Winter 1976

STUDIES OF MOLYBDENUM COMPLEXES

GREGORY WALKER ESTES

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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

Doctor of Philosophy

Graduate School

Department of Chemistry

December, 1976

This thesis has been examined and approved.

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Research Director
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Charles M Wheeler Jr.

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9/8/76

Date

TO MY PARENTS

ACKNOWLEDGEMENTS

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 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

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 all 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, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, 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, $(NH_4)_2C_2O_4 \cdot H_2O$, 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°C. Therefore, this method is likely to work only with difficulty.

Hydrolysis reactions employing such compounds as orthoesters, such as triethyl orthoformate, $HC(OC_2H_5)_3$, and ketals, such as 2,2-dimethoxypropane, $(CH_3)_2C(OCH_3)_2$, 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 $(Mo_7O_{24})^{6-} + 8NH_3 \longrightarrow 7\ MoO_4^{2-} + 8NH_4^+$ 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, $(NH_4)_2MoO_4$.

A third possibility would be to synthesize the anhydrous ammonium dimolybdate[31] $(NH_4)_2Mo_2O_7$, 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 Kjehldahl 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 $(NH_4)_2C_2O_4$: C, 19.34; H, 6.57; 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°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 Orthoformate (ml)	Solvent	Volume of Solvent (ml)	Time (Hr:Min)
0.80	50	1,2-Dimethoxyethane	100	3:00
0.70	50	methanol	100	2:10[a]
1.10	60	methanol	80	4:50
1.10	50	t-butanol	100	3:10[a]
1.20	70	acetonitrile	130	3:00
1.10	55	nitromethane	100	2:30

---

[a] Reaction was not complete as determined by the comparison of the powder patterns with those for ammonium oxalate hydrate and anhydrous ammonium oxalate.

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 (~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 methanol. 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 (~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°C the solid turned to a liquid which boiled immediately.

Anal. Calcd for $(NH_4)_2C_2O_4 \cdot 1/2C_4H_8O_2$: C, 23.36; H, 6.54; N, 18.18. Found: C, 21.38; H, 6.02; N, 18.70.

4. The Attempted Dehydration of Ammonium Paramolybdate Tetrahydrate by Triethyl Orthoformate in 1,2-Dimethoxethane

Three trials were made, which gave the same basic results.

Trial #1: 10.59 g of ammonium paramolybdate tetrahydrate were refluxed in 240 ml of 1,2-dimethoxyethane and 160 ml of triethyl orthoformate (~25 fold excess) for 9.5 hr.

Anal. Found: C, 17.28; H, 3.17; Mo, 43.29; N, 5.50.

Trial #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: C, 19.54; H, 3.07; Mo, 41.04; N, 6.26.

Trial #3: 5.10 g of ammonium paramolybdate tetrahydrate were refluxed in 175 ml of 1,2-dimethoxyethane and 70 ml of triethyl orthoformate (~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 (~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 Ammonium 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 paramolybdate tetrahydrate were refluxed in 100 ml 2,2-dimethoxypropane (~45 fold excess), 7 ml of acetic acid, and 1 ml of acetic anhydride for 2.25 hr.

Anal. Found: C, 20.13; H, 3.72; Mo, 48.90; N, 3.68.

Trial #2: 4.73 g of ammonium paramolybdate tetrahydrate were refluxed with 200 ml of 2,2-dimethoxypropane (~60 fold excess), 10 ml of acetic acid, and 0.1 ml of acetic anhydride for 5 hr.

Anal. 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 (~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 $(NH_4)_6Mo_7O_{24}\cdot 5CH_3OH$: C, 4.53; H, 3.34; Mo, 50.73; 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 (~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; 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 #1: 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 Model 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-Elmer 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.

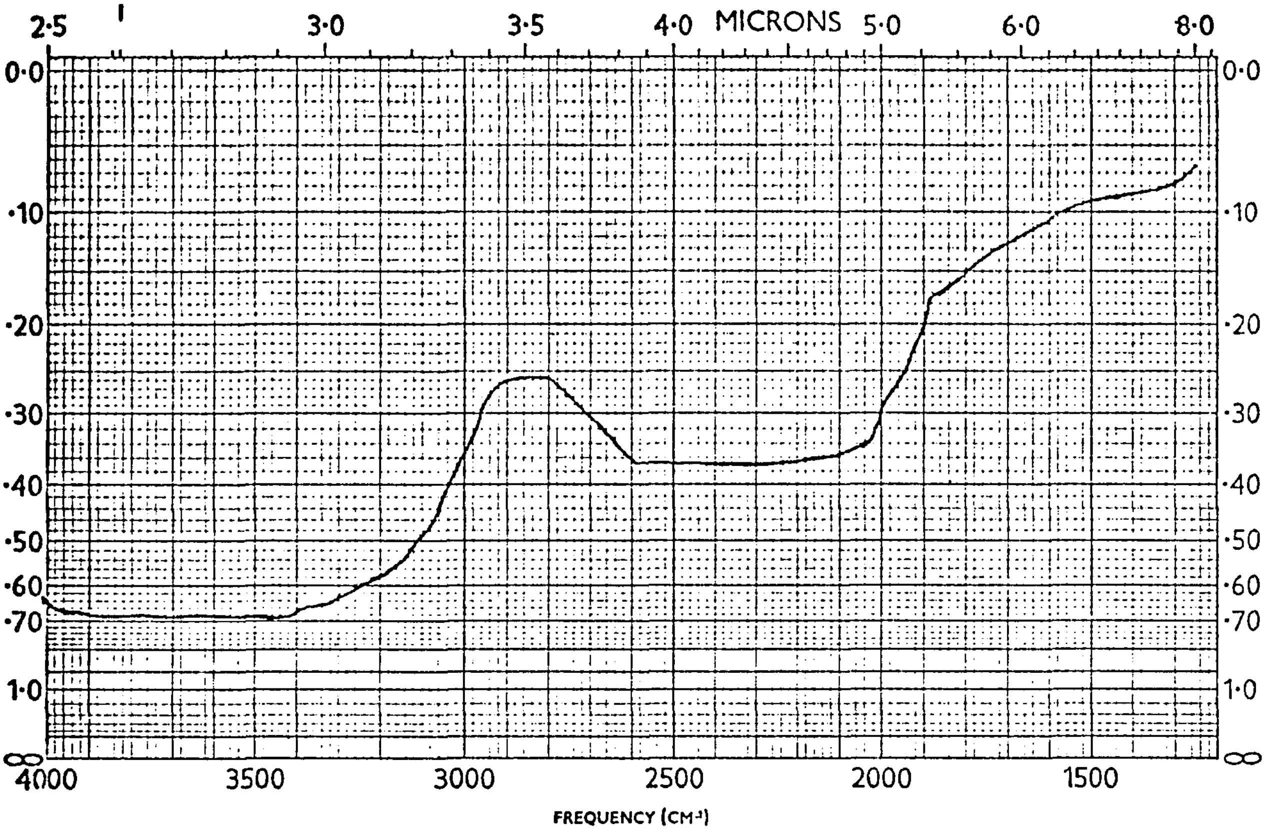
E. X-ray Powder Patterns

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 CuKα radiation, λ=1.5418 A^o.

The powder patterns are given in Tables VI and VII.

