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# STUDIES OF MOLYBDENUM COMPLEXES 

by

GREGORY W. ESTES
B. A., University of Colorado, 1971

A THESIS

Submitted to the University of New Hampshire In Partial Fulfillment of

The Requirements for the Degree

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This thesis has been examined and approved.

$918 / 76$

TO MY PARENTS

This research project was carried out in the chemistry laboratories of Parsons Hall under the direction of Dr. Helmut M. Haendler. I wish to thank $\operatorname{Dr}$. Haendler for his timely advice and guidance. I am indebted to Mrs. Deanna Cardin for the CHN analyses that she ran, to Mr. Michael Pazdon for the mass spectra that he ran, and to the Center for Industrial and Institutional Development for the use of their thermogravimetric analyzer. I would also like to express my appreciation to the University of New Hampshire for the financial support that it provided through teaching assistantships and a University of New Hampshire Summer Fellowship for Graduate Teaching Assistants.
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# ABSTRACT <br> <br> STUDIES OF MOLYBDENUM COMPLEXES 

 <br> <br> STUDIES OF MOLYBDENUM COMPLEXES}

## by

GREGORY W. ESTES

The primary goal of this research was to determine the feasibility of synthesizing anhydrous metal molybdates by the reaction of dehydrated ammonium molybdate with metal salts in nonaqueous media. In order to develop an appropriate dehydration technique, a preliminary study was made of the dehydration of ammonium oxalate monohydrate by triethylorthoformate and 2,2-dimethoxypropane. The anhydrous ammonium oxalate was prepared successfully, and the compound was characterized by infrared and mass spectrometry, chemical analysis, and by x-ray diffraction.

Triethyl orthoformate does not dehydrate ammonium paramolybdate tetrahydrate, but the hydrate does react with 2,2-dimethoxypropane, forming an methanol adduct of the molybdate with methanol produced in the dehydration by the hydrolysis of the 2,2-dimethoxypropane. This adduct is soluble in methanol, and reactions of this solution with a series of metal bromides were studied. The affinity of molybdenum for bridging oxygens is apparently so strong that it prevents formation of ionic molybdates, since only molybdenum oxides were obtained in these reactions.

In the orthoformate dehydration experiments with the ammonium molybdate a number of complex, presumably polymeric, compounds were isolated. Infrared and mass spectral data suggested that these were acid derivatives formed from the byproducts of the orthoformate reaction. In order to provide some known compounds with which to compare the spectra, the ammonium salts of the molybdenum complexes of oxalic acid, tartaric
acid, and phthalic acid were synthesized. The results indicate that only dicarboxylic acids of appropriate stereochemistry form this type of complex, and that the formate complexes, although acidic, are of a different, and perhaps new type.

## INTRODUCTION

Anhydrous metal molybdates catalyze a variety of reactions. At present, these compounds are made by one of two methods. ${ }^{1-3}$ The first method consists of mixing an aqueous solution of a molybdenum compound, such as ammonium molybdate, with an aqueous solution of some metal salt, sometimes in hot solution. The precipitate is collected and must be dehydrated prior to use. This dehydration may produce a change in structure from one in which some or a.11 of the molybdenum atoms have an octahedral environment ${ }^{4}$ to one in which all of the molybdenum atoms have tetrahedral environment. ${ }^{5}$

The second method consists of heating a mixture of molybdenum dioxide or molybdenum trioxide with a metal oxide or carbonate to a high temperature. Water is sometimes included in the mixture. The few occassions in which melts have been used as a reaction medium for the synthesis of metal molybdates also fall into this category. This method requires special handling and equipment and can result in undesirable structural imperfections.

The primary goal of this study was to determine the feasibility of synthesizing anhydrous metal molybdates in nonaqueous solvents. A logical approach is to dehydrate ammonium paramolybdate tetrahydrate, $\left(\mathrm{NH}_{4}\right){ }_{6} \mathrm{Mo}_{7} \mathrm{O}_{24} \cdot 4 \mathrm{H}_{2} \mathrm{O}$, and then react it with a metal salt in a nonaqueous solvent. Several methods of dehydrating ammonium paramolybdate tetrahydrate are possible. When possible, these methods were tested with ammonium oxalate monohydrate, $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{C}_{2} \mathrm{O}_{4} \cdot \mathrm{H}_{2} \mathrm{O}$, prior to their extension to ammonium paramolybdate tetrahydrate. Ammonium oxalate monohydrate is readily available, inexpensive, and thermally unstable, and is of interest as a reducing agent and as a source of the oxalate ligand in nonaqueous solvents.

One possible method is to thermally dehydrate ammonium paramolybdate tetrahydrate and react the dehydrated product with a metal salt in a nonaqueous solvent. Although there is some disagreement among the various reports, the thermal decomposition studies ${ }^{6-10}$ performed on ammonium paramolybdate tetrahydrate at atmospheric pressure indicate that both water and ammonia are lost near $100^{\circ} \mathrm{C}$. Therefore, this method is likely to work only with difficulty.

Hydrolysis reactions employing such compounds as orthoesters, such as triethyl orthoformate, $\mathrm{HC}\left(\mathrm{OC}_{2} \mathrm{H}_{5}\right)_{3}$, and ketals, such as 2,2-dimethoxypropane, $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{C}\left(\mathrm{OCH}_{3}\right)_{2}$, have been used successfully in dehydrating transition metal compounds. ${ }^{11-13}$ They may also be successful in dehydrating ammonium paramolybdate tetrahydrate.

Another possible method is based on the reversible formation of polyanions by ammonium molybdate with changing pH . ${ }^{14-31}$ The reaction $\left(\mathrm{Mo}_{7} \mathrm{O}_{24}\right)^{6-}+8 \mathrm{NH}_{3} \longrightarrow 7 \mathrm{MoO}_{4}^{2-}+8 \mathrm{NH}_{4}^{+}$occurs readily in aqueous solution. ${ }^{29,32}$ Since ammonium paramolybdate is a tetrahydrate, it may undergo this reaction in a nonaqueous solvent to product anhydrous ammonium molybdate, $\left(\mathrm{NH}_{4}\right) \mathrm{MOO}_{4}$.

A third possibility would be to synthesize the anhydrous ammonium dimolybdate ${ }^{31}\left(\mathrm{NH}_{4}\right)_{2} \mathrm{MO}_{2} \mathrm{O}_{7}$, and then react it with a metal salt in a nonaqueous solvent.

Once an anhydrous ammonium molybdate is synthesized, it should be easy to react it with a metal bromide, or other anhydrous metal salt, in a nonaqueous solvent. An alternative method is to combine the reaction of the metal salt and ammonium paramolybdate tetrahydrate with the dehydration reaction by triethyl orthoformate. The presence of the
metal salt is likely to make the dehydration reaction easier and more sure of success by increasing the ionic strength.

Attempts were made to synthesize several molybdenum carboxylates in order to make some comparisons with the mass spectra of the molybdenum compounds synthesized in the attempts to dehydrate ammonium paramolybdate tetrahydrate and react the product with metal bromides. Molybdenum carboxylates appear to be easily synthesized, ${ }^{33-37}$ some are good reduction catalysts, ${ }^{38}$ and carboxylic acids are often used in quantitative and qualitative analyses of various transition metals. 39,40

## CHAPTER I.

## DEHYDRATION OF INORGANIC SALTS

1. Experimental

## A. Reagents

Analytical reagent grade methanol, ACS reagent grade acetonitrile, and USP grade absolute ethanol were dried over Type 3A "Linde" Molecular Sieves. Other commercially available chemicals were used without further purifications.

## B. Elemental Analyses

CHN analyses were run by Mrs. Deanna Cardin on an F \& M Model
185 CHN Analyzer.
Ammonia was determined by Kjehldah1 method.
Molybdenum was determined gravimetrically as the 8-quinolinol complex. 41-45 The sample was initially dissolved in an acidic hydrogen peroxide solution to insure that all of the molybdenum was present as Mo(VI).

## C. Preparation of Compounds

1. Dehydration of Ammonium Oxalate Monohydrate by Triethyl

## Orthoformate

Ammonium oxalate monohydrate was refluxed with excess (~50 fold)
triethyl orthoformate in an appropriate solvent. The quantities of reagents and reaction times used are shown in Table $I$.

Anal. Calcd for $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{C}_{2} \mathrm{O}_{4}$ : $\mathrm{C}, 19,34 ; \mathrm{H}, 6.57 ; \mathrm{N}, 22.58$. Found: C, 20.09; H, 6.25; N, 22.09.

A melting point determination showed that the product decomposed to gaseous products at $225^{\circ} \mathrm{C}$. The powder pattern is different from the pattern for ammonium oxalate monohydrate. No pattern has been reported

Table I. The Quantities of Reagents and Reaction Times Used for the Dehydration of Ammonium Oxalate Monohydrate

| Ammonium Oxalate Monohydrate (g) | Triethyl <br> Orthoformate (ml) | Solvent | Volume of Solvent (m1) | $\begin{gathered} \text { Time } \\ \text { (Hr:Min) } \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: |
| 0.80 | 50 | 1,2-Dimethoxyethane | 100 | 3:00 |
| 0.70 | 50 | methanol | 100 | $2: 10^{\text {a }}$ |
| 1.10 | 60 | methanol | 80 | 4:50 |
| 1.10 | 50 | t-butanol | 100 | $3: 10^{\text {a }}$ |
| 1.20 | 70 | acetonitrile | 130 | 3:00 |
| 1.10 | 55 | nitromethane | 100 | 2:30 |

[^0]for anhydrous ammonium oxalate.
2. Dehydration of Ammonium Oxalate Monohydrate by 2,2-Dimethoxypropane
1.32 g of ammonium oxalate monohydrate were refluxed in 110 ml of 2,2 -dimethoxypropane ( $\sim 100$ fold excess), 1 ml of acetic anhydride, and 6 ml of acetic acid for 5.5 hr . The product was filtered and washed with methano1. The powder pattern was identical with the powder pattern of the product obtained by method \#1.
3. Dehydration of Ammonium Oxalate Monohydrate by 2,2-Dimethoxypropane in Dioxane
1.01 g of ammonium oxalate monohydrate were refluxed in 93 ml of 2,2 -dimethoxypropane ( $\sim 110$ fold excess), 6 ml of acetic acid, 2 ml of acetic anhydride, and 90 ml of dioxane for 3.6 hr . The product was filtered and washed with dioxane. A melting point determination showed that at $225^{\circ} \mathrm{C}$ the solid turned to a liquid which boiled immediately.

