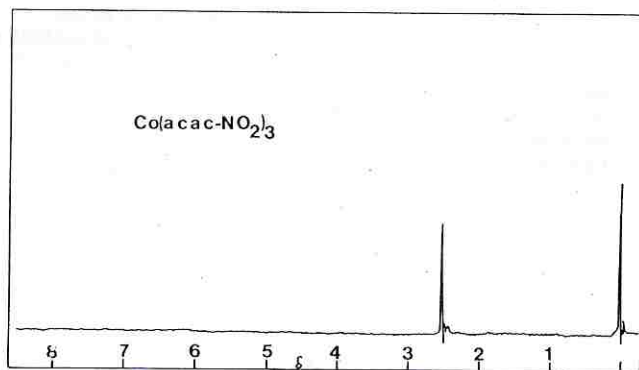


Figure 2. Student NMR of Nitrated Product.

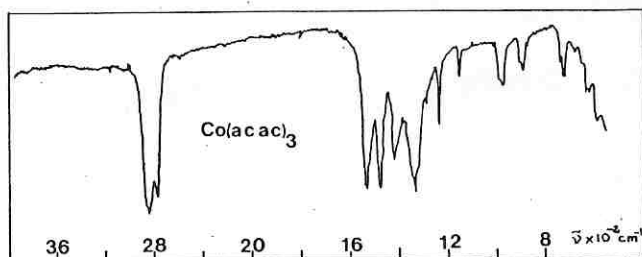


Figure 3. Infrared Spectrum of  $\text{Co}(\text{acac})_3$ .

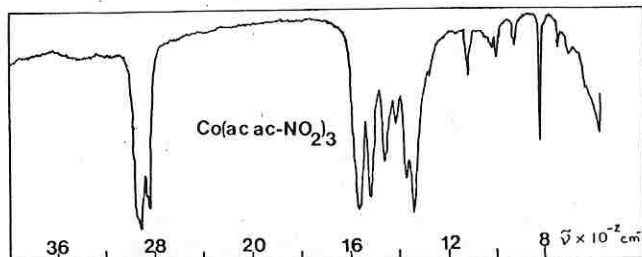


Figure 4. Infrared Spectrum of Nitrated Product.

proton NMR. Typical student spectra are shown in Figures 1 and 2. Students were able to identify the absorbances at 2.2 and 5.6 ppm as the methyl and  $\gamma$  hydrogen resonances, respectively. The integrated intensities of these peaks are in the required 6:1 ratio. Since the peak at 5.6 ppm is not present in the nitrated product, the students correctly stated that substitution occurs at the  $\gamma$  position.

Interpretation of the infrared spectra (Figs. 3 and 4) was far more difficult. The band at  $1580\text{ cm}^{-1}$  in  $\text{Co}(\text{acac})_3$  was identified as a carbonyl stretch by 80% of the class, and the prominent band at  $825\text{ cm}^{-1}$  in the spectrum of the nitrated product was correctly assigned to the nitro moiety by all but one student. Although many attempts were made to decipher the rest of the spectra, few were successful in providing the correct assignments for all the bands. The correct assignment of the entire spectra was not required, of course, but it was encouraging to see many of the students attempt to solve a problem that has been debated in the literature for some time (2). Even though many of these spectra were left unassigned, most students recognized the significant changes that occurred upon nitration.

Visible spectra of the compounds were also recorded.  $\text{Co}(\text{acac})_3$  has only one maximum in the region 350–750 nm, and it occurs at 600 nm. The students are able to calculate the crystal field splitting parameter,  $10\text{ Dq}$ , and they note that substitution on the ligand has little effect on  $10\text{ Dq}$ . This part of the experiment gives a concrete experience in a topic that

is sometimes not emphasized enough in lectures.

A number of modifications to this experiment are possible.  $\text{Co}(\text{acac})_3$  can be brominated (3) instead of, or in addition to, being nitrated; the brominated product has only one band in the  $1600\text{--}1500\text{ cm}^{-1}$  region, while the nitrated product has two bands in this region. By comparing the three spectra, students should be able to deduce that the band at  $1520\text{ cm}^{-1}$  in the nitrated product is due to the nitro group. Also,  $\text{Cr}(\text{acac})_3$  is easily prepared (4) and nitrated. The cobalt and chromium complexes could be compared with respect to visible spectra and magnetic properties. Also the chromium content of the complex can be determined spectrophotometrically as chromate ion.