Unit cells were determined by the unit cell series of computer programs (including DeWolff comparison).[51-53]

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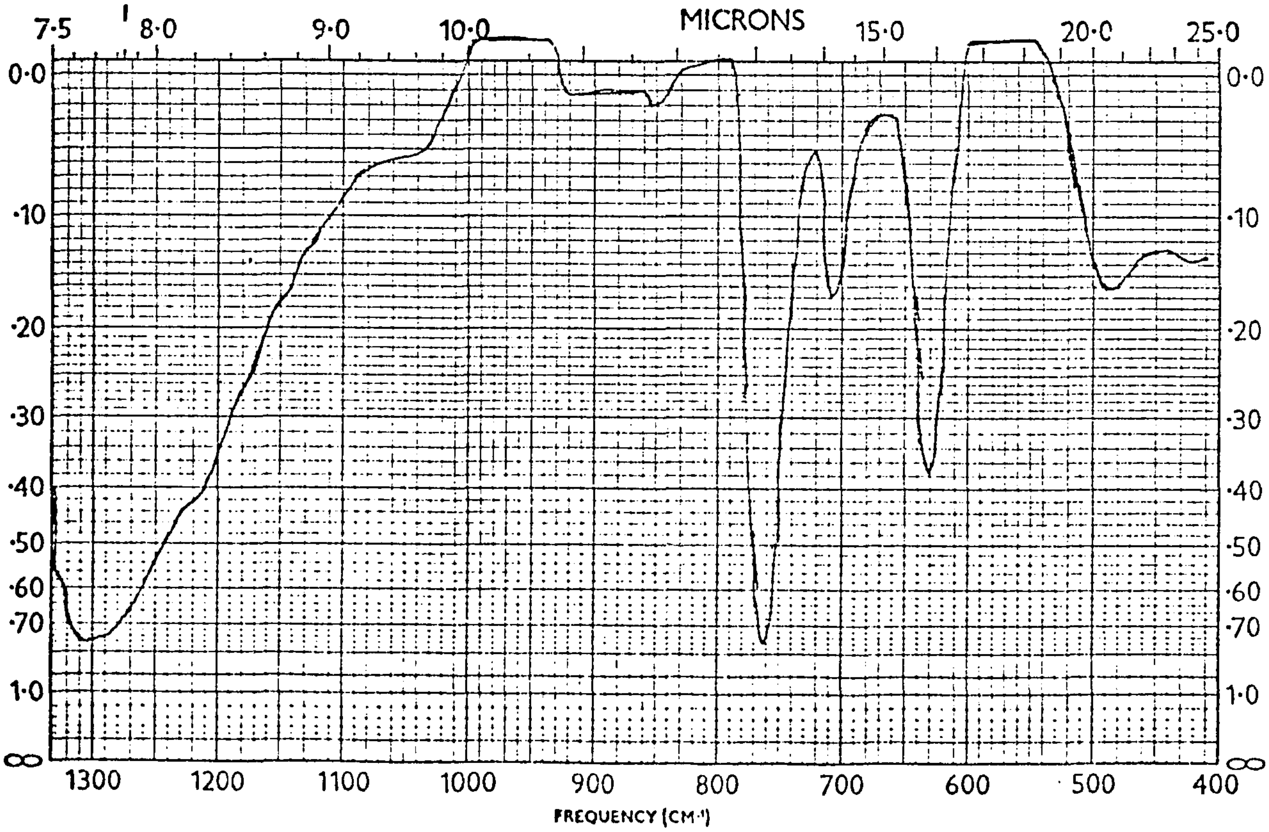
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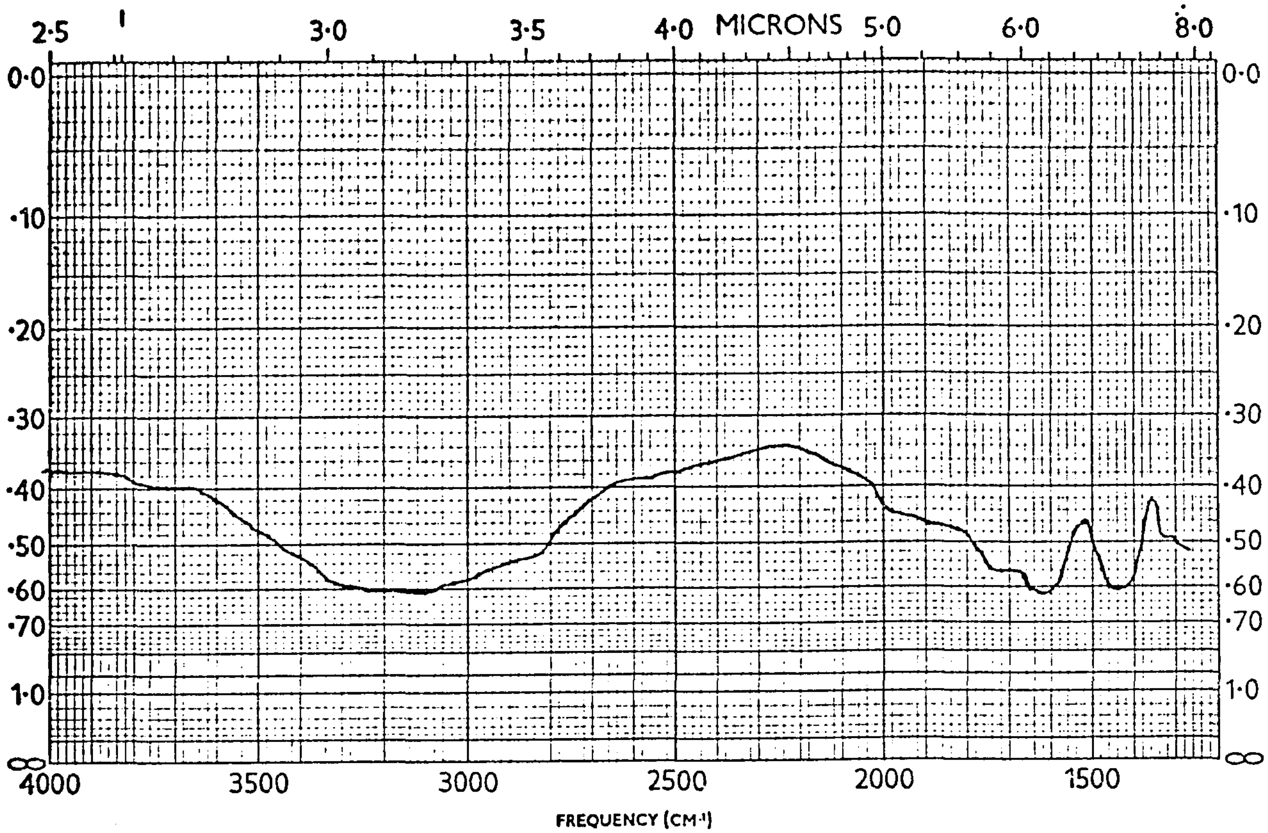
Figure 2. The Infrared Spectrum of the Ammonium Oxalate-Dioxane