

Lab 6

Inorganic Syntheses using Mo catalysts

Literature References

1. Moore, F.W., et. al., "Dialkyldithiocarbamate Complexes of Molybdenum (V) and Molybdenum (VI)", *Inorganic Chemistry* **1967**, 6, 998-1003.
2. Chen, G.J.-J., et. al., "Synthesis of Mo(IV) and Mo(V) Complexes Using Oxo Abstraction by Phosphines. Mechanistic Implications", *Inorganic Chemistry* **1976**, 15, 2612.
3. Dirand, J., et. al., "Preparation and Molecular Structure of Oxodihalgenobis (dialkyldithio carbamate) molybdenum (VI) Complexes", *J. Chem. Soc., Dalton Trans.* **1976**, 278-282).

Objective

To explore a basic set of inorganic syntheses and catalytic reactions, in this case with Mo because it is extremely stable.

Materials

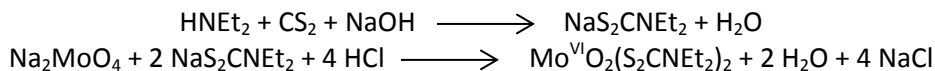
250 mL erlenmeyer flask
Watchglass
Vacuum filtration system
Filter paper
25-mL Erlenmeyer flask

Chemicals

Name	Formula	Molar Mass (g/mol)	MP/BP (°C)	Hazards
Hydrochloric acid	HCl	36.45	-62/109	corrosive, irritant
Diethylamine	C ₄ H ₁₁ N	73.14	-50/55	flammable, corrosive
Sodium hydroxide	NaOH	39.9971	318/1388	corrosive
Carbon disulfide	CS ₂	76.139	-110/46	toxic, irritant
Sodium molybdate	Na ₂ MoO ₄	241.95	687/--	--
Ethanol	C ₂ H ₆ O	46.07	-114/78	flammable
Dichloromethane	CH ₂ Cl ₂	84.93	-97/40	--
Triphenylphosphine	C ₁₈ H ₁₅ P	262.29	80/377	--
acetone	C ₃ H ₆ O	58.08	-94/56	flammable, irritant

Part I: Synthesis of dioxobis(N,N-diethyldithiocarbamato)molybdenum(VI) [MoO₂(S₂CNEt₂)₂]

Reaction Scheme

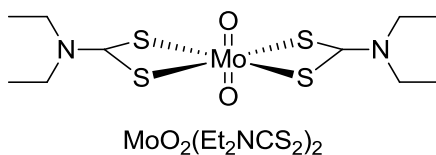


Sample Calculations

$$\begin{aligned} (3.5 \text{ g Na}_2\text{MoO}_4) / (241.95 \text{ g/mol Na}_2\text{MoO}_4) * (1 \text{ mol/1 mol}) * (424.4830 \text{ g/mol MoO}_2(\text{S}_2\text{CNEt}_2)_2) \\ = \mathbf{6.14 \text{ g MoO}_2(\text{S}_2\text{CNEt}_2)_2} \end{aligned}$$

Pre-Lab Questions

1. What is the reaction for the second part of the synthesis, addition of sodium molybdate dihydrate to the ligand?
 - a. See Reaction Scheme.
2. Draw the structure of MoO₂(S₂CNEt₂)₂.



3. Give the Mo oxidation state and valence electron count for MoO₂(S₂CNEt₂)₂.
 - a. This 16 e⁻ compound has a Mo (6+) metal center with a d⁰ electron state.

Experimental Method

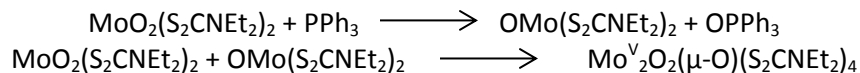
Success depends on vigorous stirring during the addition of the hydrochloric acid. Diethylamine (2.4 mL, 23 mmol) and sodium hydroxide (0.9 g, 23 mmol) are added to water (50 mL) in a 250 mL erlenmeyer flask. After stirring for 5 min, the mixture is treated with carbon disulfide (1.4 mL, 23 mmol), a watchglass is placed over the top of the flask and the solution is stirred for a further 10 min. Sodium molybdate(VI) dihydrate (3.5 g, 14.5 mmol) is added to the mixture, which is then treated dropwise (from a dropping funnel, over about a 10 min period) with a solution of 6 mL of concentrated hydrochloric acid in water (100 mL). Vigorous stirring is required during the dropwise addition; the dense yellow-brown product precipitates. The solid is isolated by vacuum filtration washed well with water (60 mL), ethanol (60 mL), then ether (60 mL) and dried. The crude material may be used in the syntheses that follow (save ~ 1.5 g). The remainder of the sample can be recrystallized by dissolving it in dichloromethane (15 mL/g), filtering, and adding ether (20 mL/g) to the clear filtrate.