Anal. Calcd for $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{C}_{2} \mathrm{O}_{4} \cdot 1 / 2 \mathrm{C}_{4} \mathrm{H}_{8} \mathrm{O}_{2}: \mathrm{C}, 23.36 ; \mathrm{H}, 6.54 ; \mathrm{N}, 18.18$. Found: C, 21.38; H, 6.02; N, 18.70.
4. The Attempted Dehydration of Ammonium Paramolybdate Tetrahydrate by Triethy1 Orthoformate in 1,2-Dimethoxethane

Three trials were made, which gave the same basic results.
 refluxed in 240 ml of 1,2 -dimethoxyethane and 160 m 1 of triethyl orthoformate ( $\sim 25$ fold excess) for 9.5 hr .

Anal. Found: $\mathrm{C}, 17.28 ; \mathrm{H}, 3.17$; Mo, 43.29; N, 5.50.
Trial 非2: 8.59 g of ammonium paramolybdate tetrahydrate were refluxed in 240 ml 1,2-dimethoxyethane and 155 ml of triethyl orthoformate $(25$ fold excess) for 19 hr .

Anal. Found: $\mathrm{C}, 19.54 ; \mathrm{H}, 3.07$; Mo, $41.04 ; \mathrm{N}, 6.26$.
Trial 非3: 5.10 g of ammonium paramolybdate tetrahydrate were refluxed in 175 ml of 1,2 -dimethoxyethane and 70 ml of triethyl orthoformate ( $\sim 100$ fold excess) for 4.3 hr .

Anal. Found: C, 17.00; H, 2.98; N, 5.30.
All three products were brown tars and appear to be the same in other respects. Two other trials apparently did not go to completion.
5. Attempted Dehydration of Ammonium Paramolybdate Tetrahydrate with Triethyl Orthoformate in Ethanol
1.74 g of ammonium paramolybdate tetrahydrate were refluxed with 9.13 g of triethyl orthoformate ( $\sim 15$ fold excess) in 50 ml of ethanol for 3 hr . The solution turned brown while it was being heated, but the color faded as it cooled. Some of the solution was distilled off and a tan solid was filtered out and washed with ethanol.

Anal. Found: C, 24.92; H, 5.34; Mo, 45.12; N, 5.49.
6. The Attempted Dehydration of Amnonium Paramolybdate

Tetrahydrate by 2,2-Dimethoxypropane in the Presence of Acetic Anhydride
Two trials were made for this synthesis, the first of which apparently did not go to completion.

Trial \#1; 2.45 g of ammonium paranolybdate tetrahydrate were refluxed in $100 \mathrm{ml} 2,2$-dimethoxypropane ( $\sim 45$ fold excess), 7 ml of acetic acid, and 1 ml of acetic anhydride for 2.25 hr .

Ana1. Found: $\mathrm{C}, 20.13 ; \mathrm{H}, 3.72 ; \mathrm{Mo}, 48.90 ; \mathrm{N}, 3.68$.
Trial \#2: 4.73 g of ammonium paramolybdate tetrahydrate were refluxed with 200 ml of $2,2-$ dimethoxypropane ( $\sim 60$ fold excess), 10 ml of acetic acid, and 0.1 ml of acetic anhydride for 5 hr .

Ana1. Found: C, 25.29; H, 4.19; Mo, 35.36; N, 3.95.
7. The Dehydration of Ammonium Paramolybdate Tetrahydrate by 2,2-Dimethoxypropane
2.08 g of ammonium paramolybdate tetrahydrate were refluxed with 100 ml of 2,2 -dimethoxypropane ( $\sim 500$ fold excess) and 7 ml of acetic acid for 2.5 hr . The white product was filtered and washed with methanol. This product appears to be soluble in methanol. The powder pattern is different from that for ammonium paramolybdate tetrahydrate or that for anhydrous ammonium paramolybdate.

Anal. Calcd for $\left(\mathrm{NH}_{4}\right)_{6} \mathrm{MO}_{7} \mathrm{O}_{24} \cdot 5 \mathrm{CH}_{3} \mathrm{OH}: \mathrm{C}, 4.53$; $\mathrm{H}, 3.34$; Mo, 50.73;
$\mathrm{N}, 6.34$. Found: C, 4.48; H, 2.81; Mo, 51.10; $N$, 5.70.
8. The Attempted Dehydration of Ammonium Paramolybdate

Tetrahydrate by 2,2-Dimethoxypropane in Acetonitrile
3.93 g of ammonium paramolybdate tetrahydrate were refluxed in 125 ml of 2,2-dimethoxypropane ( $\sim 200$ fold excess), 5 ml of acetic acid, and 70 ml of acetonitrile for 3.5 hr . The tan solid product was filtered out and washed with acetonitrile.

Anal. Found: C. 16.24; H, 3.35; Mo, 44.77; N, 4.63.
9. Control Experiment - The Reaction of Ammonium Paramolybdate Tetrahydrate with Methanol
0.84 g of ammonium paramolybdate tetrahydrate were dissolved in 200 ml of methanol and allowed to stand for 4.5 hr . Some methanol was distilled off and the white product was filtered out.

Anal. Found: C, 0.90 ; H, 1.38; Mo, $58.36 ; \mathrm{N}, 4.48$ (N/Mo mole ratio is 4/8).
10. The Reaction of Ammonium Paramolybdate Tetrahydrate with Ammonia in Methanol

Two trials were attempted for this reaction. Ammonia solutions in methanol were produced by passing ammonia through a column of barium
oxide and a glass frit into dry methanol. 46
Trial \#l: 1.47 g of ammonium paramolybdate tetrahydrate were dissolved in 200 ml of the ammonia solution in methanol and 100 ml of methanol and allowed to stand for 7 hr . The undissolved solid was filtered out, some methanol was distilled off, and the white product was filtered out.

Anal. Found: C, 0.82; H, 2.18; Mo, 56.32; N, 6.64.
Trial \#2: 1.83 g of ammonium paramolybdate tetrahydrate were dissolved in 200 ml of the ammonia solution in methanol and allowed to stand for 2.5 hr . Some methanol was distilled off and the white solid was filtered out.

Anal. Found: C, 2.25; H, 2.35; Mo, 43.87; N, 5.25.
The N/Mo mole ratio is $6 / 7$ in both cases.

## C. Infrared Spectra

Infrared spectra were run as KBr pellets on a Perkin Elmer Mode1 337 Infrared Spectrometer. The instrument was calibrated against polystyrene.

The infrared spectra are shown in Figure 1 through 7.

## D. Mass Spectra

Mass spectra were run by Mr. Michael Pazdon on a Hitachi
Perkin-E1mer Model RMU-6E Mass Spectrometer. Two computer programs have been adapted to aid in the interpretation of mass spectra ${ }^{47-50}$ (see the appendix).

The mass spectra are given in Tables II through $V$.
E. X-ray Powder Patterns

X-ray powder patterns were run using the Debye-Scherrer method, 57.3 and 114.6 mm cameras employing the Straumanis mount were used. The samples were loaded in 0.3 mm diameter capillaries and exposed to

# nickel-filtered CuK $\boldsymbol{\alpha}$ radiation, $\boldsymbol{\lambda}=1.5418$ A $^{\circ}$. <br> The powder patterns are given in Tables VI and VII. <br> Unit cells were determined by the unit cell series of computer programs (including DeWolff comparison). 5l-53 

Figure 1. The Infrared Spectrum of Anhydrous Ammonium Oxalate


Figure 2. The Infrared Spectrum of the Ammonium Oxalate-Dioxane Adduct


Figure 3. The Infrared Spectrum of the Product of the Reaction of Ammonium Paramolybdate Tetrahydrate with Triethyl Orthoformate in 1,2-Dimethoxyethane


Figure 4. The Infrared Spectrum of the Product of the Reaction of Ammonium Paramolybdate Tetrahydrate with Triethyl Orthoformate in Ethanol


Figure 5. The Infrared Spectrum of the Product of the Reaction of Ammonium Paramolybdate Tetrahydrate with 2,2-Dimethoxypropane in the Presence of Acetic Anhydride


Figure 6. The Infrared Spectrum of $\left(\mathrm{NH}_{4}\right)_{6} \mathrm{Mo}_{7} \mathrm{O}_{24} \cdot{ }^{-5 \mathrm{CH}_{3} \mathrm{OH}}$


Figure 7. The Infrared Spectrum of the Product of the Reaction of Ammonium Paramolybdate Tetrahydrate with 2,2-Dimethoxypropane in Acetonitrile


## Table II. The Mass Spectrum of Anhydrous Ammonium Oxalate

$\mathrm{m} / \mathrm{e}$ ..... $\%$
100 ..... 13
66 ..... 47
65 ..... 11
57 ..... 10
56 ..... 95
55 ..... 99
54 ..... 90
51 ..... 91
50 ..... 46
49 ..... 18
48 ..... 50
46 ..... 76
45 ..... 18
41 ..... 51
40 ..... 16
39 ..... 93
38 ..... 100
37 ..... 44
28 ..... 93
27 ..... 88
26 ..... 83
25 ..... 73
24 ..... 24

Table III. The Mass Spectrum of the Product of the Reaction of Ammonium Paramolybdate Tetrahydrate with Triethyl Orthoformate in 1,2-Dimethoxyethane

| $\mathrm{m} / \mathrm{e}$ | \% | $\mathrm{m} / \mathrm{e}$ | \% |
| :---: | :---: | :---: | :---: |
| 206 | 19 | 38 | 21 |
| 97 | 26 | 36 | 58 |
| 94 | 30 | 32 | 70 |
| 69 | 38 | 31 | 36 |
| 60 | 32 | 30 | 83 |
| 58 | 30 | 29 | 57 |
| 57 | 42 | 27 | 75 |
| 56 | 21 | 26 | 23 |
| 55 | 38 | 20 | 19 |
| 46 | 36 | 19 | 21 |
| 44 | 74 | 18 | 28 |
| 43 | 96 | 17 | 32 |
| 42 | 26 | 16 | 100 |
| 41 | 38 | 15 | 92 |
| 39 | 26 |  |  |