Adduct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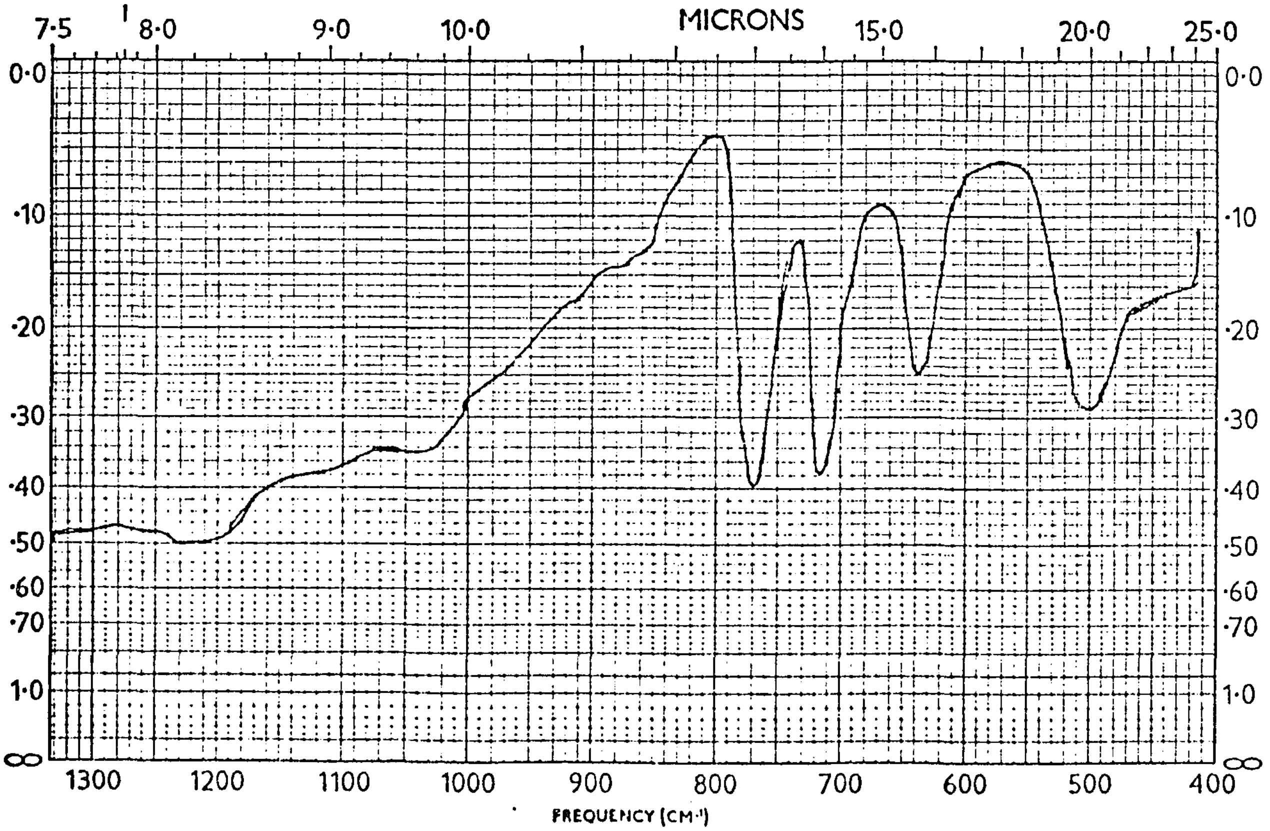
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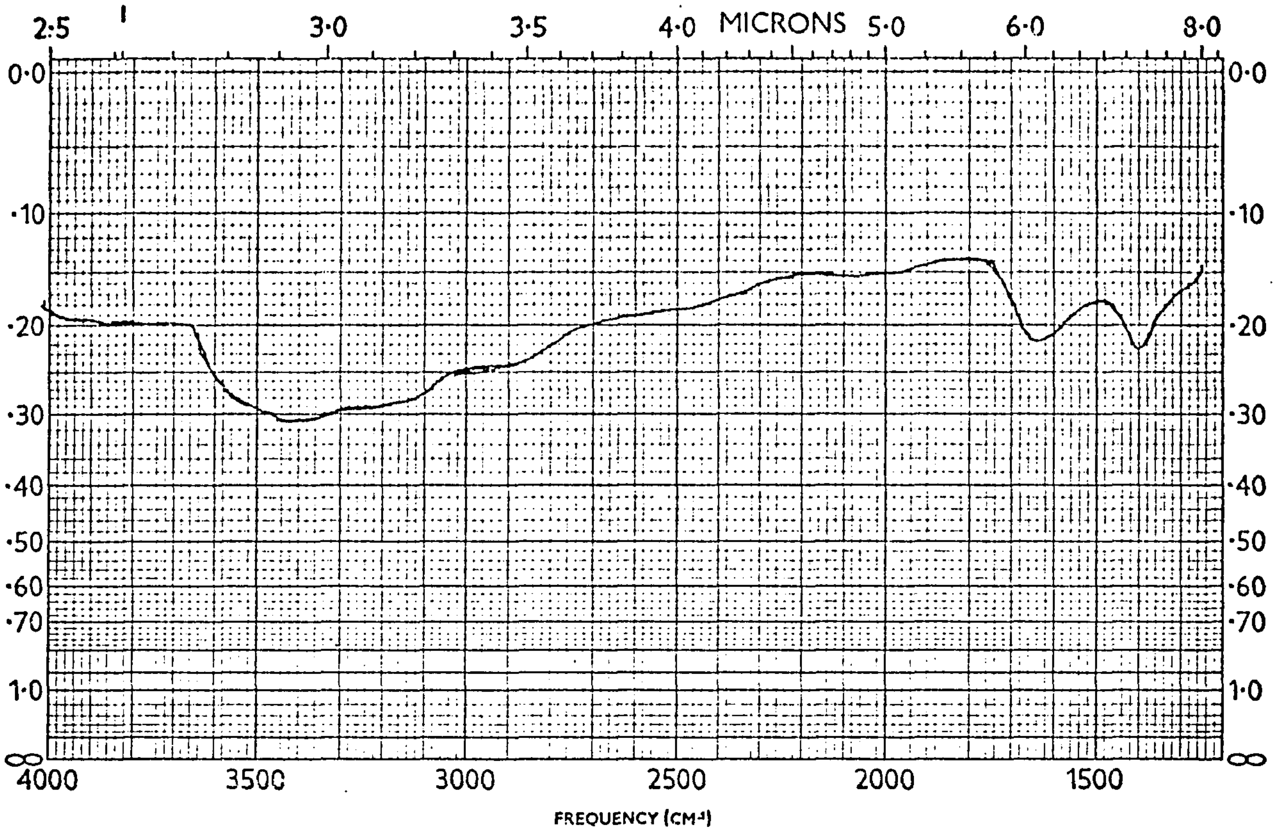
Figure 3. The Infrared Spectrum of the Product of the Reaction of Ammonium Paramolybdate Tetrahydrate with Triethyl Orthoformate in 1,2-Dimethoxyethane



