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-[(acetylacetanato)copper(II)]

First, they dissolve 5.0 grams of $Cu(NO_3)_2 .3H_2O$, or an equivalent molar amount of $CuSO_4 .2H_2O$, 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 $[Cu(NH_3)_4]^{2+}$ 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 V_2O_5 with 8 mL of H_2O and 6 mL of concentrated (18M) H_2SO_4 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 ©. In this reaction, the alcohol serves as a reducing agent, acting approximately by the equation

$$V_2O_5 + CH_3CH_2OH + 4H_3O \longrightarrow 2VO_2^+ + CH_3CHO + 7H_2O.$$

After an hour, they filter the sample through filter paper to remove any unreacted V_2O_5 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 Na_2CO_3 (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 $VO(acac)_2$, or $Cu(acac)_2$, 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.