

Synthesis and Characterization of two inorganic complexes, Cu(acac)₂ and VO(acac)₂

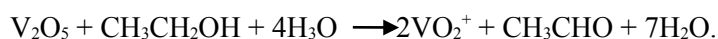
This laboratory exercise involves synthesis of two inorganic complexes, Cu(acac)₂ and VO(acac)₂, and to subsequently measure their isotropic EPR spectra. In addition, these complexes have a well-defined spectral structure, which the students must assign by consideration of the molecule's spin sublevels.

Preparation of Bis-[(acetylacetonato)copper(II)]

First, they dissolve 5.0 grams of Cu(NO₃)₂ · 3H₂O, or an equivalent molar amount of CuSO₄ · 2H₂O, in 100 mL of distilled water in a 250 mL Erlenmeyer flask. To this solution they add 7.5 mL of concentrated ammonium hydroxide. This process should form the [Cu(NH₃)₄]²⁺ complex. Next add 5.5 mL of acetylacetone (2,4- pentanedione or Hacac) in a dropwise manner while stirring the solution. A pale blue precipitate, which is the desired product, forms. They filter the precipitate and wash it with small volumes of ice-cold water, followed by ice-cold 95% ethanol. Finally, they dry the precipitate by placing it in a vacuum desiccator.

Preparation of [Bis-[(acetylacetonato) oxovanadium (IV)]

This procedure is a modification of a published one [5]. First, combine 3.0 g of V₂O₅ with 8 mL of H₂O and 6 mL of concentrated (18M) H₂SO₄ in a 250 mL Erlenmeyer flask. This solution is very acidic and the students should be warned to be careful. Next, add 15 mL of 95% ethanol and heat the solution on a hot plate for an hour, with occasional swirling. During this time the temperature of the mixture should be *ca* 80 °C. In this reaction, the alcohol serves as a reducing agent, acting approximately by the equation



After an hour, they filter the sample through filter paper to remove any unreacted V₂O₅ and collect the filtrate (which is still very acidic) in a 600 mL beaker. Next, they add 8 mL of acetylacetone to this solution and proceed to neutralize it by slowly adding a saturated solution of Na₂CO₃ (sodium carbonate). During this time, they stir the sample using a magnetic stirrer. A blue-green VO(acac)₂ product begins to precipitate at a pH near 3.5. They filter off the VO(acac)₂ precipitate and wash it sparingly with ice-cold water followed by cold 95% ethanol. Finally, they dry the sample in a vacuum desiccator.

EPR Sample Preparation and Measurement

The students dissolve their samples in a solvent that is 40% chloroform (CHCl_3): 60% toluene, by volume. The concentration of $\text{VO}(\text{acac})_2$, or $\text{Cu}(\text{acac})_2$, should be 10^{-3}M to 10^{-2}M . They then pipette a small amount of the solution(s) into an EPR tube(s).

The students then use an EPR spectrometer to measure the spectrum of the complexes. The spectral features have to be interpreted.