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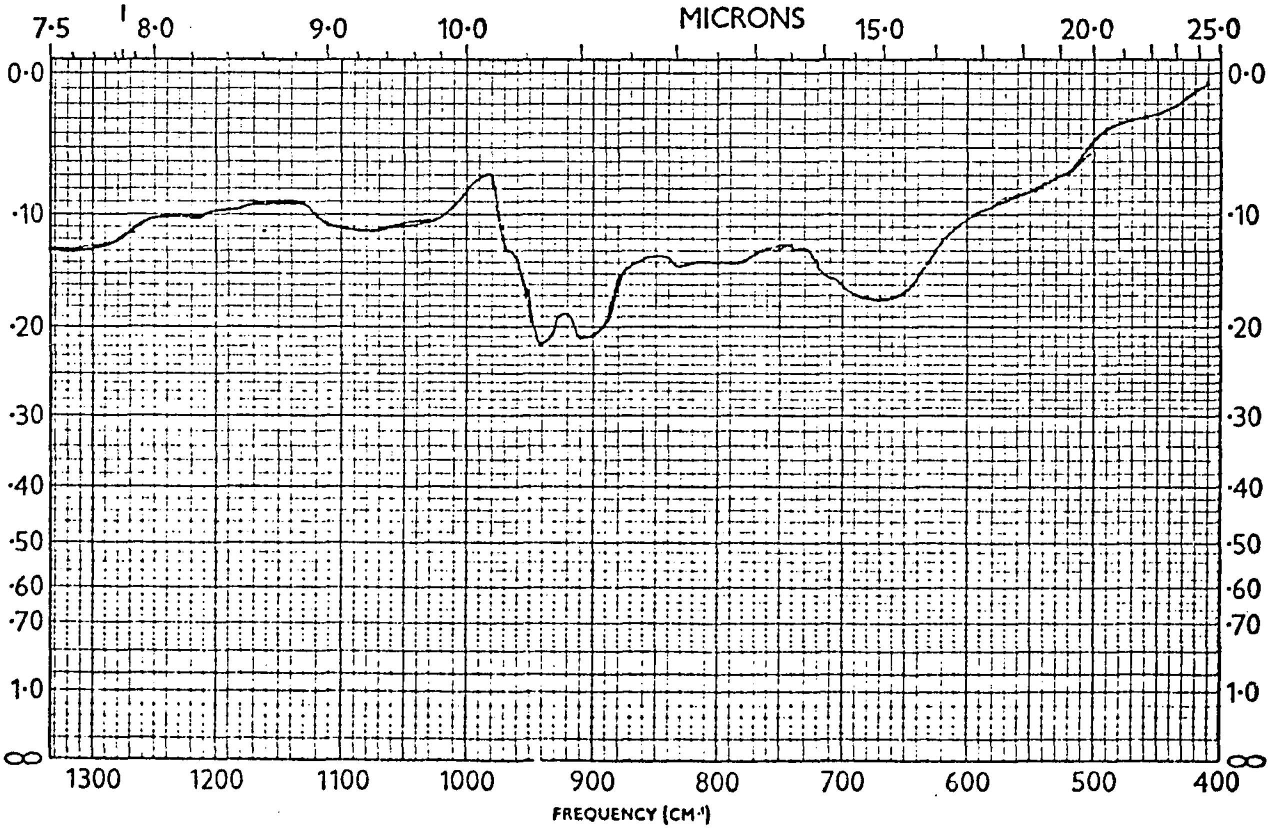