Table IV. The Mass Spectrum of the Product of the Reaction of Ammonium Paramolybdate Tetrahydrate with 2,2-Dimethoxypropane in the Presence of Acetic Anhydride

| m/e | \% | $\mathrm{m} / \mathrm{e}$ | \% | $\mathrm{m} / \mathrm{e}$ | \% |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 281 | 9 | 119 | 60 | 71 | 66 |
| 264 | 12 | 115 | 100 | 69 | 91 |
| 263 | 35 | 114 | 41 | 68 | 79 |
| 207 | 29 | 113 | 97 | 67 | 91 |
| 206 | 29 | 111 | 35 | 64 | 87 |
| 189 | 40 | 109 | 43 | 61 | 81 |
| 188 | 99 | 101 | 47 | 60 | 72 |
| 187 | 43 | 100 | 49 | 59 | 72 |
| 173 | 56 | 99 | 84 | 55 | 74 |
| 172 | 94 | 98 | 41 | 54 | 43 |
| 161 | 40 | 97 | 56 | 49 | 79 |
| 160 | 51 | 89 | 69 | 48 | 63 |
| 159 | 66 | 88 | 41 | 47 | 68 |
| 156 | 34 | 87 | 51 | 46 | 32 |
| 146 | 37 | 86 | 65 | 45 | 66 |
| 145 | 81 | 85 | 66 | 44 | 12 |
| 144 | 88 | 83 | 49 | 43 | 82 |
| 143 | 88 | 82 | 54 | 35 | 34 |
| 141 | 40 | 81 | 85 | 33 | 54 |
| 133 | 46 | 80 | 78 | 32 | 60 |
| 132 | 90 | 79 | 35 | 31 | 41 |
| 131 | 65 | 75 | 44 | 18 | 74 |
| 129 | 52 | 74 | 63 | 17 | 62 |
| 127 | 59 | 73 | 68 | 16 | 44 |
| 120 | 31 | 72 | 44 | 15 | 41 |

## Table V. The Mass Spectrum of $\left(\mathrm{NH}_{4}\right)_{6} \mathrm{Mo}_{7} \mathrm{O}_{24} \cdot{ }^{-5 \mathrm{CH}_{3} \mathrm{OH}}$

m/e ..... \%
242 ..... 26
167 ..... 28
45 ..... 86
42 ..... 11
30 ..... 68
28 ..... 100
17 ..... 22
16 ..... 28
13 ..... 39

Table VI. The Powder Pattern for Anhydrous Ammonium Oxalate ( 114.6 mm Film)

| $\mathrm{d}_{\text {obsd }}, \mathrm{A}^{\mathrm{o}}$ | $\mathrm{d}_{\text {calcd }}, \mathrm{A}^{0}$ | $\underline{I / I}$ | $h k 1{ }^{\text {a }}$ |
| :---: | :---: | :---: | :---: |
| 6.810 | 6.77874 | m | 010 |
| 6.416 | 6.39172 | vw | $0 \overline{11}$ |
| 5.681 | 5.67518; 5.62145 | m | I01, 100 |
| 5.471 | 5.49345; 5.40448 | $s$ | $\overline{110, ~} 111$ |
| 5.039 | $\begin{aligned} & 5.04591 ; 5.01857 ; \\ & 4.94711 \end{aligned}$ | m | $\overline{102, ~ 003, ~} 1 \overline{11}$ |
| 4.271 |  | vw |  |
| 3.770 | 3.76393; 3.74281 | W | 004, 111 |
| 3.591 | 3.58253; 3.57707 | S | $11 \overline{2}, \overline{120}$ |
| 3.507 | $\begin{aligned} & 3.51474 ; 3.48793 ; \\ & 3.47575 \end{aligned}$ | m | $\overline{121, ~} 104,1 \overline{13}$ |
| 3.187 | $\begin{aligned} & 3.19586 ; 3.17773 ; \\ & 3.17607 \end{aligned}$ | W | $0 \overline{2} 2,1 \overline{2} 2,014$ |
| 3.100 | 3.10247; 3.09001 | s | $\overline{211, ~} 112$ |
| 3.018 | 3.03158; 3.01114 | vs | $\overline{212, ~} 005$ |
| 2.831 | 2.84474; 2.83759 | w | 015, $\overline{202}$ |
| 2.746 | 2.74673; 2.73696 | S | $\overline{220, ~} 113$ |
| 2.652 | $\begin{aligned} & 2.66305 ; 2.63907 ; \\ & 2.65113 ; 2.63907 \end{aligned}$ | W | $\frac{201}{2 \overline{21}}, 2 \overline{1} 2, \overline{1} 24,$ |
| 2.578 | 2.57816 | m | $11 \overline{5}$ |
| 2.468 | 2.47355; 2.46739 | vw | $2 \overline{2} 2,202$ |
| 2.417 | $\begin{aligned} & 2.42250 ; 2.41809 ; \\ & 2.41769 ; 2.41694 ; \\ & 2.41680 ; 2.41089 \\ & 2.41062 ; 2.40797 \end{aligned}$ | S | $\begin{aligned} & \frac{0 \overline{1} 6}{13}, 1 \overline{3} 1,114, \\ & \frac{131}{116}, 2 \overline{13}, \end{aligned}$ |
| 2.309 | 2.31378; 2.30094 | w | $\overline{205, ~} 210$ |
| 2.276 | $\begin{aligned} & 2.28146 ; 2.28058 ; \\ & 2.27361 ; 2.27225 \end{aligned}$ | Vw | $\begin{aligned} & 2 \overline{2} 3,11 \overline{6}, 21 \overline{3}, \\ & 122 \end{aligned}$ |
|  |  |  | ued - |

Table VI. Continued

| $\mathrm{d}_{\text {obsd }}, \mathrm{A}^{\mathrm{o}}$ | $\mathrm{d}_{\text {calcd }}, \mathrm{A}^{\mathrm{O}}$ | $\underline{I / I}{ }^{0}$ | $h k 1^{\text {a }}$ |
| :---: | :---: | :---: | :---: |
| 2.222 | 2.21770 | vw | $0 \overline{32}$ |
| 2.191 | 2.18944; 2.18363 | vw | $\overline{2} 32, \overline{2} 25$ |
| 2.132 | 2.13057; 2.12954 | vw | 0333, 106 |
| 2.103 | $\begin{aligned} & 2.10677 ; 2.10580 ; \\ & 2.10472 ; 2.10325 ; \\ & 2.10294 ; 2.09758 ; \\ & 2.09648 \end{aligned}$ | m | $\begin{aligned} & \overline{2} 06, \frac{0 \overline{2} 6}{0}, \frac{\overline{2} 33,}{\overline{1} \overline{7},} \overline{11}, \overline{126}, \end{aligned}$ |
| 2.058 | $\begin{aligned} & 2.05522 ; 2.05482 ; \\ & 2.05432 ; 2.05313 \end{aligned}$ | w | $\begin{aligned} & \overline{3} 12, \overline{3} 11, ~ \\ & 204 \end{aligned} \overline{3} 4,$ |
| 1.981 | 1.98013; 1.97913 | w | $\overline{3} 23,2 \overline{3} 3$ |
| 1.896 | $\begin{aligned} & 1.89857 ; 1.89857 ; \\ & 1.89173 ; 1.89162 \end{aligned}$ | vw | $\frac{\overline{135}}{027}, 21 \overline{6}, \overline{3} 03,$ |
| 1.866 | $\begin{aligned} & 1.87084 ; 1.87066 ; \\ & 1.86835 ; 1.86728 ; \\ & 1.86680 ; 1.86237 \end{aligned}$ | vw | $\begin{aligned} & 22 \overline{1}, 13 \overline{2}, \overline{2} 35, \\ & 034,205,130 \end{aligned}$ |
| 1.847 | 1.84835; 1.84369 | w | $\overline{3} 31,22 \overline{3}$ |
| 1.704 | $\begin{aligned} & 1.70549 ; 1.70130 ; \\ & 1.70049 \end{aligned}$ | vw | 143, 206, 041 |
| 1.637 | 1.63720; 163378 | w | 22 $\overline{6}$, 223 |
| 1.615 | $\begin{aligned} & 1.61753 ; 1.61734 ; \\ & 1.61691 ; 1.61494 \end{aligned}$ | w | $\frac{2 \overline{1} 7}{137}, 1 \overline{3} \overline{7}, \overline{2} 37,$ |
| 1.480 | 1.47886 | vw | 313 |
| 1.439 | $\begin{aligned} & 1.44019 ; 1.44003 ; \\ & 1.43962 ; 1.43755 ; \\ & 1.43691 \end{aligned}$ | vw | $\frac{4 \overline{2} 2}{402}, \overline{1} 51, \overline{4}, \overline{2} 52,$ |
| 1.042 | 1.04268; 1.04191 | vw | 424, $25 \overline{6}$ |
| 1.001 | 1.00174; 1.00039 | vw | 614, $1 \overline{7} 4$ |
| 0.991 | 0.99129; 0.99116 | vw | 4717, 254 |

a. Based on the unit cell given in the text on page 34 .

Table VII. The Powder Pattern of $\left(\mathrm{NH}_{4}\right){ }_{6} \mathrm{Mo}_{7} \mathrm{O}_{24} \cdot \mathrm{SCH}_{3} \mathrm{OH}$ (114.6 mm Film)

| $\mathrm{d}_{\mathrm{obsd}}, \mathrm{~A}^{\mathrm{o}}$ | $\mathrm{d}_{\text {calcd }}, \mathrm{A}^{0}$ | $\underline{I / I}{ }_{0}$ | $h k 1^{\text {a }}$ |
| :---: | :---: | :---: | :---: |
| 10.704 | 10.91108; 10.75385 | $s$ | 010, 100 |
| 9.707 | 9.76362 | 5 | $0 \overline{11}$ |
| 9.137 | 9.03552 | S | $\overline{101}$ |
| 8.124 | 8.03851 | s | 110 |
| 7.762 | 7.84314 | s | 002 |
| 7.381 | 7.44769; 7.32880 | s | 111, 110 |
| 6.948 | $\begin{aligned} & 7.02797 ; 6.94905 ; \\ & 6.89229 \end{aligned}$ | $s$ | 11I, $0 \overline{12}, \overline{111}$ |
| 6.398 | 6.45785 | S | $\overline{102}$ |
| 5.405 | $\begin{aligned} & 5.44609 ; 5.37692 ; \\ & 5.36407 \end{aligned}$ | m | $\overline{021}, 200, \overline{112}$ |
| 5.025 | $\begin{aligned} & 5.05699 ; 5.02662 ; \\ & 5.01996 ; 5.01592 ; \\ & 5.00966 \end{aligned}$ | W | $\begin{aligned} & \overline{120}, \frac{201,}{210} \\ & 1121 \end{aligned}$ |
| 4.345 | $\begin{aligned} & 4.35630 ; 4.35091 ; \\ & 4.33991 \end{aligned}$ | w | 202, 12 $\overline{2}, 211$ |
| 4.162 | 4.16126, 4.14514 | W | 022, $\overline{212}$ |
| 3.924 |  | w |  |
| 3.818 | 3.82965; 3.80724 | W | 212, $\overline{2} 21$ |
| 3.676 | 3.68440; 3.66440 | w | 22], 220 |
| 3.494 |  | S |  |
| 3.330 |  | $s$ |  |
| 3.208 |  | m |  |
| 3.102 |  | m |  |
| 2.937 |  | m |  |
| 2.780 |  | VW |  |
| 2.644 |  | vw |  |

Table VII. Continued

| $\mathrm{d}_{\text {obsd }}, \mathrm{A}^{\mathrm{o}}$ | $\mathrm{d}_{\text {calcd }}, \mathrm{A}^{\mathrm{o}}$ | $\underline{I / I}{ }_{0}$ | $h k 1^{\text {a }}$ |
| :---: | :---: | :---: | :---: |
| 2.412 |  | w |  |
| 2.356 |  | w |  |
| 2.316 |  | w |  |
| 2.201 |  | vw |  |
| 2.083 |  | vw |  |
| 1.971 |  | vw |  |
| 1.904 |  | vw |  |
| 1.804 |  | vw |  |
| 1.734 |  | vw |  |
| 1.568 |  | vw |  |
| 1.472 |  | vw |  |
| 1.330 |  | vw |  |

a. Indices determined on the basis of the unit cell described in the text on page 35.

