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Synthesis and Characterization of Tris(diethyldithiocarbamato) cobalt(III) as an Undergraduate Inorganic Laboratory

C. T. Eagle,* D. G. Farrar, G. N. Holder, D. M. Gooden, A. B. Goodman, and S. W. Wyatt

Department of Chemistry, Appalachian State University, Boone, NC 28608, eaglect@appstate.edu

Abstract: The synthesis of tris(diethyldithiocarbamato) cobalt(III) by the reaction of sodium diethyldithiocarbamate and cobaltous chloride is described. The recovered crystals of the cobalt complex are characterized by magnetic susceptibility, IR and NMR spectroscopy, and cyclic voltammetry.

Introduction

It can be quite challenging to arrive at an inorganic synthetic procedure that is accessible to the skills of junior-level inorganic students and yet provides fundamental instruction in instrumental methodology as well. Typical examples involving ferrocene or simple metal–ammine complexes give the visual stimulation so important to student engagement, yet the spectroscopic and/or voltammetric behavior of these compounds is so predictably prosaic as to offer little more than training exercises in instrumental usage. What is needed to pique undergraduate interest is a synthesis designed to be straightforward enough to complete within a scheduled lab period and obtainable in reasonably purity and yield, and provide some instructive surprises with respect to both the reaction itself and compound characterization.

In order to satisfy these criteria, we have developed a two-part laboratory experiment to synthesize and characterize $Co[S_2CN(C_2H_5)_2]_3$ from readily obtainable and inexpensive starting materials of low-toxicity. The purity of the recrystallized product can be determined by magnetic susceptibility, while structural characteristics of the complex can be verified by IR and ^1H NMR spectroscopy. Cyclic voltammetry can be used to determine the electron-transfer behavior of the purified compound.

Dithiocarbamates and their derivatives are well-known substances [1], and typically syntheses of formulations with various metals are straightforward [2]. Dithiocarbamates have been exploited in rubber chemistry, inorganic analysis, and biochemistry. The wide variety of applications is largely due to the diversity of metal dithiocarbamate complexes that form. Dithiocarbamate compounds have been employed as inhibitors in research on enzymes. A famous dithiocarbamate complex, tetraethylthiuram disulfide (Antabuse) blocks the action of alcohol dehydrogenase and is used in the treatment of chronic alcoholism [3]. Recently, dithiocarbamates have been utilized as nonchromophoric chelating ligands to tune sensitizer absorption properties in pursuit of compounds useful in light-to-electrical energy conversion [4].

Experimental

Materials. The hydrated sodium salt of diethyldithiocarbamate, 30% hydrogen peroxide solution, $CDCl_3$ (99.8 atom % D), acetone-d_6 (99.9 atom % D), 1,2-dichloroethane (HPLC grade), tetra-*n*-butylammonium bromide, and potassium hexafluorophosphate were obtained from Aldrich Chemical Company. Dichloromethane (Mallinckrodt AR grade), KBr (infrared grade), and ethanol (95%) were obtained from VWR. All materials were used as received without further purification.

Safety Precautions and Waste Considerations. Chlorinated hydrocarbons are suspected carcinogens, and therefore were handled in a well-ventilated area while wearing gloves. The hydrogen peroxide solution (30%) can cause burns, and thus gloves were worn while handling it. All waste from this laboratory experiment was placed in a waste bottle labeled with the identity of its contents and disposed of by our waste management company, Laidlaw Safety Kleen.

Synthesis. Dissolve, with warming, 1.5 g $NaS_2CN(C_2H_5)_2$ in 10 mL of distilled water. The resulting solution is pale yellow. In another beaker, dissolve 0.500 g of cobalt(II) chloride hydrate (*toxic, irritant*) in 10 mL of distilled water; the resulting solution will be red. Add the $NaS_2CN(C_2H_5)_2$ solution to the cobalt(II) chloride solution with stirring; a thick green precipitate will form. Add 5 mL of 30% hydrogen peroxide and stir for 5 minutes. No visible change will be detected. Collect the green, air-stable complex by vacuum filtration, wash twice with distilled water (2 × 5–10 mL), and three times with ethanol (3 × 5 mL). The product, $Co[S_2CN(C_2H_5)_2]_3$, can be dried on the filtration apparatus for 15 minutes or dried in vacuo [5].

Recrystallization. Recrystallize 0.5 g of the crude $Co[S_2CN(C_2H_5)_2]_3$ for characterization purposes. Dissolve the crude product in a minimum amount of hot dichloromethane, filter, then heat the filtrate and add just enough ethanol to cause the solution to become cloudy. Cool the mixture in an ice bath and filter to recover dark green, air-stable crystals. Although exact amounts of the solvents needed vary (due largely to the dryness of the sample), typical amounts are 7 mL of dichloromethane and 5 mL of ethanol. The yield of the recrystallization is typically 30%.

Characterization

Measurements. Magnetic susceptibility measurements were performed with a Johnson Matthey Magnetic Susceptibility Balance, Type MSB.