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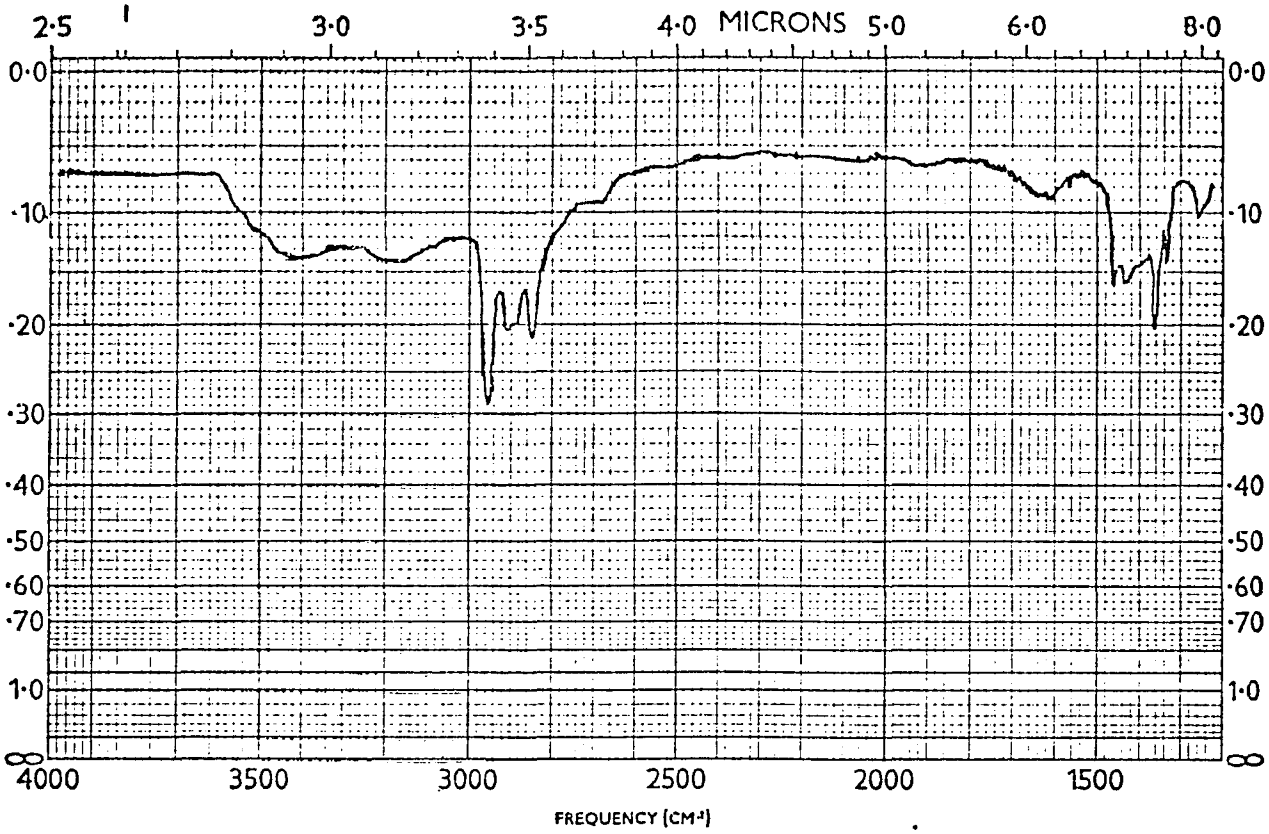
Figure 4. The Infrared Spectrum of the Product of the Reaction of Ammonium Paramolybdate Tetrahydrate with Triethyl Orthoformate in Ethanol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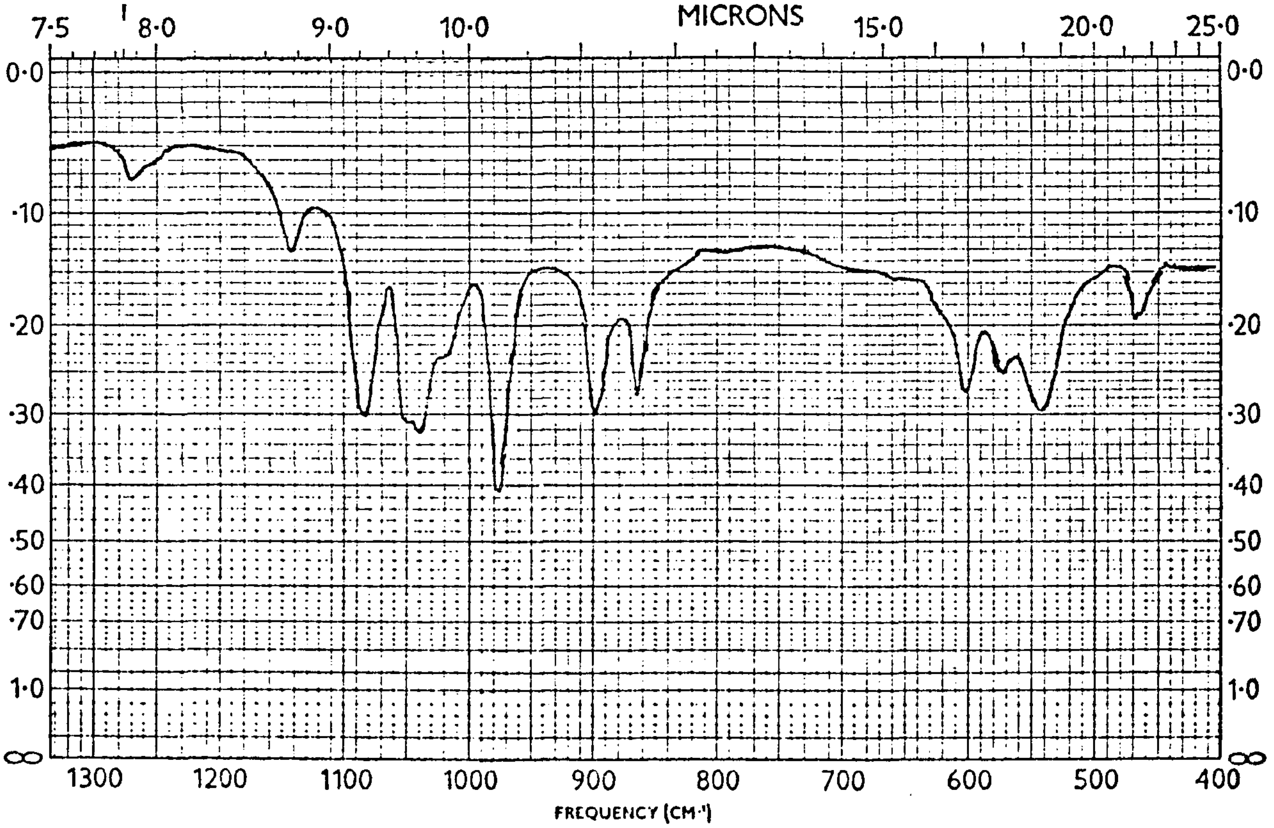
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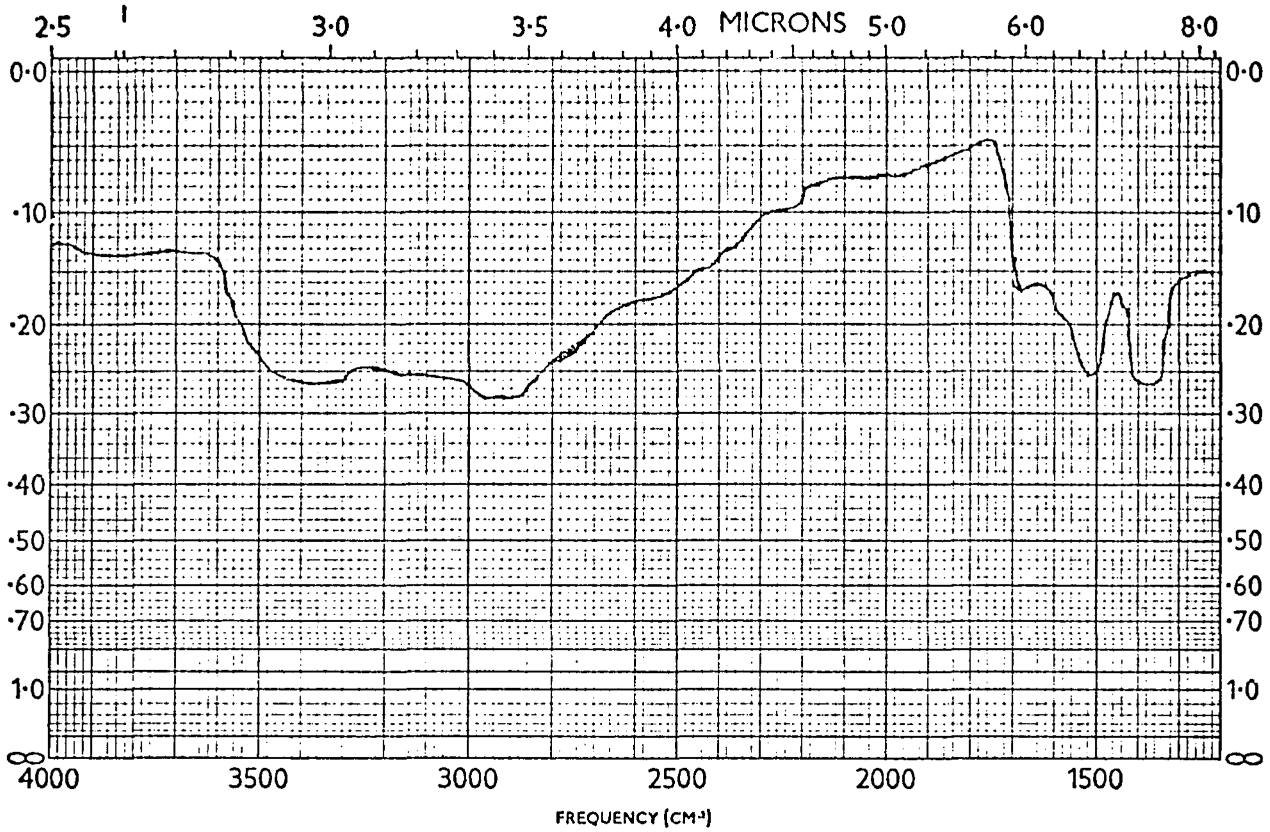