## 2. Results and Discussion

## A. Ammonium Oxalate

The fact that the products of the reaction of ammonium oxalate hydrate with the various dehydrating agents in various solvents decompose at $225^{\circ} \mathrm{C}$ (Erdey, Gal, and Liptay ${ }^{6}$ reported that ammonium oxalate monohydrate decomposes at $235^{\circ} \mathrm{C}$ ) is a good indication that the products are ammonium oxalates. The elemental analysis is also in reasonable agreement with the calculated values.

The mass spectrum of the "anhydrous" ammonium oxalate contains a number of fragments that correspond to some of the decomposition products, such as formic acid ( $\mathrm{m} / \mathrm{e}=46$ ) and carbon monoxide ( $\mathrm{m} / \mathrm{e}=28$ ) . The infrared spectrum contains the usual band for the ammonium ion at about $2400 \mathrm{~cm}^{-1}$ (probably lowered because of hydrogen bonding). The infrared band above $3500 \mathrm{~cm}^{-1}$ is at too high a frequency to be a water peak and is attributable to hydrogen bonding between the ammonium ion and the oxygens in the oxalate group. The band at about $1380 \mathrm{~cm}^{-1}$ can be attributed to carbon-oxygen vibrations and the band at 760 can be attributed to C-C vibrations.

The reaction of ammonium oxalate with 2,2 -dimethoxypropane in dioxane yields a product that decomposes to a liquid that immediately boils away. This indicates, probably, that the ammonium oxalate decomposes, leaving the dioxane (b. p. $101^{\circ} \mathrm{C}$ ) which would immediately boil. The infrared spectrum has the usual ammonium ion ( $3200 \mathrm{~cm}^{-1}$ ) and $C=0\left(1620 \mathrm{~cm}^{-1}\right)$ absorptions, as well as a broad band at about $1220 \mathrm{~cm}^{-1}$ which is attributable to cyclic $\mathrm{C}-0$ vibrations. There are also bands which correspond to $C-C$ vibrations ( $770 \mathrm{~cm}^{-1}$ and $720 \mathrm{~cm}^{-1}$ ) and $\mathrm{CH}_{2}$ vibrations ( $640 \mathrm{~cm}^{-1}$ ).

The data indicate that all of the techniques tried were successful in dehydrating ammonium oxalate monohydrate. The reaction in dioxane probably leads to a dioxane adduct. Although the required reaction time apparently varies with the solvent chosen, there is no correlation with any of the usual solvent properties, such as boiling point, dielectric constant, etc. The data are not sufficient to test the presure/volume approach discussed by Dack. 54

The unit cell determination for anhydrous ammonium oxalate gave a triclinic cell with the parameters $a=6.213 \mathrm{~A}^{\circ}, b=7.385 \mathrm{~A}^{\circ}$, $c=15.406 \mathrm{~A}^{\circ}, \alpha=90.3, \beta=101.2^{\circ}$, and $Y=112.2^{\circ}$.

## B. Ammonium Paramolybdate

The infrared spectra of the products of the reactions of ammonium paramolybdate tetrahydrate with triethyl orthoformate and the reaction of ammonium paramolybdate tetrahydrate with 2,2-dimethoxypropane and acetic anhydride have aborptions near $1600 \mathrm{~cm}^{-1}$ that indicate $C=0$ vibrations, and near $3400 \mathrm{~cm}^{-1}$ that indicate the presence of the ammonium ion. The mass spectra of the products of the reaction of ammonium paramolybdate tetrahydrate with triethyl orthoformate in 1,2-dimethoxyethane and the product of the reaction of ammonium paramolybdate tetrahydrate with 2,2-dimethoxypropane and acetic anhydride have $m / e$ peaks at 44 , which corresponds to a $\mathrm{CO}_{2}$ fragment from an organic acid, and at 18 , which corresponds to an ammonium ion, These compounds may be polymeric acid derivatives. It is known that metal molybdates catalyze the hydrogenation of the carbonyl groups of esters. 55, 56

The product of the reaction of ammonium paramolybdate with 2,2-dimethoxypropane is probably not an acid derivative, in spite of the infrared absorption at about $1600 \mathrm{~cm}^{-1}$, because there is no mass spectrum peak at $m / e=44$ from a $\mathrm{CO}_{2}$ fragment of an acid. The infrared absorption at about $1600 \mathrm{~cm}^{-1}$ is attributable to an NH vibration or to an overtone of an Mo-O vibration that occurs at a lower frequency. The presence of $0-\mathrm{H}\left(1420 \mathrm{~cm}^{-1}\right), \mathrm{C}-0\left(1030 \mathrm{~cm}^{-1}\right)$, and $\mathrm{CH}_{2}\left(1320 \mathrm{~cm}^{-1}\right.$, $930 \mathrm{~cm}^{-1}$ ) bands in infrared spectrum indicate that this compound may be a methanol adduct. Molybdenum compounds in which alcohols are coordinated to molybdenum have been reported for manitol, ${ }^{57,} 58$ chloral hydrate ${ }^{59}$ (which is a geminal diol ${ }^{60}$ ), ethanol, ${ }^{61}$ and methanol. ${ }^{62,} 63$ The infrared absorption at $3200 \mathrm{~cm}^{-1}$ indicates that it is an ammonium salt. The unit cell determination gave two triclinic cells that fit the powder pattern equally well and are probably variations of the same cell. The first cell has the parameters $a=10.808 \mathrm{~A}^{\circ}, b=11.112 \mathrm{~A}^{\circ}, c=15.920 \mathrm{~A}^{\circ}, \boldsymbol{\alpha}=99.56^{\circ}$, $\beta=91.37^{\circ}$, and $\gamma=94.98^{\circ}$. The second cell has the parameters $a=11.673 \mathrm{~A}^{\circ}$, $b=11.974 \mathrm{~A}^{\circ}, c=15.347 \mathrm{~A}^{\circ}, \quad \propto=103.19^{\circ}, \boldsymbol{\beta}=92.59 \mathrm{~A}^{\circ}$, and $\boldsymbol{\gamma}=111.98^{\circ}$. A qualitative inspection of the indices for the d values generated by the two cells indicates that the first cell may be the correct one because it gives simpler indices. The indices based on the first cell are given in Table VII.

The reaction of ammonium paramolybdate tetrahydrate with 2,2-dimethoxypropane in acetonitrile yielded a tar. It is an ammonium salt (infrared absorbtion at $3150 \mathrm{~cm}^{-1}$ ). It probably is not a nitrile adduct since there is no $\mathrm{C} \cong \mathrm{N}$ absorption at about $2000 \mathrm{~cm}^{-1}$. A nitrile will hydrolyze in acid solution, and this could cause an acid derivative to be synthesized with an infrared absorption at $1600 \mathrm{~cm}^{-1}$.

The only reaction that appears to have occured when ammonium paramolybdate tetrahydrate was dissolved in a solution of ammonia in methanol was the replacement of some water of hydration by some methanol. When ammonium paramolybdate was dissolved in methanol, the $N /$ Mo mole ratio decreased from $6 / 7$ to about $4 / 8$, possibly because of the reactions $\left(\mathrm{NH}_{4}\right)_{6} \mathrm{Mo}_{7} \mathrm{O}_{24} \longrightarrow\left(\mathrm{NH}_{4}\right)_{4} \mathrm{H}_{3} \mathrm{MO}_{7} \mathrm{O}_{24}+3 \mathrm{NH}_{3}$ and $\left(\mathrm{NH}_{4}\right)_{4} \mathrm{H}_{3} \mathrm{MO}_{7} \mathrm{O}_{24} \longrightarrow$ $\left(\mathrm{NH}_{4}\right)_{3} \mathrm{H}_{4} \mathrm{Mo}_{7} \mathrm{O}_{24}+\mathrm{NH}_{3}$. This is supported by the fact that 4 M solutions of ammonia in methanol can be prepared easily. 46 The acid-base properties of the ammonium paramolybdate may be affected by the change in solvent to a large enough extent to allow this reaction to occur. The resulting molybdenum compound could also lose water of hydration, in a manner similar to the reaction of ammonium paramolybdate tetrahydrate in the solutions of ammonia in methanol.

## 3. Conclusions

Ammonium oxalate monohydrate and ammonium paramolybdate tetrahydrate were dehydrated by 2,2-dimethoxypropane in the presence of small amounts of acetic acid to give anhydrous ammonium oxalate and a methanol adduct of ammonium paramolybdate with five coordinated methanol molecules. Ammonium oxalate was also dehydrated by triethyl orthoformate, and this reaction shows some solvent effects. Ammonium paramolybdate tetrahydrate reacted with triethyl orthoformate to give tars and this reaction also showed some solvent effects. Attempts to form anhydrous ammonium molybdates by reacting ammonium paramolybdate tetrahydrate with ammonia in methanol were also unsuccessful.

## CHAPTER II.

METAL MOLYBDATES

1. Experimental

## A. Reagents

See Chapter I, page 4.

## B. Analyses

CHN Analyses were run by Mrs. Deanna Cardin on an F \& M Model
185 CHN Analyser.
The analysis for molybdenum is that described in Chapter $I$, page 4. EDTA was added as a masking agent for the other metals. 42,43

Copper was determined gravimetrically as the 8-quinolinol complex, 41,44 the anthranilate, ${ }^{64}$ or the thiocyanate. ${ }^{65-67}$

Cadmium was determined gravimetrically as the 8-quinolinol complex ${ }^{41,} 44$ or the thiourea reinickate. 68

Bismuth was determined volumetrically as the EDTA complex ${ }^{69}$ or gravimetrically as the oxychloride. ${ }^{70}$

Bromide was determined by the Mohr method.
C. Compound Preparation

1. Metal Bromides

Copper(II), cadmium(II), bismuth(III), and tin(IV) bromides were
prepared by adding increments of elemental bromine to the metal in dry methanol until all of the metal had reacted. ${ }^{71}$ Solid $\mathrm{CuBr}_{2}$ could be dissolved directly in methanol with no apparent affect on the results.