### Experimental

$\text{Co}(\text{acac})_3$  is prepared by the method of Bryant and Fernelius (5) with minor changes. A mixture of 2.5 g  $\text{CoCO}_3$  (Alfa Inorganics) and 20 ml of acetylacetone (Aldrich) is heated with a steam bath to approximately  $85^\circ\text{C}$ . When 30 ml of 10%  $\text{H}_2\text{O}_2$  is added dropwise to the mixture it becomes green in color. When effervescence ceases, the reaction is complete. The flask is chilled in an ice-salt bath and is vacuum filtered. The product is then washed with cold ethanol and dried at  $110^\circ\text{C}$  for 15 min. Dissolve the  $\text{Co}(\text{acac})_3$  in boiling toluene (50 ml), filter if necessary, then add about 70 ml of heptane and cool in an ice bath to precipitate the product. Filter the sample, air dry for a few minutes, then dry in a  $110^\circ\text{C}$  oven. Yield is approximately 6 g.

The complex was nitrated by two methods (6, 7) to compare the techniques. No significant differences were observed; therefore, the method that appeared in *this Journal* (7) is now used. It is repeated here for completeness.

Copper nitrate trihydrate (2.6 g) is crushed and added to 40 ml of acetic anhydride in a dry flask.  $\text{Co}(\text{acac})_3$  (1.0 g) is then added to the mixture; the flask is stoppered and the mixture is stirred vigorously at room temperature for 30 min. The mixture is poured into a beaker containing 120 ml of water, sodium acetate (3 g), and 120 g of ice. It is stirred vigorously. Then the product usually separates as an oil (green in the cobalt complex, red for chromium). To solidify the oil, add ethanol and stir vigorously. Then the product can be filtered, washed with 5 ml of ethanol, and recrystallized from methylene chloride-ethanol. Yield is about 0.6 g of product.

Infrared spectra are run as Nujol mulls, and NMR samples are dissolved in deuterated chloroform. Visible spectra are recorded as toluene solutions.

### Literature Cited

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- (2) Nakamoto, K., "Infrared and Raman Spectra of Inorganic and Coordination Compounds," 3rd Ed., Wiley, New York, 1978.
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## A Versatile and Inexpensive Pipet Bulb

Students experience more difficulty and frustration in attempting to use a volumetric pipet properly than any other piece of basic laboratory apparatus. Much of the difficulty stems from problems involved with the use of the simple rubber suction bulb to fill the pipet. For the student, it is a challenge to attach and remove the rubber bulb from the pipet in the process of delivering the calibrated volume. In recent years several modifications have been suggested<sup>1</sup>; however, the following is simple and works well.

About a year ago, in attempting to adapt a 2-oz rubber bulb with a standard bore to fill a 1-ml volumetric pipet with a much smaller outside diameter, an Eppendorf pipet tip<sup>2</sup> was inserted and fixed in the open end of the rubber bulb. This modification worked well for the 1-ml pipet and proved useful for all pipets ranging in volume from 1 to 50 ml. The tapered tip fits the open end of the pipet making a sufficiently tight seal to draw liquid into the pipet and fill it, and pulling and twisting is unnecessary to remove the bulb, simply lift the bulb out and away. At Rhode Island College the use of these tips has resulted in a significant improvement in pipetting technique and reduction in breakage and injury from broken pipets.

<sup>1</sup> Harris, W. E. and Kratochvil, B., *J. CHEM. EDUC.* 53, 253 (1976); Hanson, R. H., *J. CHEM. EDUC.* 54, 434 (1977); Hickling, G. G., *J. CHEM. EDUC.* 55, 541 (1979); Van Atta, R. E. and Kamback, D. O., *J. CHEM. EDUC.* 56, 756 (1979).

<sup>2</sup> Brinkman Instruments Inc., Cat. No. 22-35-130-3: disposable polypropylene tips for sampling with 1 to 100  $\mu\text{l}$  pipets.

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