Figure 5. The Infrared Spectrum of the Product of the Reaction of Ammonium Paramolybdate Tetrahydrate with 2,2-Dimethoxypropane in the Presence of Acetic Anhydride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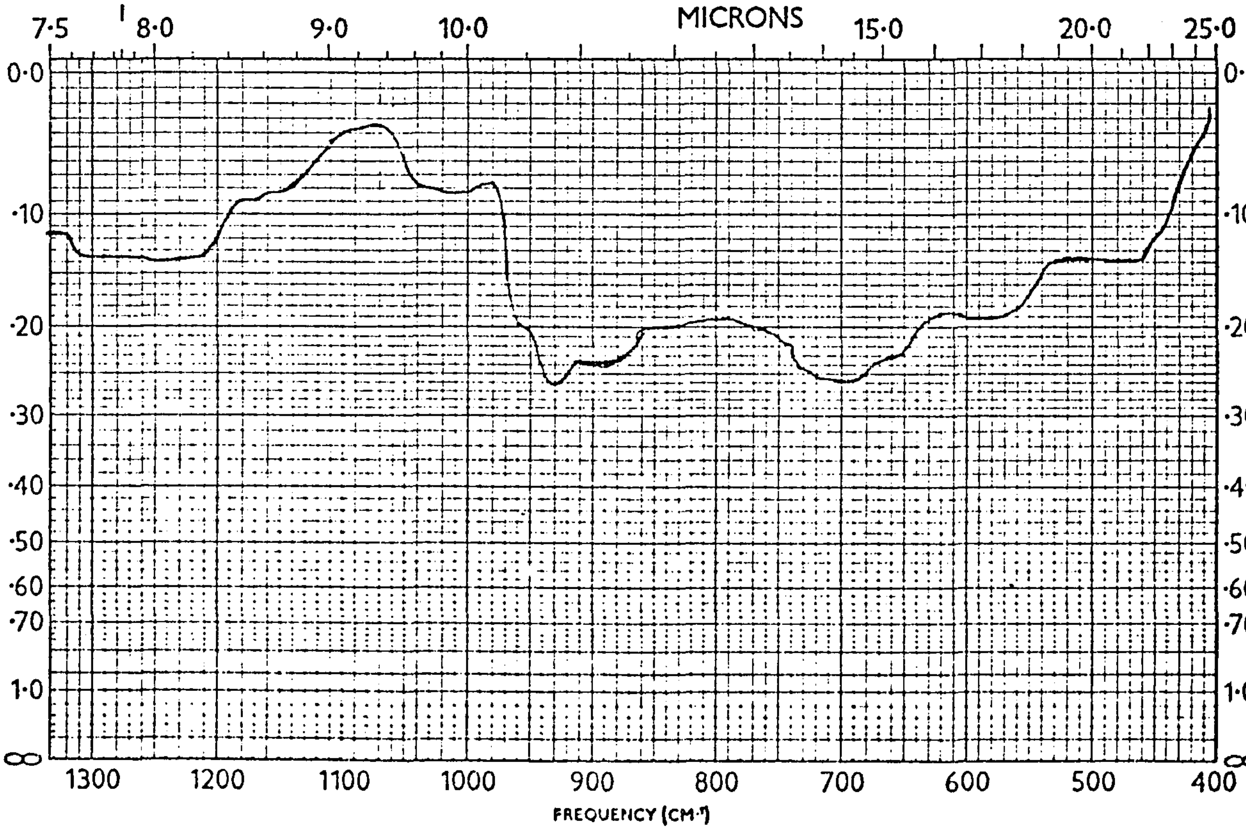
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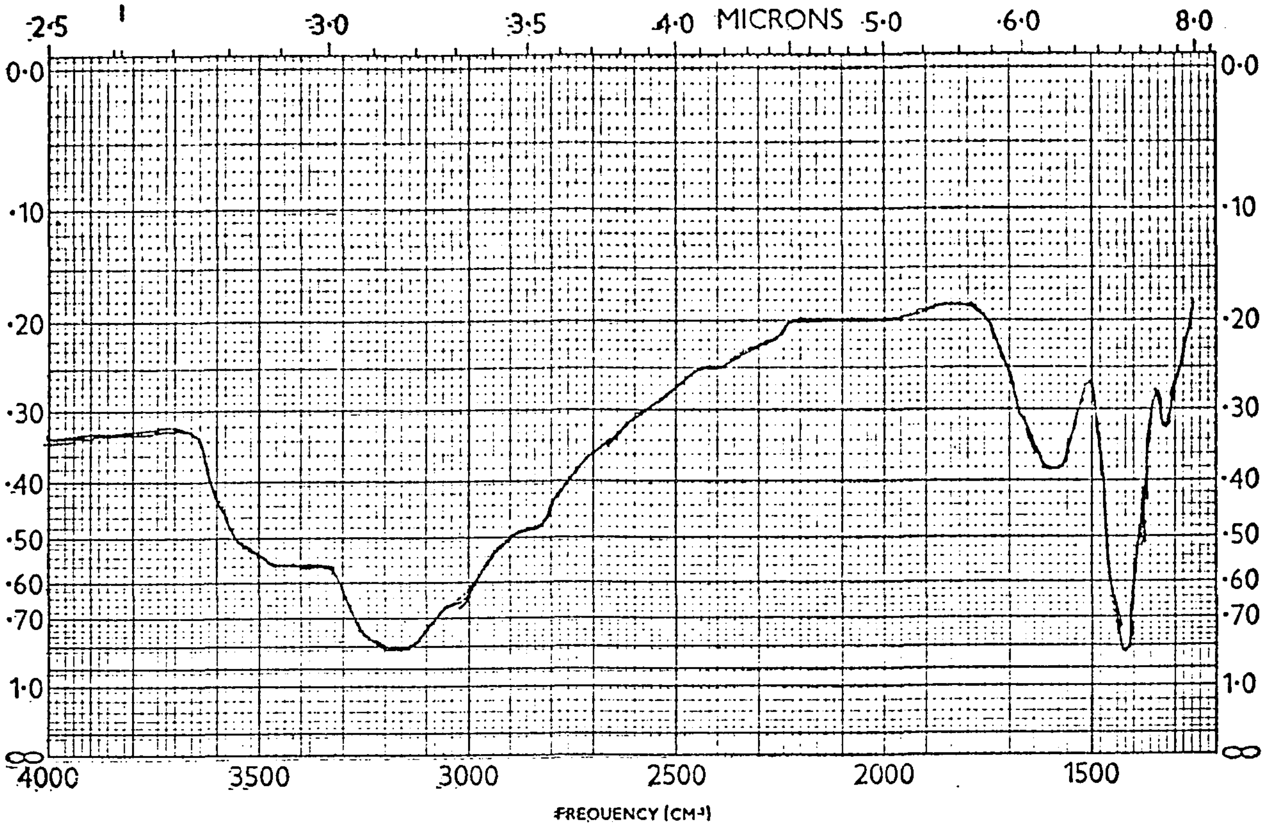
Figure 6. The Infrared Spectrum of $(NH_4)_6Mo_7O_{24} \cdot 5CH_3OH$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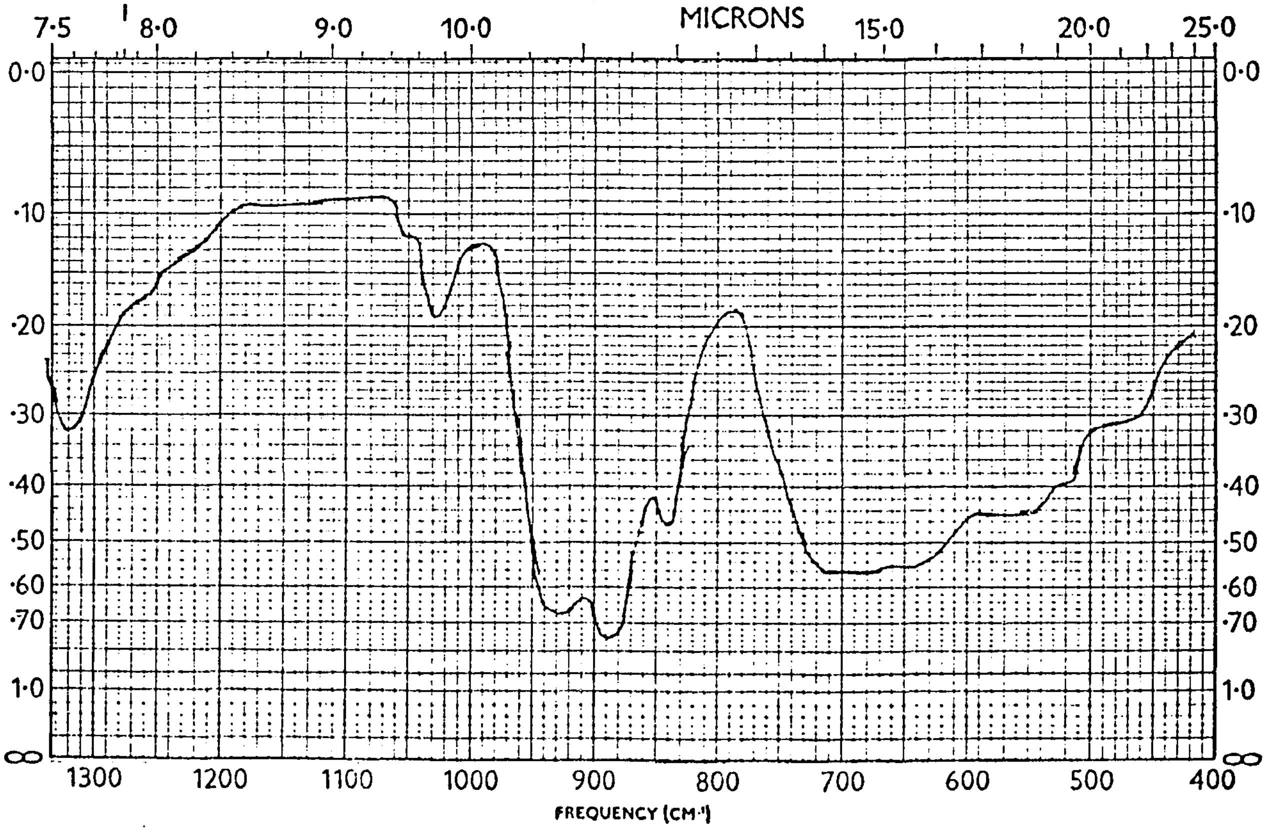