## 2. Anhydrous Ammonium Paramolybdate

Anhydrous ammonium paramolybdate was prepared by refluxing
ammonium paramolybdate tetrahydrate with 2,2-dimethoxypropane and
acetic acid in a manner similar to the described in Chapter $I$. The fact that no hydrolysis products of the metal bromides were observed indicates that the reaction was probably successful.

## 3. Attempted Synthesis of Cadmium Molybdate

Cadmium bromide was made from 2.35 g ( 0.021 moles) of cadmium and 2.0 ml of bromine in 50 ml of methanol. Anhydrous ammonium paramolybdate was made from 3.20 g ( 0.0026 moles) of ammonium paramolybdate tetrahydrate, 190 ml of 2,2 -dimethoxypropane, and 9 ml of acetic acid. 55 ml of methanol, the anhydrous ammonium paramolybdate, and the solution of $\mathrm{CdBr}_{2}$ were mixed and stirred for 5.5 hr . The product was filtered out and washed and methanol.

Anal. Found: H, 1.64; Cd, 3.37; Mo, 47.34.
Another trial with a different reaction time and a different ratio of reactants gave the same results.
4. Attempted Synthesis of Tin Molybdate

Tin bromide was made from 0.43 g ( 0.0036 moles) of tin and 1.8 ml of bromine in 43 ml of methanol. Anhydrous ammonium paramolybdrate was made from 1.51 g ( 0.0012 moles) of ammonium paramolybdate tetrahydrate, 190 ml of 2,2-dimethoxypropane, and 4 ml of acetic acid. The anhydrous ammonium paramolybdate, 47 ml of methanol, and the solution of tin bromide were mixed and stirred for 3.5 hr . Analysis of the powder pattern and qualitative chemical tests showed that the product probably contained tin bromide, ammonium bromide, and an ammonium molybdate or a molybdenum oxide. Another trial with a different reaction time and a different ratio of reactants gave the same results.
5. Attempted Synthesis of Bismuth Molybdate.

Method \#1: Bismuth bromide was made from 4.9 g ( 0.023 moles) of bismuth and 3.7 ml of bromine in 50 ml of methanol. Anhydrous
ammonium paramolybdate was made from 7.07 g ( 0.0057 moles) of ammonium paramolybdate tetrahydrate, 220 ml of 2,2-dimethoxypropane, and 6 ml of acetic acid. The anhydrous ammonium paramolybdate, 75 ml of methanol, and the bismuth bromide solution were mixed and stirred for 8 hr . The product, when dried, was a yellow solid with blue streaks.

Anal. Found: H, 3.30; Bi, 8.25; Mo, 24.89; N, 11.47. The powder pattern showed that a molybdenum oxide was produced that is similar to that producted in the reaction of anhydrous ammonium paramolybdate with cadmium bromide. The bismuth may have been in the form of bismuth bromide. Other reaction times and other ratios of reactants were tried with the same results.

Method \#2: Bismuth bromide was made from 2.84 g ( 0.014 moles) of bismuth and 4 ml of bromine in 55 ml of methanol. Anhydrous ammonium paramolybdate was made from 4.34 g ( 0.0035 moles) of ammonium paramolybdate tetrahydrate, 180 ml of 2,2-dimethoxypropane, and 5 ml of acetic acid. The anhydrous ammonium paramolybdate, 45 ml of methanol, and the bismuth bromide solution were mixed and refluxed for 3.25 hr .

Anal. Found: C, 1.12; H, 1.47; Bi, 1.91; Mo, 46.94. Other reaction times and reactant ratios were tried with similar results.
6. Attempted Synthesis of Copper Molybdate

Method \#1: Anhydrous ammonium paramolybdate was made from
4.61 g ( 0.0037 moles) of ammonium paramolybdate tetrahydrate, 200 ml of 2,2-dimethoxypropane, and 7 ml of acetic acid. The anhydrous ammonium paramolybdate, 4.60 g ( 0.0 ic moles) of copper(II) bromide, and 140 ml of methanol were mixed and stirred for 0.5 hr .

Anal. Found: C, 0.93; H, 1.82; Cu, 3.36; Mo, 56.44; N, 4.35. The powder pattern showed that the copper was in the form of anhydrous
copper(II) bromide. Other reaction times and reactant ratios were tried with the same results.

Method \#2: Copper(II) bromide was made from 0.73 g ( 0.011 moles) of copper metal and 2 ml of bromine in 55 m 1 of methanol. Anhydrous ammonium paramolybdate was made from 4.34 g ( 0.0035 moles) of ammonium paramolybdate tetrahydrate, 200 ml of 2,2 -dimethoxypropane, and 3 ml of acetic acid. The copper(II) bromide solution, and the anhydrous ammonium paramolybdate, were mixed and refluxed for 50 min .

Anal. Found: $\mathrm{C}, 1.52$; $\mathrm{H}, \mathrm{1.76;}$ Mo, 47.46 .
Other reaction times, reactant ratios, and commercial copper(II) bromide were used with the same results.

Method 非3: 2.26 ( 0.010 moles) of copper(II) bromide, 4.78 g ( 0.0039 moles) of ammonium paramolybdate tetrahydrate and 14.84 g ( 0.10 moles) of triethyl orthoformate were refluxed in 65 ml of methanol for 2 hr. A green solid was filtered out that contained copper and bromine, but no molybdenum, and whose powder pattern has lines in common with the reported pattern for $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{CuBr}_{4} \cdot 2 \mathrm{H}_{2} \mathrm{O}$. When some methanol was stripped off of the filtrate, a white solid was isolated.

Anal. Found: $\mathrm{C}, 1.13 ; \mathrm{H}, 1.64 ; \mathrm{Mo}, 57.28 ; \mathrm{N}, 3.65$. The $N /$ Mo mole ratio is $1 / 2$. Other reactant times and ratios of reactants were tried with no effect on the results. Using ethanol instead of methanol as the solvent also did not affect the results.

## D. X-ray Powder Patterns

X-ray powder patterns were run as described in Chapter 1 page 9.

## E. Infrared Spectra

Infrared spectra were run as described in Chapter I page 9.

Figure 8. The Infrared Spectrum of the Product of the Reaction of Ammonium Paramolybdate Tetrahydrate, Cupric Bromide, and Triethyl Orthoformate in Methanol.


## 2. Results and Discussion

The reaction of ammonium paramolybdate tetrahydrate with copper(II) bromide and triethyl orthoformate apparently gave a hydrated copper(II) bromide and an ammonium molybdate $\left(\mathrm{NH}_{4}^{+}\right.$infrared absorbtion at $3200 \mathrm{~cm}{ }^{-1}$ ). The copper (II) bromide seemed to act as a better dehydrating agent than triethyl orthoformate.

The reactions of anhydrous ammonium paramolybdate with metal bromides gave molybdenum oxides. The ammonia may have been lost in a manner similar to the process that takes place when ammonium paramolybdate tetrahydrate is dissolved in methanol. The equilibrium may have been shifted by the presence of the metal bromide and the absence of water of hydration.

CHAPTER III.

## MOLYBDENUM CARBOXYLATE

## 1. Experimental

## A. Reagents

See Chapter I, page 4. Molybdenum trioxide was dried at $135^{\circ} \mathrm{C}$ overnight prior to use. 72 Anthranilic acid had been recrystalized previously.

## B. Analyses

CHN analyses were as described in Chapter I, page 4.
The procedure for the molybdenum analysis was that described in Chapter $I$, page 4 . The precipitate in the case of the oxalate complex was red and the value obtained did not agree with the calculated value. This is probably due to two factors:

1. Oxalic acid will react with the molybdenum oxinate, when heated, to give molybdenum trioxide. 45
2. 8-Quinolinol reacts with the $M o(V)$ oxalate complex to form a red complex with the molybdenum/oxalate/oxine ratio of $2: 2: 2 .{ }^{73}$

Mixed oxine/acid complexes might have formed in a few of the other cases also.

## C. Preparation of Compounds

1. Method 非1

The method described by Killefer and Linz, ${ }^{33}$ Kay and Mitche11, ${ }^{34}$ Henderson et al, 35,36 and Gopalakrishman et a1. ${ }^{37}$ was attempted for all of the ligands. A solution of the ammonium salt of the carboxylic acid was produced either by dissolving the ammonium salt itself in water or by dissolving the acid in water and adding enough ammonium hydroxide to
bring the pH to about 7. Table VIII gives the quantities of reagents used. A l:1 mole ration was used in all cases. The solution was brought

Table VIII. The quantities of Reagents used in the Synthesis of the Molybdenum Carboxylates

| Acid | grams of <br> acid used | grams of <br> ammonium salt <br> used | ml 15 M <br> $\mathrm{NH}_{4} \mathrm{OH}$ | grams <br> MoO <br> used |
| :--- | :--- | :--- | :--- | :--- |
| acetic | (4.1ml) | 2.7011 | - | 4.7693 |
| benzoic | 4.0537 | - | 2.15 | 4.6315 |
| oxalic | 0.7572 | 8.1939 | - | 4.6188 |
| succinic | 4.0446 | - | 4.60 | 4.7406 |
| tartaric | 5.1147 | - | 4.40 | 4.6370 |
| anthranilic | 4.4260 | - | 2.70 | 4.6082 |
| mandelic | 4.9223 | - | 2.30 | 4.7050 |
| phthalic | 5.3324 | - | 4.50 | 4.7050 |

to a boil and the $\mathrm{MoO}_{3}$ was added in small increments. Each increment was allowed to dissolve before the next was added. The undissolved material was filtered out, and the solution was heated until the product started to precipitate out. The solution was cooled in an ice bath, and the product was filtered and washed with cold water.

