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Synthesis of bis(diethyldithiocarbamato)manganese(II) and tris(diethyldithiocarbamato)manganese(III)

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Abstract: An ideal undergraduate introduction to the challenges of synthesis and characterization of air-sensitive compounds is accomplished in the preparation of bis(diethyldithiocarbamato)manganese(II). This economical experiment employs a glovebag, low-cost and low-toxicity chemicals, and is completed in one undergraduate laboratory period. For comparison purposes, the synthesis and characterization of air-stable tris(diethyldithiocarbamato)manganese(III) is also described.

Introduction

Teaching students inert-atmosphere techniques for inorganic synthesis is important because these skills are necessary for success in graduate school and beyond; however, it is difficult to find inorganic syntheses that are (1) low-cost; (2) use low-toxicity chemicals and (3) can be completed in a three-to-four-hour laboratory period. In two well-known inorganic laboratory manuals, *The Synthesis and Characterization of Inorganic Compounds* [1] and *Synthesis and Technique in Inorganic Chemistry* [2], the majority of the inert atmosphere syntheses presented require costly Schlenk glassware or a glovebox, highly toxic chemicals, and long laboratory periods making them unsuitable as undergraduate laboratory experiments at most institutions. This laboratory experiment offers a solution to this pedagogical problem. The synthesis and characterization of bis(diethyldithiocarbamoto)-manganese(II) is low-cost, uses low-toxicity chemicals, and can be completed in one laboratory period.

Experimental

Materials. Sodium diethyldithiocarbamate hydrate (NaDTC), 1,2-dichloroethane (HPLC grade), tetra-*N*-butylammoniumhexafluorophosphate, lithium perchlorate, and a small glove bag (Cat# 211, 283-6) were obtained from Aldrich Chemical Company. Manganese(II) chloride tetrahydrate ($MnCl_2•4H_2O$), KBr (infrared grade), acetonitrile, and methanol (ACS, anhydrous) were obtained from Van Waters & Rogers. Nitrogen gas (99.99% pure) was used as supplied from National Welders.

Safety Precautions and Waste Considerations. Chlorinated hydrocarbons are suspected carcinogens; therefore, they were handled in a well-ventilated area while wearing gloves. All waste from this laboratory experiment was placed in a properly labeled waste bottle and disposed of by our waste management company, Laidlaw Safety Kleen, Inc.

Synthesis. Bis(diethyldithiocarbamato)manganese(II), $Mn(DTC)_2$. In separate beakers, 4.18 g of NaDTC and 1.9 g of $MnCl_2•4H_2O$ are dissolved in 10 mL of methanol. Each solution is stirred while the other materials are collected for the experiment. The NaDTC solution is heated to aid dissolution. Reagent solutions are poured into sample vials, labeled, and capped tightly. No vial should be more than half full.

Preparing the nitrogen environment carefully is crucial to a successful synthesis. The following are placed inside the glove bag:

2 vials of methanol (15mL each)
vial of $MnCl_2•4H_2O$ solution
vial of NaDTC solution
2 empty vials, weighed
150-mL beaker
250-mL beaker
stemless glass funnel
fluted filter paper
spatula
10 disposable glass pipets
scupula
magnetic susceptibility tube (preweighed)
watchglass
latex gloves [3]

A rubber hose is used to connect the nitrogen line to the gas inlet of the glove bag; a disposable pipet is fitted to the terminus inside the glove bag. The gas outlet of the glove bag is fitted with a similar rubber hose that is connected to an oil bubbler [4]. While no work is being done in the glove bag, a rate of 100 bubbles of nitrogen per min should be maintained.

The atmosphere in the bag is purged by filling it with nitrogen gas and then deflating it by pushing on the exterior of the glove bag until virtually all the nitrogen is squeezed out. The bag is then refilled with nitrogen until it reaches the desired oil-bubbler rate, and then, it is purged once more.