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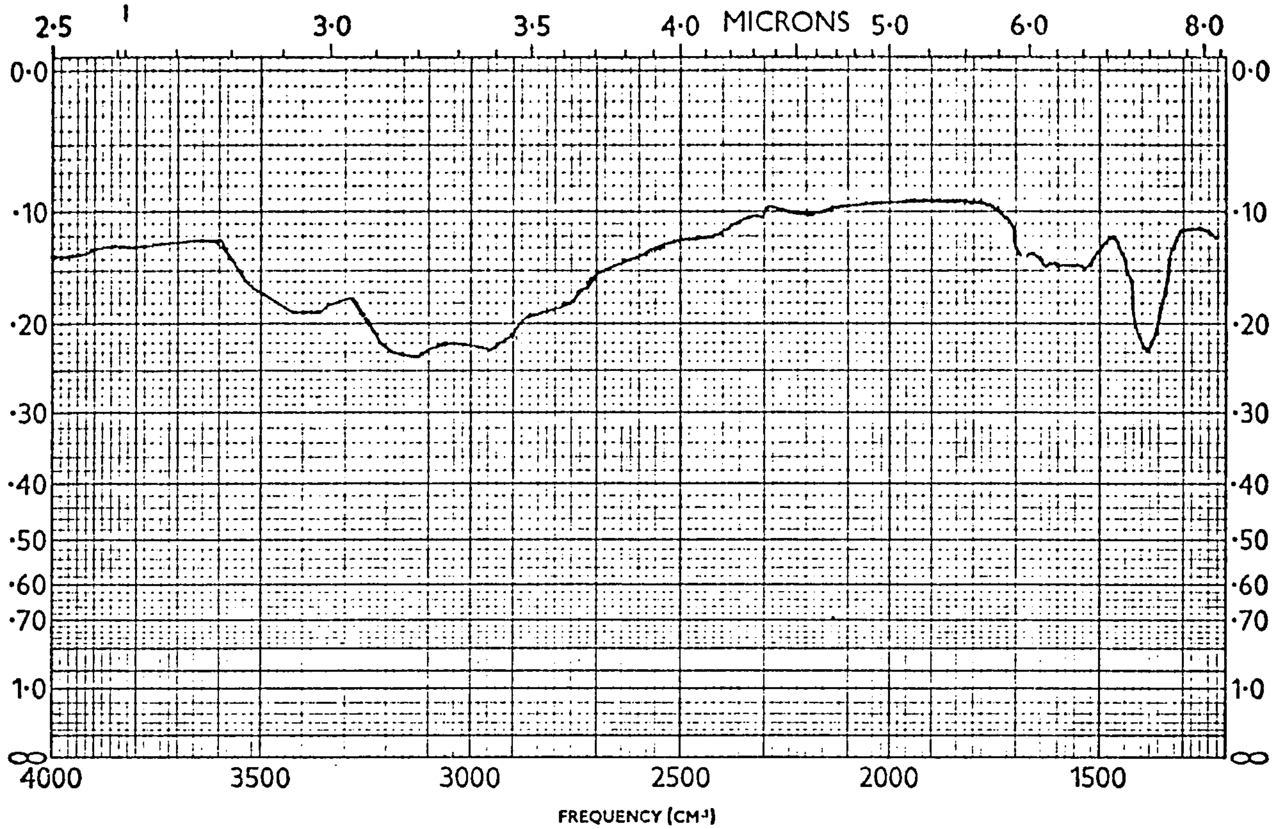
Figure 7. The Infrared Spectrum of the Product of the Reaction of Ammonium Paramolybdate Tetrahydrate with 2,2-Dimethoxypropane in Acetonitrile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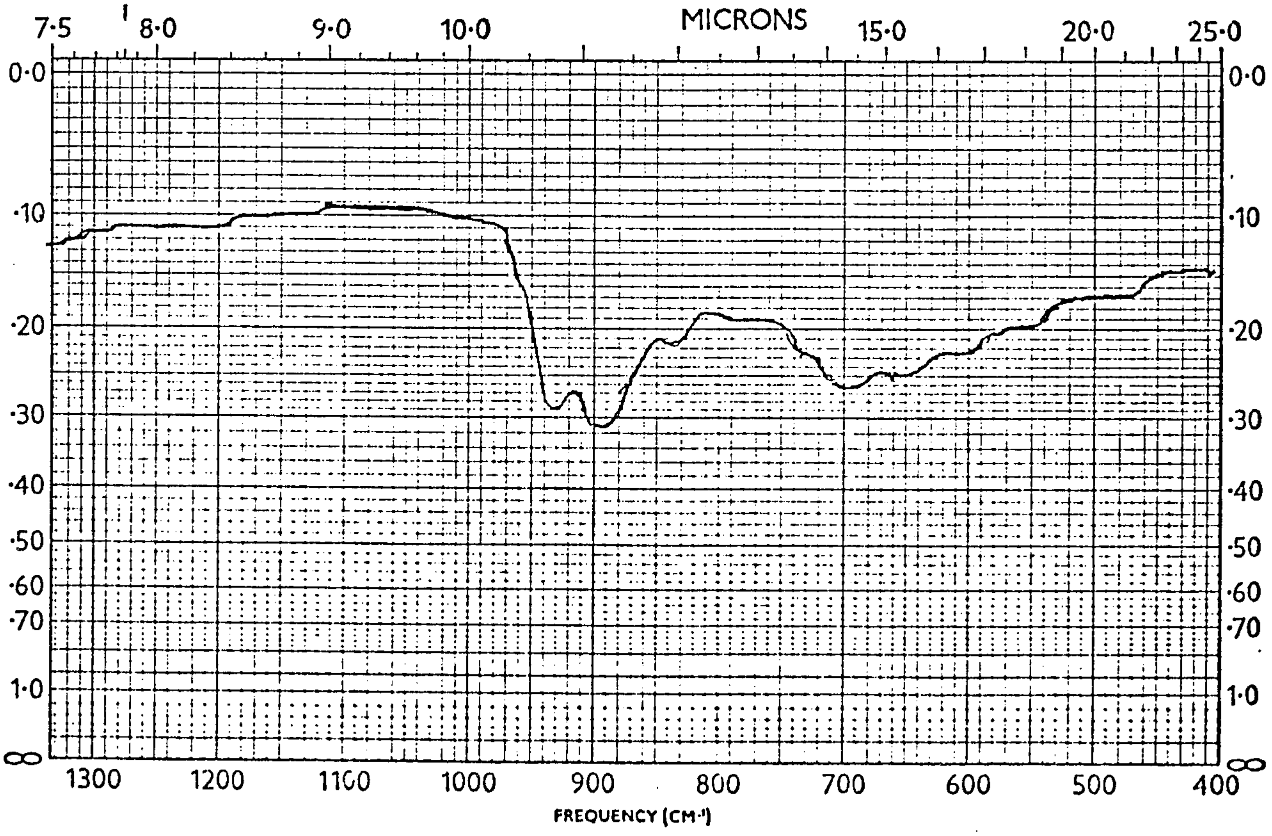
MICRONS
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8·0
9·0
10·0
15·0
20·0
25·0
0·0
·10
·20
·30
·40
·50
·60
·70
1·0
∞
1300
1200
1100
1000
900
800
700
600
500
400
FREQUENCY (CM-1)