The reaction of mandelic acid with molybdenum trioxide gave a blue solution, probably caused by molybdenum blue (a reduced form of molybdenum), and gave off a distinct odor like that of benzaldehyde. The elemental analyses of the other products are given in Table IX.
2. Method \#1 2

A second method was attempted for anthranilic acid. 6.06 g ( 0.0049 mole ) of ammonium paramolybdate tetrahydrate were dissolved in

Table IX．Elemental Analyses for the Products of Method $⿰ ⿰ 三 丨 ⿰ 丨 三 ⿻$

| Acid |  | \％ C | \％ H | \％Mo | \％ | 플 | n |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Acetic | Calc | 10.04 | 3.79 | 40.14 | 5.86 | 1 | 1 |
|  | Found | 2.29 | 1.20 | 51.80 | 4.52 |  |  |
| Benzoic | Calc | 28.00 | 3.36 | 31.98 | 4.67 | 1 | 1 |
|  | Found | 3.03 | 2.81 | 51.06 | 6.63 |  |  |
| Oxalic | Calc | 8.39 | 3.52 | 33.54 | 9.79 | 2 | 1 |
|  | Found | 10.70 | 3.94 | 20.66 | 10.94 |  |  |
| Tartaric | Calc | 13.87 | 4.08 | 27.72 | 8.09 | 2 | 1 |
|  | Found | 13.92 | 3.81 | 25.24 | 8.06 |  |  |
| Phthalic | Calc | 26.51 | 3.90 | 26.50 | 7.74 | 2 | 1 |
|  | Found | 26.64 | 4.03 | 23.00 | 7.70 |  |  |
| Succinic | Calc | 15.28 | 4.49 | 30.55 | 8.92 | 2 | 1 |
|  | Found | 6.93 | 2.70 | 43.99 | 6.43 |  |  |
| Anthranilic＊ | Calc | 26.58 | 3.83 | 30.36 | 8.86 | 1 | 1 |
|  | Found | 60.97 | 5.00 | 1.99 | 10.44 |  |  |

＊Calc for anthranilic acid $\mathrm{C}, 61.13 ; \mathrm{H}, 5.13 ; \mathrm{N}, 10.22$.

75 ml of water and 25 ml of buffer solution. The buffer solution was made up of 4 parts of a $50 \%(v / v)$ acetic acid solution and 3 parts of a $50 \%$ (w/v) ammonium acetate solution. 4.50 g ( 0.033 mole) of anthranilic acid were dissolved in 39 ml of a 1 F sodium hydroxide solution. The anthranilic acid solution was filtered and diluted to 100 ml with water. The ammonium paramolybdate solution was brought to a boil, and the anthranilic acid solution was added. A brown precipitate formed immediately, then gradually changed color to light tan as the solution stood. The solid was filtered out and washed once with hot water and three times with cold water.

Anal. Found: C, 4.56; H, 1.24; Mo, 52.51; N, 3.27.
3. Reaction of Ammonium Molybdenum Oxalate with Copper(II) Chloride

The ammonium molybdenum oxalate complex was reacted with copper(II) chloride as follows: A solution containing 0.5778 g (. 0034 mole) of copper(II) chloride was mixed with a solution containing 0.5893 g (. 002 mole ) of the ammonium molybdenum oxalate complex. The blue solid was filtered out and washed with water.

The product did not contain any molybdenum and its powder pattern contained a large number of lines in common with the file pattern for copper(II) oxalate.

## D. Infrared Spectra

Infrared spectra were run as described in Chapter I, page 9.
The infrared spectrum of ammonium molybdenum oxalate was like that reported by Gopalakrishman, et al. 37 The infrared spectra of the tartrate and phthalate complexes are shown in Figure 9 and 10.

## E. Thermogravimetric Analyses

Thermogravimetric analyses were run on a DuPont Model 950 Thermogravimetric Analyzer.

The thermogravimetric analyses for the tartrate and phthalate complexes are shown in Figure 11 and 12.

## F. Mass Spectra

The mass spectra were determined as described in Chapter I, page 9.
The mass spectra for the oxalate, tartrate, and phthalate complexes are given in Tables X through XII.

## G. X-ray Powder Patterns

The X-ray powder patterns and unit cell determinations were carried out as described in Chapter $I$, page 9.

The powder patterns for the oxalate, tartrate, and phthalate complexes are given in Tables XIII through XV.

Figure 9. Infrared Spectrum of Ammonium Molybdenum Tartrate.


Figure 10. Infrared Spectrum of Ammonium Molybdenum Phthalate.




Table X. The Mass Spectrum of Ammonium Molybdenum Oxalate
m/e $\quad$ \%
14430
$45 \quad 36$
$44 \quad 42$
$43 \quad 67$
423
37 8
$35 \quad 23$
$29 \quad 11$
$28 \quad 14$
$27 \quad 6$
19
100
18 73

1742
1
27

Table XI. The Mass Spectrum of Ammonium Molybdenum Tartrate.

| $\mathrm{m} / \mathrm{e}$ | \% | $\mathrm{m} / \mathrm{e}$ | \% |
| :---: | :---: | :---: | :---: |
| 146 | 2 | 44 | 17 |
| 108 | 2 | 43 | 8 |
| 100 | 2 | 42 | 2 |
| 98 | 4 | 41 | 8 |
| 94 | 2 | 38 | 6 |
| 92 | 2 | 36 | 15 |
| 84 | 8 | 35 | 4 |
| 83 | 4 | 30 | 4 |
| 69 | 6 | 29 | 4 |
| 67 | 8 | 28 | 65 |
| 65 | 4 | 27 | 4 |
| 56 | 10 | 20 | 6 |
| 55 | 2 | 19 | 8 |
| 54 | 10 | 18 | 100 |
| 53 | 2 | 17 | 92 |
| 52 | 2 | 16 | 63 |

Table XII. The Mass Spectrum of Ammonium Molybdenum Phthalate.
m/e ..... \%
350 ..... 42
166 ..... 10
149 ..... 16
148 ..... 56
125 ..... 6
122 ..... 68
106 ..... 62
105 ..... 100
98 ..... 10
77 ..... 16
76 ..... 76
57 ..... 11
56 ..... 5
45 ..... 1
44 ..... 2
38 ..... 9
36 ..... 29
28 ..... 54
18 ..... 78
17 ..... 89
16 ..... 61
1 ..... 7

Table XIII. The Powder Pattern of Ammonium Molybdenum Oxalate (114.6 mm Film)

| $\mathrm{d}_{\text {obsd }}, \mathrm{A}^{\mathrm{o}}$ | $\mathrm{d}_{\text {calc }}, \mathrm{A}^{\mathrm{o}}$ | $\underline{I / I}{ }_{0}$ | $h k 1^{\text {a }}$ |
| :---: | :---: | :---: | :---: |
| 12.6090 | 12.51362 | m | 110 |
| 7.5122 | 7.51316; 7.46826 | m | 200; 001 |
| 6.7071 | 6.73534; 6.63950 | S | 130; 111 |
| 6.2623 | $\begin{aligned} & 6.25681 ; 6.23081 ; \\ & 6.20818 \end{aligned}$ | m | 220; 021; 111 |
| 5.1022 | 5.10697; 5.06979 | VW | 13I; 201 |
| 4.8982 | 4.90270; 4.89015 | w | 131; 310 |
| 4.5314 | 4.51613; 4.50633 | w | 240; 041 |
| 4.3322 | 4.32911 | VW | 150 |
| 4.1558 | 4.17121 | VW | 330 |
| 3.7903 | $\begin{aligned} & 3.78895 ; 3.77369 \text {; } \\ & 3.76733 \end{aligned}$ | S | 151; 241; 060 |
| 3.5297 | 3.54562; 3.52901 | VW | 022; 331 |
| 3.3240 | $\begin{aligned} & 3.33154 ; 3.32414 ; \\ & 3.31975 \end{aligned}$ | $s$ | 42 $\overline{1} ; 13 \overline{2} ; 22 \overline{2}$ |
| 3.1523 | 3.15706 | vw | 170 |
| 3.0228 | 3.02386 | W | 261 |
| 2.9280 | 2.92817 | w | 171 |
| 2.8550 | $\begin{aligned} & 2.86518 ; 2.85767 ; \\ & 2.84764 \end{aligned}$ | W | $\overline{152 ; ~ 511 ~ ; ~} 312$ |
| 2.7849 | 2.79142; 2.79141 | m | 152; 530 |
| 2.6602 | 2.66009; 2.65209 | m | 460; 062 |
| 2.5865 | 2.59239 | W | $37 \overline{1}$ |
| 2.5183 | 2.51862 | W | $28 \overline{1}$ |
| 2.4346 | $\begin{aligned} & 2.43911 ; 2.43406 ; \\ & 2.43114 ; 2.43041 ; \\ & 2.42945 \end{aligned}$ | W | $\begin{aligned} & 51 \overline{2} ; \overline{1} 7 \underline{2} ; 023 ; \\ & \frac{203 ; ~ 55 \overline{1}}{} \end{aligned}$ |

Table XIII. Continued

| $\mathrm{d}_{\text {obsd }}, \mathrm{A}^{\mathrm{o}}$ | $\mathrm{d}_{\text {calc }}, \mathrm{A}^{\circ}$ | $\underline{I / I}{ }_{0}$ | $h k 1^{\text {a }}$ |
| :---: | :---: | :---: | :---: |
| 2.3642 | 2.36681 | w | $\overline{133}$ |
| 2.2464 | $\begin{aligned} & \text { 2.24907; } 2.24511 ; \\ & 2.24224 \end{aligned}$ | W | 37-2; 390; 641 |
| 2.2090 | 2.21317 | VW | $33 \overrightarrow{3}$ |
| 2.1734 | 2.17480; 2.17397 | W | 391; $60 \overline{2}$ |
| 2.1337 | $\begin{aligned} & 2.13700 ; 2.13484 ; \\ & 2.13388 ; 2.13114 ; \\ & 2.21966 \end{aligned}$ | vw | $\begin{aligned} & 710 ; 62 \overline{2} ; 153 ; \\ & 243 ; 42 \overline{3} \end{aligned}$ |
| 2.0794 | 2.07876: 2.07694 | m | 192; 063 |
| 2.0094 | 2.00936; 2.00676 | VW | 552; 711 |
| 1.9271 | 1.92717 | m | 590 |
| 1.8777 | $\begin{aligned} & 1.87942 ; 1.87940 ; \\ & 1.87829 ; 1.87807 \end{aligned}$ | w | $\begin{aligned} & 443 \overline{3} ; 46 \overline{3} ; 800 ; \\ & 73 \overline{2} \end{aligned}$ |
| 1.8268 | $\begin{aligned} & 1.82794 ; 1.82768 ; \\ & 1.82642 \end{aligned}$ | m | 62 ${ }^{\text {\% }}$; 22 $\overline{4}$; 114 |
| 1.7751 | 1.77435; 1.77281 | VW | 204; 044 |
| 1.7229 | 1.72299; 1.72285 | W | $68 \overline{2} ; 82 \overline{2}$ |
| 1.6922 | 1.69286 | vw | 244 |
| 1.6551 | 1.65519 | VW | 2,10, $\overline{3}$ |
| 1.6208 | $\begin{aligned} & 1.62077 ; 1.61954 ; \\ & 1.61908 \end{aligned}$ | vw | 174; 802; 643 |
| 1.5728 | 1.57156 | VW | 791 |
| 1.5399 | 1.53844 | VW | 2,14,1 |
| 1.5027 | $\begin{aligned} & 1.50380 ; 1.50263 ; \\ & 1.50263 ; 1.50211 ; \\ & 1.50193 \end{aligned}$ | VW | $\begin{aligned} & 374 ; 284 ; 10,0,0 ; \\ & 0,12,3 ; \frac{194}{194} \end{aligned}$ |
| 1.3960 | $\begin{aligned} & 1.39678 ; 1.39576 ; \\ & 1.39571 ; 1.39571 ; \\ & 1.39541 \end{aligned}$ | w | $\begin{aligned} & \overline{3} 55 ; 10,4, \overline{2} ; \\ & 2,10,4 ; 10,6,0 ; \\ & 245 \end{aligned}$ |