Three equipment purge cycles are then performed. Each cycle consists of (1) blowing nitrogen all around the glassware and equipment (this requires moving items to get above and below the surface) and (2) purging all solutions and solvents for 2 min each by bubbling nitrogen through each solution for 2 min to displace dissolved air. A different pipet must be used for each reagent; Thus, one pipet is used to blow nitrogen gas around the glassware (and all equipment), to outgas the methanol, and to outgas the $MnCl_2·4H_2O$ solution. Then the pipet is replaced with a clean one and the Na(DTC) solution is outgassed. Finally, the atmosphere in the glove bag was purged as described in the previous paragraph.

The glove bag is inflated to a comfortable working size and pressure. This requires lowering the nitrogen flow rate. The $MnCl_2•4H_2O$ solution is poured into the 150-mL beaker. While swirling the beaker, the $Na(DTC)_2$ solution is added. Bright-yellow $Mn(DTC)_2$ immediately precipitates from solution. The product

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Table 1. Magnetic Suseptibilities, χ_{eff}, of Mn(DTC)$_2$ and Mn(DTC)$_3$ in Bohr Magnetons, μ_B

	Mn(DTC)$_2$^{a}	Mn(DTC)$_2$^{b}	Mn(DTC)$_3$^{c}
Experimental value	5.65	5.29	4.96
Literature value $^{d, e}$	5.65		4.90

^{a} Compound was yellow in color while measurement was made. The value is an average of three trials. ^{b}Obtained by exposing yellow Mn(DTC)$_2$ to air for 24 hours. Compound was brown in color while measurement was made. The value is an average of three trials. ^{c}compound was brown in color from intentional synthesis of Mn(DTC)$_3$. The value is an average of three trials. ^{d} ref 5. ^{e}ref 6.

mixture is bubbled with nitrogen for 1 min to hinder oxidation from adventitious air. The product is gravity-filtered and rinsed with two 10-mL aliquots of methanol. The filter paper containing the product is removed from the funnel and dried under a stream of nitrogen. The nitrogen flow rate is adjusted to approximately 100 bubbles per min and the glove bag can be left unattended until drying is complete. (During this time, the Mn(DTC)$_3$ was prepared.) The average yield of Mn(DTC)$_2$ was 90%.

Tris(diethyldithiocarbamato)manganese(III), Mn(DTC)$_3$

In separate beakers, 6.9 g of NaDTC and 1.9 g of MnCl$_2$•4H$_2$O are dissolved in 10 mL of methanol. The Na(DTC) solution is then added to the MnCl$_2$•4H$_2$O with stirring. A thick dark brown product forms immediately. The solution is mixed for 5 min and the product collected by gravity filtration. The product is rinsed with two 10-mL portions of methanol and recrystallized by dissolving it in 20 mL of dichloromethane and then adding 10 mL of ethanol. The product is collected on filter paper, rinsed with ethanol, and allowed to air dry (while the Mn(DTC)$_2$ is characterized). The average recrystallized yield of Mn(DTC)$_3$ is 70%.

Characterization. As is typical of air-sensitive compounds, characterization is complicated by the tendency of Mn(DTC)$_2$ to decompose, forming Mn(DTC)$_3$ in addition to other products. This can be followed visually and confirmed by comparison of characterization data for decomposed Mn(DTC)$_2$ with that of Mn(DTC)$_3$. The characterization methods described here can be expanded upon, depending on the facilities available. Inert atmosphere analysis of Mn(DTC)$_2$ via UV–vis spectroscopy and/or IR spectroscopy (utilizing airtight liquid cells) is certainly an additional possibility for characterization.

Equipment

Magnetic susceptibility measurements are performed with a Johnson Matthey magnetic susceptibility balance, Type MSNB.

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

Cyclic voltammograms are collected on a Bioanalytical Systems, Inc., (BAS) Model 100B/W electrochemical workstation. A platinum or glassy carbon disk (BAS) serves as the working electrode; a Pt coil functions as the auxiliary electrode. The reference is a saturated calomel electrode. Potentials are not corrected for liquid junction, but are calibrated daily against an internal reference (ferrocene). Voltammograms are obtained under a blanket of nitrogen.

Magnetic Susceptibility Measurements

Samples of Mn(DTC)$_2$ are prepared in the glove bag using preweighed sample tubes. The Mn(DTC)$_2$ is not ground. Once prepared, the samples are quickly removed from the glove bag and analyzed. As time elapses, the decomposition of Mn(DTC)$_2$ is visually evident and can be followed by magnetic susceptibility.