Observations

- 0.893 g NaOH
- 3.535 g Na₂MoO₄
- Yellow solution turns to a cranberry coloring. When HCl solution is added dropwise, a precipitate begins to form, and the mixture becomes yellow → yellow brown.
- Didn't wash with ether, as instructed by TA's. Only water and ethanol.
- Crude mass: 4.352 g. Yield: 70.9% MP: decomposed at 155 °C.
- Saved 1.509 g crude product to be used in Lab 6.2.
- 2.843 g used to recrystallize in 15 mL DCM. Didn't use ether in recrystallization. Dried until next class

Part II: Synthesis of μ -oxo-dioxo-tetrakis(diethyldithiocarbamato)molybdenum(V)
[Mo₂O₂(μ -O)(S₂CNEt₂)₄]

Reaction Scheme

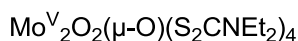
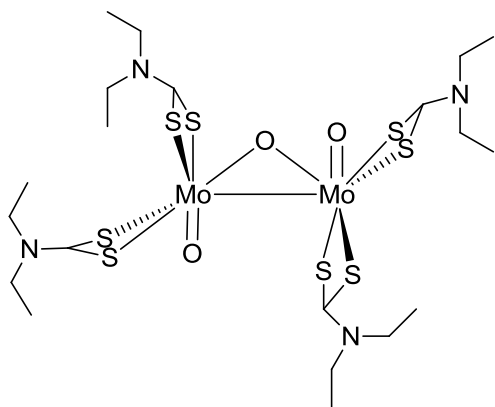


Sample Calculations

$$(0.5 \text{ g MoO}_2(\text{S}_2\text{CNEt}_2)_2) / (424.4830 \text{ g/mol MoO}_2(\text{S}_2\text{CNEt}_2)_2) * (1 \text{ mol} / 2 \text{ mol}) * (832.9666 \text{ g/mol Mo}^{\text{V}}_2\text{O}_2(\mu\text{-O})(\text{S}_2\text{CNEt}_2)_4) = \mathbf{0.49 \text{ g Mo}^{\text{V}}_2\text{O}_2(\mu\text{-O})(\text{S}_2\text{CNEt}_2)_4}$$

Pre-Lab Questions

1. Write out the equation(s) for this reaction.
 - a. See Reaction Scheme.
2. What does μ -oxo mean?
 - a. It means the oxygen is a bridging complex.
3. Draw the structure of this μ -oxo complex.



4. Give the Mo oxidation state and the valence electron count for the complex [Mo₂O₂(μ -O)(S₂CNEt₂)₄].
 - a. This symmetrical bridging compound has Mo (5+) metal centers, each with a d¹ electron state.

Experimental Method

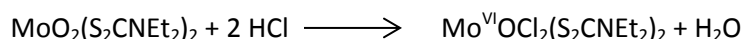
A solution of crude MoO₂(S₂CNEt₂) (0.5 g, 1.2 mmol) in dichloromethane (5 mL) is filtered through a fluted filter paper into a 25-mL Erlenmeyer flask, then the filtrate is treated with a solution of triphenylphosphine (0.16 g, 0.6 mmol) in methanol (10 mL). The mixture is swirled for a few seconds then left to stand for 15 min (longer times may be employed if the flask is tightly stoppered). The purple solid formed is vacuum filtered, washed with methanol and dried. The true color of the compound is revealed only when a sample is crushed on a white surface (e.g., tile or paper).

Observations

- Rxt Product 1 melting point: 149 °C. Crude melting point: turned black.
- Vial mass: 9.951 g. Product 1 mass: 1.770 g. Product looks like crumbled, burnt graham crackers.
- Triphenylphosphine: 0.161 g.
- After performing suction filtration, liquid filtrate is fuschia. Solid filtrate on top is black, and turned dark green after it set briefly.
- Black/green product mass: 0.233 g, melting point: decomposed at 179 °C. Yield: 47.5%

Part III: Synthesis of oxodichlorobis(N,N-diethyldithiocarbamato)molybdenum(VI) [MoOCl₂(S₂CNEt₂)₂]

Reaction Scheme

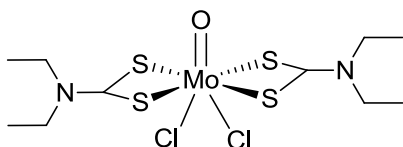


Sample Calculations

$$(0.5 \text{ g MoO}_2(\text{S}_2\text{CNEt}_2)_2) / (424.4830 \text{ g/mol MoO}_2(\text{S}_2\text{CNEt}_2)_2) * (1 \text{ mol} / 1 \text{ mol}) * (479.3900 \text{ g/mol Mo}^{\text{VI}}\text{OCl}_2(\text{S}_2\text{CNEt}_2)_2) = \mathbf{0.56 \text{ g Mo}^{\text{VI}}\text{OCl}_2(\text{S}_2\text{CNEt}_2)_2}$$

Pre-Lab Questions

1. Draw the structure of Mo^{VI}OCl₂(S₂CNEt₂)₂.



2. Give the valence electron count for Mo^{VI}OCl₂(S₂CNEt₂)₂.
 - a. This 16 e⁻ compound has a Mo (6+) metal center with a d⁰ electron state.
3. The oxygen is in the axial position. Why?
 - a. Steric factors play a major part in this configuration, especially with a 7-coordinate geometry system such as this.