Table XIII. Continued

| $\mathrm{d}_{\text {obsd }}, \mathrm{A}^{0}$ | $\mathrm{d}_{\text {calcd }}, \mathrm{A}^{0}$ | $\underline{I / I}{ }_{0}$ | $h k 1^{\text {a }}$ |
| :---: | :---: | :---: | :---: |
| 1.3516 | 1.35182; 1.35137 | w | 10,0,2; 10,6,1 |
| 1.3020 | $\begin{aligned} & 1.30261 ; 1.30258 ; \\ & 1.30182 \end{aligned}$ | w | $\frac{11,3,2}{645} ; 11,3,1 ;$ |
| 1.2640 | 1.26412; 1.26411 | vw | 735; 10,6, $\overline{3}$ |
| 1.2499 | 1.24978 | vw | 10,10, $\overline{1}$ |
| 1.1749 | $\begin{aligned} & 1.17555 ; 1.17502 ; \\ & 1.17466 ; 1.17455 \end{aligned}$ | vw | $\begin{aligned} & 10,6,3 ; 715 ; \\ & 10,12,0 ; 536 \end{aligned}$ |
| 1.1523 | $\begin{aligned} & 1.15242 ; 1.15237 ; \\ & 1.15225 ; 1.15221 ; \\ & 1.15162 \end{aligned}$ | vw | $\begin{aligned} & 11,1,4 ; 11,1,3 ; \\ & 266 ; 954 ; 626 \end{aligned}$ |
| 1.1308 | 1.13093; 1.13046 | vw | 685; $95 \overline{5}$ |
| 1.1198 | 1.12020 | vw | 805 |
| 1.0122 | 1.01228; 1.01209 | vw | 886; 975 |
| 0.96826 | 0.96839 | vw | 2,14,6 |
| 0.92365 | 0.92365 | vw | 5,23,1 |
| 0.92207 | 0.92178 | vw | 667 |
| 0.83884 | 0.83891 | vw | 2,12,8 |

a. Based on the unit cell given in Table XVI.

Table XIV. The Powder Pattern for Ammonium Molybdenum Tartrate ( 114.6 mm Film)

a. Based on the Powder pattern given in Table XVI

Table XV. The Powder Pattern of Ammonium Molybdenum Phthalate (114.6 mm Film)


Table XV. Continued

| $\mathrm{d}_{\text {obsd }}, \mathrm{A}^{\mathrm{o}}$ | $\mathrm{d}_{\mathrm{calcd}}, \mathrm{~A}^{\mathrm{o}}$ | $I / I_{0}$ | hki ${ }^{\text {a }}$ |
| :---: | :---: | :---: | :---: |
| 2.8965 | 2.89610 | $s$ | 224 |
| 2.7942 | 2.79901 | VW | $33 \overline{1}$ |
| 2.7385 | 2.73635 | w | 514 |
| 2.7095 | 2.70855; 2.70384 | VW | 333, $\overline{2} 04$ |
| 2.6442 | 2.64331 | vw | 315 |
| 2.5865 | 2.58766 | vW | 005 |
| 2.5349 | $2.53720 ; 2.53597$ | vw | $33 \overline{2}, 622$ |
| 2.4144 |  | m |  |
| 2.3583 |  | w |  |
| 2.3020 |  | Vw |  |
| 2.1684 |  | vw |  |
| 2.1001 |  | w |  |
| 2.0592 |  | w |  |
| 1.9848 |  | m |  |
| 1.9375 |  | vw |  |
| 1.8791 |  | VW |  |
| 1.8473 |  | VW |  |
| 1.8142 |  | VW |  |
| 1.7601 |  | m |  |
| 1.7353 |  | W |  |
| 1.7163 |  | w |  |
| 1.6628 |  | VW |  |
| 1.6203 |  | w |  |
| 1.5725 |  | w |  |
| 1.5509 |  | m |  |
| 1.5148 |  | VW |  |
|  |  | continued - |  |

Table XV. Continued

| $\mathrm{d}_{\text {obsd }}, \mathrm{A}^{\mathrm{o}}$ | $\mathrm{d}_{\text {calcd }}, \mathrm{A}^{\mathrm{o}}$ | $\underline{I / I}{ }_{0}$ | $h k 1^{a}$ |
| :---: | :---: | :---: | :---: |
| 1.5000 |  | VW |  |
| 1.4809 |  | VW |  |
| 1.4553 |  | VW |  |
| 1.4179 |  | vw |  |
| 1.3969 |  | w |  |
| 1.3752 |  | vw |  |
| 1.3530 |  | VW |  |
| 1.3324 |  | vw |  |
| 1.3136 |  | vW |  |
| 1.2847 |  | VW |  |
| 1.2568 |  | vw |  |
| 1.1820 |  | vw |  |
| 1.1624 |  | VW |  |
| 1.1480 |  | Vw |  |
| 1.1246 |  | VW |  |
| 1.0975 |  | VW |  |
| 1.0284 |  | VW |  |
| 0.86143 |  | VW |  |
| 0.84463 |  | vw |  |
| 0.80515 |  | VW |  |
| 0.80242 |  | VW |  |
| 0.78474 |  | vw |  |
| 0.78327 |  | VW |  |
| 0.77752 |  | VW |  |
| 0.77589 |  | VW |  |

a. Based on the unit cell given in Table XVI.

## 2. Results and Discussion

Oxalic acid, tartaric acid, and phthalic acid all formed stable 1:1 complexes of the type $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{MoO}_{3}(\mathrm{Acid}) \cdot \mathrm{H}_{2} \mathrm{O}$. The oxalate complex was studied by Gopalskrishman et al. ${ }^{37}$ Henderson and Barr ${ }^{35}$ made the complex $\mathrm{MoO}_{2}\left(\mathrm{NaC}_{4} \mathrm{H}_{4} \mathrm{O}_{6}\right)_{2} \cdot 3 \mathrm{H}_{2} \mathrm{O}$ by dissolving $\mathrm{MoO}_{3}$ in a boiling solution of sodium hydrogen tartrate in a 1:2 mole ratio. The difference in the constitution between the complex of Henderson and Barr ${ }^{35}$ and the complex reported here is probably due to the difference in the mole ratios of the reactants used ( $1: 1$ mole ratio in this work). Prasad and Pandey ${ }^{74}$ showed that, for citric acid, the Mo/ligand ratio in the complex depended on the mole ratio in the reaction mixture. The phthalate complex has not been reported in the literature. A11 three complexes have the infrared absorptions for the ammonium ion (about $3100 \mathrm{~cm}^{-1}$ ) and for the carbonyl group (about $1600 \mathrm{~cm}^{-1}$ ). The oxalate and tartrate complexes have the expected $m / e$ peaks at 44 in their mass spectra, also indicating that they are carboxylic acid derivatives. The phthalate complex loses the expected $\mathrm{C}_{6} \mathrm{H}_{4}{ }^{+}$fragment $(\mathrm{m} / \mathrm{e}=76)$, but does not have a significant peak at $\mathrm{m} / \mathrm{e}=44$, probably because the benzene ring forms the more stable cation. By analogy to the oxalate complex, ${ }^{37}$ the presence of three infrared absorptions ( $920 \mathrm{~cm}^{-1}, 875 \mathrm{~cm}^{-1}$, and $750 \mathrm{~cm}^{-1}$ ) which can be attributed to MoO vibrations indicates that the phthalate complex may be an oxo-bridged dimer. The fact that two bands ( $875 \mathrm{~cm}^{-1}$ and $710 \mathrm{~cm}^{-1}$ ) can be attributed to MoO vibrations appear in the infrared spectrum for the tartrate complex indicates that it may also be a dimer. The data are insufficient to support other structural conclusions. The thermogravimetric analyses show that the oxalate complex ${ }^{37}$ and the tartrate
complex do not lose the ligand until about $200^{\circ} \mathrm{C}$, while the phthalate complex starts to lose the ligand at about $160^{\circ} \mathrm{C}$. This indicates that the phthalate ligand is fairly loosely bound, while the oxalate and tartrate ligands are more tightly bound. The unit cell determinations of the three complexes all produced a number of satisfactory cells. The volumes, and other data for the oxalate and tartrate complexes indicate that all of the cells are variations of the same cell. The unit cell determination of the phthalate complex produced only one cell with other than triclinic symmetry. Table XVI gives the simplest monoclinic cell for each complex.

Table XVI. Unit Cells for the Three Carboxylate Complexes. (a, b, and $c$ are in $A^{\circ}, \boldsymbol{\beta}$ is in degrees).

|  | Phthalate | Tartrate | Oxalate |
| :---: | :---: | :---: | :---: |
| a | 17.3128 | 25.9572 | 15.0889 |
| b | 10.7517 | 15.6677 | 22.6056 |
| c | 13.7746 | 9.1901 | 7.4999 |
| $\beta$ | 69.941 | 83.324 | 95.250 |
| Cell Type | Monoclinic | Monoclinic | Monoclinic |
| ntering | C | C | C |

None of the other ligands formed stable complexes. Apparently, for complexes to be formed by this method, the ligand must have two acidic functional groups that are held closely enough together (either by their position in the ligand or by coordination through other sites) for them to be in a position to form a chelate. In oxalic acid and phthalic acid, the carboxyl groups are held rigidly in position by the carbon skeleton; in tartaric acid, the two carboxyl groups would be brought closer together by the coordination of the alcohol functional groups to the
molybdenum atom. Although succinic acid has two acidic functional groups, they would be relatively far apart. None of the other potential ligands had two acidic functional groups. Unfortunately mandelic acid decomposed, so that it may not be readily classified in this scheme. Some other acids will also reduce $\operatorname{Mo}(\mathrm{VI})$ to $\mathrm{Mo}(\mathrm{V})$. ${ }^{33}$

## POSSIBLE FUTURE STUDIES

A variety of possible extensions of this study have presented themselves during the course of the work.

First, since some molybdenum carboxylates and metal molybdates catalyze oxidation-reduction reactions, the oxidation-reduction potentials of the ones that can be easily synthesized could be studies by cyclic voltametry. They could also be studied by such techniques as uv-visible spectroscopy, magnetic circular dichroism, X-ray photoelectron spectroscopy, and ESR in order to elucidate their structures and to relate their structures to the reaction mechanisms.