Mn^{2+} has a d^5 configuration, which can be either high spin or low spin. Similarly, the d^4 configuration of Mn^{+3} can be either high spin or low spin. The students are encouraged to predict the number of unpaired electrons after considering the tendencies of manganese and DTC.

The spin-only method is used to calculate χ_{eff} for Mn(DTC)$_2$ and Mn(DTC)$_3$. The results are given in Table 1.

A comparison of the magnetic susceptibility data above can produce a teaching moment. If Mn(DTC)$_2$ decomposes to Mn(DTC)$_3$, then why don't the χ_{eff} values match? Asking students to write a balanced chemical equation for the decomposition of Mn(DTC)$_2$ to Mn(DTC)$_3$ typically leads them to a logical conclusion. The presence of other products changes the measured magnetic susceptibility reading. To confirm that Mn(DTC)$_2$ decomposes to Mn(DTC)$_3$, the decomposed sample can be recrystallized. The recrystallized sample has a χ_{eff} of 4.96 Bohr magnetons. Thus, not only can the decomposition of Mn(DTC)$_2$ be followed by magnetic susceptibility, the technique can be used to identify the decomposition product.

IR Spectroscopy. IR spectra of both Mn(DTC)$_2$ and Mn(DTC)$_3$ were identical (See Figure 1). In fact, whether the IR sample was prepared in the glove bag or in the air, we visually observed the yellow Mn(DTC)$_2$ turn brown as we ground the sample in the mortar. This provided a pedagogical opportunity to propose reasons for the accelerated decomposition. The IR spectra matched exactly the published spectrum for Mn(DTC)$_3$. It is well-known that Mn(DTC)$_2$ decomposes to Mn(DTC)$_3$ upon exposure to air. Although this process is slow enough to allow us to perform magnetic susceptibility measurements, the decomposition rate is obviously accelerated by grinding the sample, perhaps due to the increased surface area that grinding affords. Other sampling techniques (ATR, nujol mull, and sprinkling the unground solid on top of KBr) give the same result.

Cyclic Voltammetry. Acetonitrile was dried by distillation over CaH$_2$ and kept over molecular sieves; 1,2-dichloroethane (HPLC) used as received. Supporting electrolytes were *t-N*-butylammoniumhexafluorophosphate or lithium perchlorate, both kept in a desiccator cabinet and used as received.

Within the solvent window defined by these solvent/supporting electrolyte combinations, one metal-based oxidation and one metal-based reduction are observed. Even in rigorously deaerated solvents, noticeable decomposition of the Mn(DTC)$_2$ product was observed within 10 to 15 min. This window of time, however, is more than sufficient to conduct the electrochemical analysis, because the entire scan is completed in a few seconds. Excess diethyldithiocarbamate has its own characteristic electron-transfer mechanism, which has been published [7]. A representative example of a cyclic voltammogram of Mn(DTC)$_2$, taken in MeCN, on a glassy carbon electrode is shown in Figure 2. No waves characteristic of free DTC are observed. Cyclic voltammetric diagnostic criteria [8] applied to each wave are as follows. For the reduction ($E_{1/2}$ = –0.340V), the half-wave potential ($E_{1/2}$) is relatively stable between 0.050 V s^{-1} and 2.000 V s^{-1}, drifting slightly cathodically over that range by 0.030 V. Anodic/cathodic peak separation (ΔE_p) increases from 0.152 V (0.050 V s^{-1}) to 0.417 V (2.000 V s^{-1}). Current ratio ($i_{p,a}/i_{p,c}$)