Infrared spectra were recorded on a Nicolet Magna-IR 550 FT infrared spectrometer using a deuterated triglycine sulfate (DTGS) detector. Spectra were obtained from the DRIFT sampling technique. The resolution was set at 4 cm^{-1} and 4–16 transients were taken. Typically, 1–5% by mass of the sample was ground with KBr.

NMR spectra were recorded on a 300-MHz Varian Gemini 2000 spectrometer. Typically, 10 mg of sample were dissolved in approximately 0.75 mL solvent (acetone-d_6 for $NaS_2CN(C_2H_5)_2$ and $CDCl_3$ for $Co[S_2CN(C_2H_5)_2]_3$). Either TMS or residual protiosolvent was used as the reference. Typically, 16 transients were taken.

Cyclic voltammograms were collected on a Bioanalytical Systems, Inc., (BAS) Model 100B/W electrochemical workstation. A platinum or glassy carbon disk (BAS) served as the working electrode, a Pt coil functioned as the auxiliary electrode. The reference was a saturated

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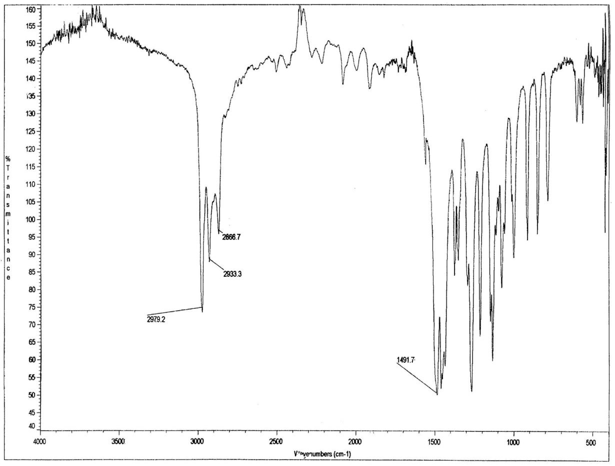

Figure 1. Infrared spectrum of $CO(S_2CN(C_2H_5)_2)_3$. Thioureide ion band at 1492cm^{-1} is marked. Also marked are the sp^3-hybridized C–H stretches at 2979, 2933, and 2867 cm^{-1}.

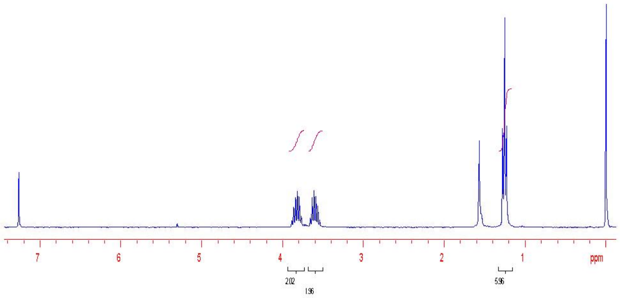

Figure 2. ^{1}H NMR ($CDCl_3$) spectrum of $CO(S_2CN(C_2H_5)_2)_3$, showing multiplets at 3.83 ppm (centroid) and 3.60 ppm (centroid) arising from magnetically nonequivalent methylene protons.

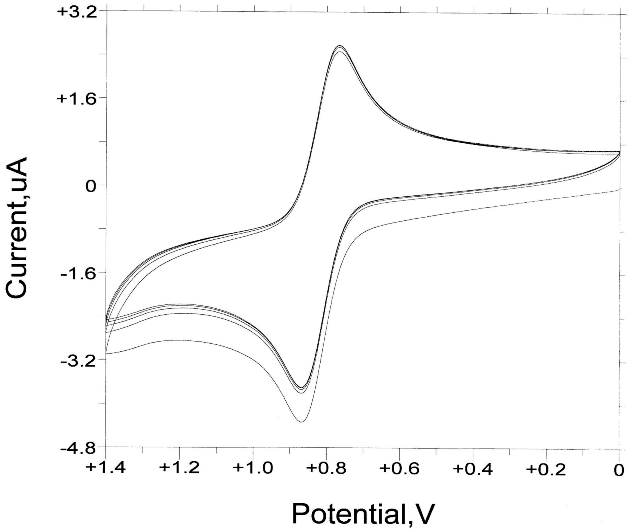

Figure 3. Cyclic voltammogram (0.200 V s^{-1}) of $CO[S_2CN(C_2H_5)_2]_3$ in 1,2-dichloromethane/0.1 M $[(C_4H_9)_4N][PF_6]$.

calomel electrode. Potentials were not corrected for liquid junction, but were calibrated daily against an internal reference (ferrocene). Voltammograms were obtained under a blanket of N_2. This, however, is unnecessary as exposure to air does not degrade the electrochemical response.

Magnetic Susceptibility. Tris(diethyldithiocarbamato)cobalt(III) is a diamagnetic complex exhibiting octahedral geometry and approximate D_3 symmetry [6]. As its melting point cannot be used to establish purity due to complex decomposition, characterization should include magnetic susceptibility. The presence of any paramagnetic impurities (such as Co^{2+}) will cause μ_{eff} to be > 0. This measurement can be done quantitatively or qualitatively quite easily using a magnetic susceptibility balance. We used this technique qualitatively on both the crude and the purified product to demonstrate effective purification by recrystallization.