Experimental Method

A solution of crude MoO₂(S₂CNEt₂)₂ (0.5 g, 1.2 mmol) in acetone (35.0 mL) is filtered through a fluted filter paper, then the filtrate is treated with concentrated hydrochloric acid (2.5 mL, excess) and the mixture stirred for 20 min. Leave the product crystallizing until the next lab. The product is isolated by filtration, washed with 10 mL of acetone and dried under vacuum.

Observations

- 0.496 g crude product used as starting reagent.
- After filter, compound has the color of dark apple juice.
- After HCl, compound is colored like pea soup, then a blue-green.
- On Day 4, product is washed with acetone and appears lime green.
- Product 3 mass: 0.263 g, melting point: 206-210. Yield: 47.0 %

Results

The aforementioned set of introductory inorganic syntheses was analyzed by melting point, TLC, and IR plots (along with product yield). The crude product was a golden yellow solid with a mass of 4.352 g, a yield of 70.9 %, an R_f value of 0.66 in pure ethyl acetate, and a melting point of 155°C (decomposition). Product 1 was a dark brown, crumbly solid with a mass of 1.770 g (from 2.843 g crude product), an R_f value of 0.66 in pure ethyl acetate, and a melting point of 149°C. Product 2 was a black-green solid with a mass of 0.233 g, a yield of 47.5 %, an R_f value of 0.66 in pure ethyl acetate, and a melting point of 179°C (decomposition). Product 3 was a lime green solid with a mass of 0.263 g, a yield of 47.0 %, an R_f value of 0.59 in pure ethyl acetate, and a melting point of 206-210°C. Analysis of IR plots can be seen in attached data sheets.

Discussion

The IR peaks for all three products are very similar in both position and intensity. Happily, the peaks shown in the IR spectra do correlate with the predicted peak pattern of each product. Specific positions are labeled and assigned with a corresponding functional group in the data sheet for each compound. The C-S peak was not labeled in the table below the raw plot, which made it harder to identify. However, the one we chose fell within the accepted range consistently among all three plots.

A standard melting point could not be found for the second and third products ($\text{Mo}^{\text{V}}\text{O}_2(\mu\text{-O})(\text{S}_2\text{CNEt}_2)_4$ and $\text{Mo}^{\text{VI}}\text{OCl}_2(\text{S}_2\text{CNEt}_2)_2$ respectively), and so we are not able to draw any conclusions for these. However, the standard melting point of the first product ($\text{Mo}^{\text{VI}}\text{O}_2(\text{S}_2\text{CNEt}_2)_2$) was found to be 133°C. This is rather close to the melting point we gathered for the first product, 149°C. The color of the first product should be more orange-yellow, although we gathered a brown, crumbled solid. For these reasons, along with the results of the IR plot, we conclude that the first compound does contain $\text{Mo}^{\text{VI}}\text{O}_2(\text{S}_2\text{CNEt}_2)_2$, but it is not a homogeneous mixture. Impurities are present and riddle our first product with dark brown chunks.

The hues of our second and third products seem to be much better, though. As we would expect, our third product is a vibrant shade of green and our second product (though it appears dark green when solid) returns to its magenta coloring when dissolved in ethyl acetate. If we had the opportunity at a later date, we should probably perform the TLC on each product over again. It was a little strange that the crude, first product, and second product all had the same R_f value. As such, the R_f values for each of the four products (including crude) were rather high and should be developed in a more non-polar solution, such as hexanes.

Conclusion

The IR plot was the most helpful tool in confirming the presence and quality of these products. This would be more helpful, however, if it was a plot of our specific products since we have no other quantifiable way of comparing them all together. Based on the qualitative appearance of our products, we believe that the second and third products are successfully synthesized $\text{Mo}^{\text{V}}\text{O}_2(\mu\text{-O})(\text{S}_2\text{CNEt}_2)_4$ and $\text{Mo}^{\text{VI}}\text{OCl}_2(\text{S}_2\text{CNEt}_2)_2$ respectively, and that the first product contains $\text{Mo}^{\text{VI}}\text{O}_2(\text{S}_2\text{CNEt}_2)_2$, but with impurities. Overall, it was interesting to see how one crude product can be molded into so many different compounds with such little adjustments.