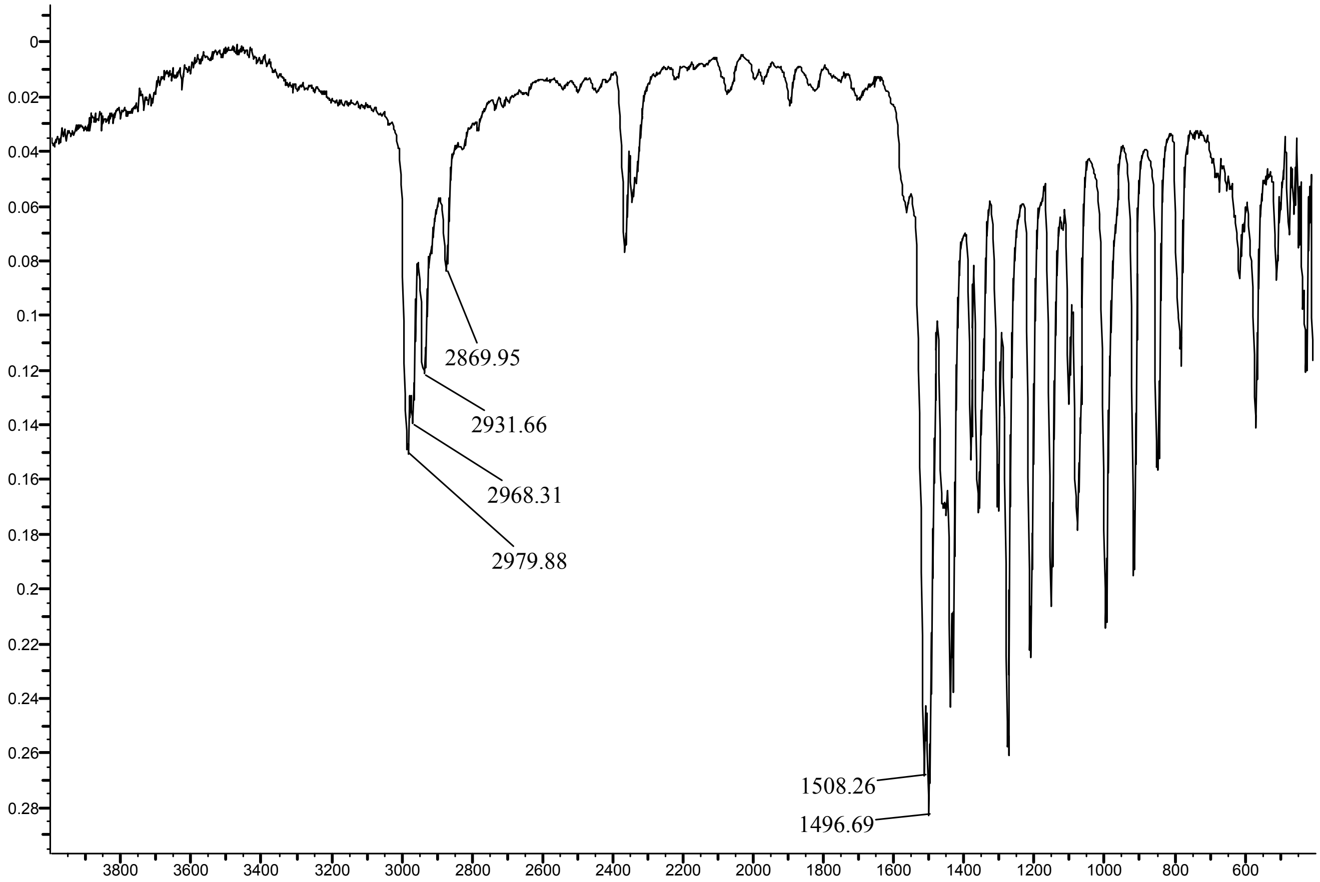

Figure 1. IR spectrum of Mn(DTC)$_2$, sample ground in the glove bag. Sample turned brown upon grinding. Spectrum matches that of Mn(DTC)$_3$.

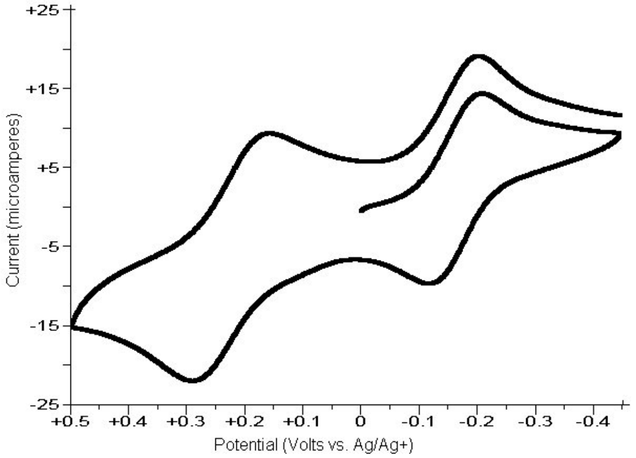

Figure 2. Cyclic voltammetric behavior of Mn(DTC)$_2$ complex showing metal-based electron-transfer processes.