Infrared Spectroscopy. The diethyldithiocarbamate ligands chelate through the two sulfur atoms; this endows the carbon–nitrogen bond with significant double-bond character that appears at a characteristic frequency, aiding in identification. This strong absorption band (1542–1480 cm^{-1}) is known as the thioureide ion band (Figure 1) [7]. A strong absorption in this region of the spectrum gives a good indication that the cobalt complex has been satisfactorily prepared. In addition to the thioureide ion band, the usual bands for sp^3-hybridized carbon–hydrogen stretches are observed (3000–2840 cm^{-1}), which are very similar to those the sodium salt of diethyldithiocarbamate [8] and thus the thioureide band is more diagnostic for characterization.

Nuclear Magnetic Resonance Spectroscopy. NMR spectra (^{1}H) taken in $CDCl_3$ (Figure 2) show ligand methyl protons as a triplet at 1.25 ppm. Ligand methylene protons appear as two multiplets centered at 3.60 ppm and 3.83 ppm. The integration pattern for the three signals is 3:1:1. This should be a surprise to students, and present a moderate challenge in explanation, as the spectrum of the sodium diethyldithiocarbamate exhibits a single resonance for the two methylene protons, giving the familiar triplet-and-quartet pattern with integrations of 3:2 that one expects from an ethyl group. Furthermore, there is no immediately obvious reason for the complexed ligand to behave differently. Careful inspection of the cobalt complex using simple molecular modeling software (or a model kit) should demonstrate that the two geminal methylene protons are diastereotopic (and thus magnetically nonequivalent). This gives rise to a separate signal for each of the methylene protons. The splitting pattern is a consequence of an incompletely resolved doublet (geminal AB coupling, H_A—C—H_B) of quartets (vicinal AX coupling, H_A—C—C—H_{3_X}). This has been observed for several *N,N*-dialkyldithiocarbamate complexes of cobalt [6]. The other peaks in the spectrum are TMS (0 ppm), H_2O (1.55 ppm), and $CHCl_3$ (7.26 ppm).

Cyclic Voltammetry. Tetra-*n*-butylammoniumhexafluorophosphate was prepared from tetra-*n*-butylammonium bromide and potassium hexafluorophospate. The supporting electrolyte was then washed with water to remove all traces of bromide, dried in vacuo, and kept in an oven at 110 °C prior to use. The anodic behavior of the cobalt complex was observed in 1,2-dichloroethane with 0.1 M tetra-*n*-butylammoniumhexafluorophosphate as supporting electrolyte (Figure 3). Within the solvent window, one oxidation was observed with a half-wave potential ($E_{1/2}$) of 819 mV. Both anodic and cathodic waves move symmetrically with the scan rate; that is, the value of $E_{1/2}$ does not change. Scan rates were varied from 50 to 500 mV/s. Diagnostic criteria applied to this wave (see Figure 3) as part of a scan-rate dependence study are: peak ratio ($i_{p,c}/i_{p,a}$) for the oxidation is unity and is invariant with scan rate, peak separation (ΔE_p) increases with increasing scan rate (from 100 mV at 50 mV/s to 157 mV at 500 mV/s), and current function ($i_p \cdot$(scan rate)$^{-0.5}$) remains steady with increasing scan rate. All these criteria are indicative of a quasi-reversible electron transfer, i.e., one characterized by moderately sluggish electron-transfer kinetics according to the definition of Matsuda and Ayabe [9]. No processes indicative of complex dissociation following electron transfer are evident.

Conclusions

What makes this an appropriate laboratory experiment? The synthesis is safe, easy, and inexpensive. The yields (95% crude, 30% purified) are good and provide more than enough material for adequate characterization. It can easily be completed in two 3-h laboratory periods, and it gives students an opportunity to work with various methods of instrumental analysis. The complex has no special handling needs above and beyond the cautions that should be afforded all compounds as a matter of safe routine, and the product obtained is air-stable. The major impurity in the crude product is paramagnetic (most likely a Co^{2+} complex), and thus magnetic susceptibility can be used to quickly determine the success of one's recrystallization technique. Infrared spectroscopy can be used in a manner that is not usual for the inorganic laboratory, that is, to give a clear and definitive indication of complex formation through the presence of the thioureide band. The ^1H NMR spectrum is unexpectedly nontrivial. This presents a reasoning challenge, putting into application material learned from symmetry and structure lectures. The simple complex is an excellent example of the effect of molecular symmetry on spectral appearance; those who deduce the diastereotopic nature of the methylene protons are imbued with a deeper understanding of the NMR technique. The cyclic voltammetry experiment is instructive without being overly difficult; there are opportunities to deduce an electron-transfer mechanism from diagnostic criteria without the characteristic complexities (especially specific adsorption) observed in many other formulations of diethyldithiocarbamates [10]. The time-domain dependence of the electron-transfer mechanism offers more intellectual challenge to the student than an obvious reversible case; ferrocene is the usual substrate for such an exercise.

In summation, we believe this experiment represents a worthwhile and rewarding expansion of the traditional junior–senior level inorganic laboratory into the realm of instrumental analysis.

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