Second, the limited thermodynamic data ${ }^{75-77}$ should be extended. Third, the wave function basis set for molybdenum ${ }^{78}$ and the data on the organomolybdenum compounds that show aromaticity ${ }^{79}$ may allow theoretical studies that could shed some light on the orbital interactions involved in the reactions catalyzed by molybdenum compounds, possibly in terms of pericyclic reactions.

Fourth, crown ethers ${ }^{84-98}$ have been studied extensively because they coordinate with the cations of ionic compounds, and allow these compounds to be dissolved in nonpolar organic solvents. Some crown ethers are very selective about the cations with which they will coordinate. It would be of interest to study the complexation of both ammonium and metal molybdates with crown ethers and to study the ability of the complexes to undergo dehydration reactions, substitution reactions, and other reactions in nonaqueous solvents. They may be useful in the development of a synthesis of anhydrous metal molybdates.

Finally, although I was unable to form metal molybdates in
nonaqueous solvents, this part of the study should be continued, especially in the area of the reactions of ammonium dimolybdate.

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#### Abstract

APPENDIX

These computer programs are written in Fortran IV (IBM 360 Compiler). ${ }^{48}$ They are intended to be used together to aid in the interpretation of mass spectra.

The first program (UNH-39) is based on the program described by Schrader. ${ }^{47}$ It determines all of the empirical formulas containing carbon, hydrogen, nitrogen, oxygen, and any one, two, or th as heteroatoms of choice, that correspond to an $m / e$ peak of a mass spectrum to within a specified error limit. The program automatically restricts the number of hydrogens in the fragment formula to a number that is reasonable based on the number of carbons, and nitrogens in the formula. This program has the advantage over other mass spectrum analysis programs, such as those described by Beech ${ }^{49}$ and by Isenhour and Jurs, ${ }^{50}$ that inorganic compounds can be analysed, as well as organic compounds.

The second program (UNH-40) will determine all of the possible $\mathrm{m} / \mathrm{e}$ values that can appear in a mass spectrum for an empirical formula containing carbon, hydrogen, nitrogen, oxygen, and any one, two, or three heteroatoms. As in UNH-39, the number of hydrogens in any given fragment is restricted to a reasonable quantity. The input instructions, and program lists are given in the following pages.


## Title: MASS SPECTRUM FRAGMENT FORMULAS

Object: To calculate possible fragment formulas for the m/e peaks of a mass spectrum, based on $C, H, N, O$, and up to 3 other hetero atom types.

Comment: Based on Appendix $C$ of Shrader, Stephen R. "Introductory Mass Spectrometry", Allyn and Bacon, Boston, Mass., 1971.

Input: TITLE = any information
LN = maximum number of nitrogen atoms in any fragment
LO $=$ maximum number of oxygen atoms in any fragment
LH = total number of all hetero atoms, including nitrogen and oxygen, allowable in any fragment
$E R=$ maximum allowable difference between calculated and observed masses for any fragment.
H1 = maximum number of hetero atoms of type 1 in any fragment
H 2 = maximum number of hetero atoms of type 2 in any fragment
H3 = maximum number of hetero atoms of type 3 in any fragment
Note: $\mathrm{LN}+\mathrm{LO}+\mathrm{H} 1+\mathrm{H} 2+\mathrm{H} 3=\mathrm{LH}$
ATOM1, ATOM2, ATOM3 = name of each hetero atom, of type 1,2 , or 3 WH1, WH2, WH3 = corresponding atomic weight EXPM $=$ experimental $\mathrm{m} / \mathrm{e}$ values

Cards: (1) TITLE $=$ any information, all columns, FORMAT(20A4)
(2) Number and error, FORMAT (315,F10.5)

Columns 1-5 LN = number of nitrogen atoms, as XXXXX
6-10 LO $=$ number of oxygen atoms, as XXXXX
11-15 LH = total number of all hetero atoms, XXXXX
16-25 ER = allowable error (difference) between calculated and observed $\mathrm{m} / \mathrm{e}$, XXXX. XXXXX
(3) Hetero atoms, FORMAT (3I5)

Columns 1-5 HI = number of hetero atoms of type 1 , XXXXX
6-10 H2 $=$ number of hetero atoms of type 2 , XXXXX
11-15 H3 $=$ number of hetero atoms of type 3 , XXXXX
(4) Hetero atoms, descriptions, FORMAT(6A4, F10.5)

Columns 1-24 ATOML = name of hetero atom of type 1 25-34 $\mathrm{WH}=$ atomic weight, as $\mathrm{XXXX} . \mathrm{XXXXX}$
Repeat with separate cards for ATOM2 and ATOM3, if present.
(5) Data cards, FORMAT (F10.5)

Columns 1-10 EXPM = experimentally observed m/e ratio, as $\mathrm{XXXX} . \mathrm{XXXXX}$
(6) Stop card, blank in columns $1-10$; end of calculation

Output: Output lists the names and weights of the hetero atoms and tabulates the experimental, calculated, and difference m/e values for possible fragment formulas, which are given.




```
    IF(NHC-NHI95,54,54 39R-0970
54 [NH=FLODT(NH)
    CAN=FLCAT(NN)
    CNC=FLCAT(NC)
    DAS=FLOAT(NO)
    CNI=FLCAT(NL)
    ON.2=FLOAT(N2)
    CN3=FLOAT(N3)
    CALC=12.00*CNC+1.007825*QNF+14.003074*ONN+15.95491*DNO+WH1*DN1+ 3GR-1050
    1ht 2*CN2+WH3*CN3
    [IFF=CALC-EXPM
    IF(ERTOIFF)80,55,55
55 IF(FR-DIFF)&C,50,56 39R-1090
50 [IFF=DIFF*10C0.0
    Y=RCUND(DIFF)
    Y=RCUND(DIFF)
    KRITE(PFINTR,2Oち)EXPM,NC,NH,NN,NC,N1,N2,N3,CALC,ICF 3GR-1130
80 NC=NC-1
    NH=NH+12
    GL TC 53
C5 CONTINUE
GG CCNTINUF
S7 CCNTINUE
G8 CONTINUE
sg CRNTINUE
100GGTC 50 3-1220
101 STOP 39R-1230
ZO1 FCRNAT(3I5,F10.5) 35R-1240
2C2 FCRMAT(3I5)
203 FCRNAT(F10.5)
ZO4 FCRMATIIH, 3X,'EXPM',5X,'C',5X,'H',5X,'N',5X,'口',5X,'H1',4X,'H2', 39R-1270
    14X,'H3',7X, '(ALC', 4X,'DIFFERENCE* 100C.0') 39R-1280
205 FNRNAT(IF,IX,F&.4,7(2X,I4),2X,F&.4,2X,I 8) 3SR-12SO
2CG FORNAT(2OA4) 39R-1300
¿C6 FORMAT(2OA4)
¿C7 FERMAT (6A4,F10.5)
208 FCRMAT(1H1,2CA4)
ZCG FCRNAT(IH, EX,'HETERGATUM H1 IS', 2X,6A4)
210 FORMAT(1H,EX,'ATUMIC WEIGHT =', 2X,F1O.5)
Z11F[:RNAT(1H, EX,'HETERUATCM #2 IS',2X,6A4) 3SR-1350
Z12 F(RMAT(1H, EX,'HETEROATOM &3 IS',2X,6A4) 39R-1360
    END 39R-1370
    FUNCTICN RCUNC(B) 39R-1380
    X=AINT(B) 3GR-1390
    TF(E-X-0.5)3CC,301,301 39R-1400
201 }x=x+1.
300 RCUNE = X
    RETURN
    EAD
    39R-0980
    39R-09G0
    35P-1000
    39R-1010
    39R-1020
    39R-1030
    3GR-1050
    39R-1060
    39R-1070
    39R-1080
    39R-1100
    3GR-1110
    39R-1120
    3R-1130
    39R-1140
    39R-1150
    39R-1160
    39R-1170
    39R-1180
    39R-1190
    39R-1200
    39R-1210
100GGTC 50 3-1220
    3GR-1240
    39R-1250
39R-1310
20 FORMLTIIH,EX,ATLMIC WEIGHT =', 2X,F10.5) 39R-1340
39R-1410
3SR-1420
39R-1430
39R-1440
```


# U.N.H. Program No. 40 

Title: PREDICTED MASS SPECTRUM

Object: To calculate the possible fragment m/e values for any empirical formula.

Input: TITLE = any information
$C=$ number of carbon atoms in the formula
$\mathrm{H}=$ number of hydrogen atoms in the formula $N=$ number of nitrogen atoms in the formula $0=$ number of oxygen atoms in the formula H1 = number of hetero atoms of type 1 in the formula H2 = number of hetero atoms of type 2 in the formula H3 = number of hetero atoms of type 3 in the formula

ATOM1, ATOM2, ATOM3 = name of the corresponding hetero atom WH1, WH2, WH3 = atomic weight of the corresponding hetero atom
$A=$ control parameter
Cards: (1) TITLE $=$ any information, all columns, FORMAT(20A4)
(2) Formula and control parameter, FORMAT(7F5.1,I2)

Columns 1-4 $\mathrm{C}=$ number of carbons, as XXXX
6-9 $\quad \mathrm{H}=$ number of hydrogens, as XXXX
11-14 $N=$ number of nitrogens, as XXXX
16-19 $\quad 0=$ number of oxygens, as XXXX
21-24 $\mathrm{H} 1=$ number of type 1 hetero atoms, as XXXX
26-29 H2 = number of type 2 hetero atoms, as XXXX
31-34 H3 = number of type 3 hetero atoms, as XXXX
$37 \mathrm{~A}=0$ for last data set
1 for all except the last
(3) Hetero atom descriptors, FORMAT (6A4,F10.5) Columns 1-24 ATOM1 = name of type 1 hetero atom 25-34 WH1 = atomic weight of type 1 hetero atom, as XXXX. XXXXX

Repeat with separate cards for ATOM2 and ATOM3.
Repeat cards (1), (2), and (3) for each data set. Note "A" value.
Output: Output lists the title, name, and weight of each hetero atom, the formulas and m/e values for the possible fragments (in ordered, tabular format), and the m/e value for the molecular ion peak.
 óo
PRJGRAM UNH-4O PREDICTED MASS SPECTFUM.
CALCULATES ALL POSSIBLE M/E PEAKS FROM THE EMPIRICAL FORMULA.


 2. $\mathrm{C} * \mathrm{DNR}+1.0 \mathrm{Cl}$
$\mathrm{H} 2+\mathrm{WH} 3 \approx \mathrm{CNH} 3$
$=\mathrm{CALC}$

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[^0]:    $a_{\text {Reaction }}$ was not complete as determined by the comparison of the powder patterns with those for ammonium oxalate hydrate and anhydrous ammonium oxalate.