decreases from 0.800 (0.100 V s^{-1}) to 0.685 (2.000 V s–^{1}). The current function ($i_p/v^{1/2}$) remains virtually constant with scan rate. Fitting the voltammograms to curves derived from fundamental equations (Digi-Sim, version 2.1, BAS, Inc.) results in an electron-transfer rate constant of $1.487 \times 10^{-3} \pm 2.60 \times 10^{-4}$ cm s^{-1} for this quasireversible electron transfer.

For the oxidation ($E_{1/2}$ = 0.080V), $E_{1/2}$ is also relatively stable, drifting slightly anodic (0.035 V). Peak separation increases from 0.109 to 0.265 V over the investigated range; however, as most of this shift is accounted for in the most extreme scan rate (2.000 V s^{-1}), this shift is probably the result of uncompensated resistance in the cell and not an artifact of a chemically coupled electron transfer. The current ratio is consistently close to unity at all scan rates while the current function remains virtually constant with scan rate. Fitting the voltammograms to curves derived from fundamental equations results in an electron-transfer (ET) rate constant of $5.189 \times 10^{-3} \pm 1.571 \times 10^{-3}$ cm s^{-1} for this quasi-reversible electron transfer.

The recrystallized Mn(DTC)$_3$ showed a more complex ET behavior. After one cycle where Mn(DTC)$_3$ is oxidized, there is another oxidation and reduction. The additional oxidation and reduction are observed at potentials identical to free DTC ligand. This indicates at least one ligand is dissociating (slowly, as indicated by low current values) upon oxidation of the complex.

Thus, Mn(DTC)$_2$ and Mn(DTC)$_3$ exhibit similar electron-transfer mechanisms. Mn(DTC)$_2$ exhibits one-electron oxidation and reduction. Both are quasireversible (slow to moderately slow heterogeneous ET kinetics). Mn(DTC)$_3$ exhibits one-electron oxidation and reduction at approximately the same potentials as Mn(DTC)$_2$; however, the Mn(DTC)$_3$ oxidation is followed by dissociation of one or more DTC ligands, as confirmed by appearance of an additional oxidation and reduction, which correspond exactly to the potentials observed by a solution of free DTC. Thus, the two compounds can be easily identified and differentiated by cyclic voltammetry.

Conclusion

This exercise represents an ideal first exposure to the problems associated with air-sensitive compounds and their manipulations. The complexation of manganese(II) with diethyldithiocarbamate is simple conceptually from the viewpoint of synthesis and characterization. The advantages of this experiment include: (1) inexpensive equipment and reagents, (2) low health and environmental hazards. From the student perspective, success is immediately obvious from the extreme color changes observed and the characterization data; thus, a premium is placed on student laboratory acumen. The synthesis of $Mn(DTC)_2$ requires that there not be atmospheric air present. The introduction of air causes the bright-yellow $Mn(DTC)_2$ to turn brown almost immediately. This gives students a visual indication of their technique. The synthesis of $Mn(DTC)_3$ allows students to identify the decomposition product of $Mn(DTC)_2$. Careful preparation, attention to detail, and good technique are rewarded with excellent results. Characterization of air-sensitive compounds affords its own challenge, and here again, $Mn(DTC)_2$ and $Mn(DTC)_3$ represent appropriate levels of difficulty. Especially fortunate is the well-behaved voltammetric behavior, easily defined and mechanistically accessible. This allows for the calculation of heterogeneous electron-transfer rate constants, an exercise not normally meaningful (if performed at all) at this level. In addition, this experiment can be performed in one laboratory period.

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References and Notes

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3. Latex gloves aid in dexterity within the glove bag.
4. The bubbler was constructed from 5-mm (i.d.) glass tubing submerged 1 cm deep into mineral oil.
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