Table II. The Mass Spectrum of Anhydrous Ammonium Oxalate

m/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

m/e	%	m/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	%	m/e	%	m/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 $(NH_4)_6Mo_7O_{24}\cdot 5CH_3OH$

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)

d_{obsd}, A°	d_{calcd}, A°	I/I_o	hkl[a]
6.810	6.77874	m	010
6.416	6.39172	vw	$0\bar{1}1$
5.681	5.67518; 5.62145	m	$\bar{1}01$, 100
5.471	5.49345; 5.40448	s	$\bar{1}10$, $\bar{1}11$
5.039	5.04591; 5.01857; 4.94711	m	$\bar{1}02$, 003, $1\bar{1}1$
4.271		vw	
3.770	3.76393; 3.74281	w	004, 111
3.591	3.58253; 3.57707	s	$11\bar{2}$, $\bar{1}20$
3.507	3.51474; 3.48793; 3.47575	m	$\bar{1}21$, $\bar{1}04$, $1\bar{1}3$
3.187	3.19586; 3.17773; 3.17607	w	$0\bar{2}2$, $1\bar{2}2$, 014
3.100	3.10247; 3.09001	s	$\bar{2}11$, 112
3.018	3.03158; 3.01114	vs	$\bar{2}12$, 005
2.831	2.84474; 2.83759	w	$0\bar{1}5$, $\bar{2}02$
2.746	2.74673; 2.73696	s	$\bar{2}20$, 113
2.652	2.66305; 2.63907; 2.65113; 2.63907	w	201, $2\bar{1}2$, $\bar{1}24$, $2\bar{2}1$
2.578	2.57816	m	$11\bar{5}$
2.468	2.47355; 2.46739	vw	$2\bar{2}2$, 202
2.417	2.42250; 2.41809; 2.41769; 2.41694; 2.41680; 2.41089 2.41062; 2.40797	s	$0\bar{1}6$, $1\bar{3}1$, 114, $\bar{1}31$, 024, 121, $\bar{1}16$, $2\bar{1}3$
2.309	2.31378; 2.30094	w	$\bar{2}05$, 210
2.276	2.28146; 2.28058; 2.27361; 2.27225	vw	$2\bar{2}3$, $11\bar{6}$, $21\bar{3}$, 122

continued –

Table VI. Continued

d_{obsd}, A^{o}	d_{calcd}, A^{o}	I/I_{o}	hkl[a]
2.222	2.21770	vw	$0\bar{3}2$
2.191	2.18944; 2.18363	vw	$\bar{2}32$, $\bar{2}25$
2.132	2.13057; 2.12954	vw	$0\bar{3}3$, 106
2.103	2.10677; 2.10580; 2.10472; 2.10325; 2.10294; 2.09758; 2.09648	m	$\bar{2}06$, $0\bar{2}6$, $\bar{2}33$, $0\bar{1}7$, $\bar{1}17$, $\bar{1}26$, $12\bar{5}$
2.058	2.05522; 2.05482; 2.05432; 2.05313	w	$\bar{3}12$, $\bar{3}11$, $1\bar{3}4$, 204
1.981	1.98013; 1.97913	w	$\bar{3}23$, $2\bar{3}3$
1.896	1.89857; 1.89857; 1.89173; 1.89162	vw	$\bar{1}35$, $21\bar{6}$, $\bar{3}03$, $0\bar{2}7$
1.866	1.87084; 1.87066; 1.86835; 1.86728; 1.86680; 1.86237	vw	$22\bar{1}$, $13\bar{2}$, $\bar{2}35$, 034, 205, 130
1.847	1.84835; 1.84369	w	$\bar{3}31$, $22\bar{3}$
1.704	1.70549; 1.70130; 1.70049	vw	$\bar{1}43$, 206, $0\bar{4}1$
1.637	1.63720; 163378	w	$22\bar{6}$, 223
1.615	1.61753; 1.61734; 1.61691; 1.61494	w	$2\bar{1}7$, $1\bar{3}7$, $\bar{2}37$, $\bar{1}37$
1.480	1.47886	vw	313
1.439	1.44019; 1.44003; 1.43962; 1.43755; 1.43691	vw	$4\bar{2}2$, $\bar{1}51$, $\bar{2}52$, $\bar{4}02$, $14\bar{4}$
1.042	1.04268; 1.04191	vw	424, $25\bar{6}$
1.001	1.00174; 1.00039	vw	$\bar{6}14$, $1\bar{7}4$
0.991	0.99129; 0.99116	vw	$4\bar{7}1$, 254

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

Table VII. The Powder Pattern of $(NH_4)_6Mo_7O_{24}\cdot 5CH_3OH$ (114.6 mm Film)

d_{obsd}, A^o	d_{calcd}, A^o	I/I_o	hkl^a
10.704	10.91108; 10.75385	s	010, 100
9.707	9.76362	s	$0\bar{1}1$
9.137	9.03552	s	$\bar{1}01$
8.124	8.03851	s	$\bar{1}10$
7.762	7.84314	s	002
7.381	7.44769; 7.32880	s	$1\bar{1}1$, 110
6.948	7.02797; 6.94905; 6.89229	s	$11\bar{1}$, $0\bar{1}2$, $\bar{1}11$
6.398	6.45785	s	$\bar{1}02$
5.405	5.44609; 5.37692; 5.36407	m	$0\bar{2}1$, 200, $\bar{1}12$
5.025	5.05699; 5.02662; 5.01996; 5.01592; 5.00966	w	$\bar{1}20$, 201, $1\bar{2}1$, 112, $\bar{2}10$
4.345	4.35630; 4.35091; 4.33991	w	202, $12\bar{2}$, 211
4.162	4.16126, 4.14514	w	022, $\bar{2}12$
3.924		w	
3.818	3.82965; 3.80724	w	212, $\bar{2}21$
3.676	3.68440; 3.66440	w	$22\bar{1}$, 220
3.494		s	
3.330		s	
3.208		m	
3.102		m	
2.937		m	
2.780		vw	
2.644		vw	

continued -

Table VII. Continued

d_{obsd}, A°	d_{calcd}, A°	I/I_o	hkl[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°C (Erdey, Gal, and Liptay[6] reported that ammonium oxalate monohydrate decomposes at 235°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 (m/e=46) and carbon monoxide (m/e=28). The infrared spectrum contains the usual band for the ammonium ion at about 2400 cm^{-1} (probably lowered because of hydrogen bonding). The infrared band above 3500 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 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°C) which would immediately boil. The infrared spectrum has the usual ammonium ion (3200 cm^{-1}) and C=O (1620 cm^{-1}) absorptions, as well as a broad band at about 1220 cm^{-1} which is attributable to cyclic C-O vibrations. There are also bands which correspond to C-C vibrations (770 cm^{-1} and 720 cm^{-1}) and CH_2 vibrations (640 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 A°, b=7.385 A°, c=15.406 A°, α=90.3, β=101.2°, and γ=112.2°.

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 cm^{-1} that indicate C=O vibrations, and near 3400 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 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 cm^{-1}, because there is no mass spectrum peak at m/e=44 from a CO_2 fragment of an acid. The infrared absorption at about 1600 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 O-H (1420 cm^{-1}), C-O (1030 cm^{-1}), and CH_2 (1320 cm^{-1}, 930 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 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 A^o, b=11.112 A^o, c=15.920 A^o, α=99.56°, β=91.37°, and γ=94.98°. The second cell has the parameters a=11.673 A^o, b=11.974 A^o, c=15.347 A^o, α=103.19°, β=92.59 A^o, and γ=111.98°. 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 cm^{-1}). It probably is not a nitrile adduct since there is no $C\equiv N$ absorption at about 2000 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 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 $(NH_4)_6Mo_7O_{24} \longrightarrow (NH_4)_4H_3Mo_7O_{24} + 3NH_3$ and $(NH_4)_4H_3Mo_7O_{24} \longrightarrow (NH_4)_3H_4Mo_7O_{24} + NH_3$. 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 $CuBr_2$ 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 $CdBr_2$ 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 (0.021 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 ml 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: C, 1.52; H, 1.76; Mo, 47.46.

Other reaction times, reactant ratios, and commercial copper(II) bromide were used with the same results.

Method #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 $(NH_4)_2CuBr_4 \cdot 2H_2O$. When some methanol was stripped off of the filtrate, a white solid was isolated.

Anal. Found: C, 1.13; H, 1.64; Mo, 57.28; 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.

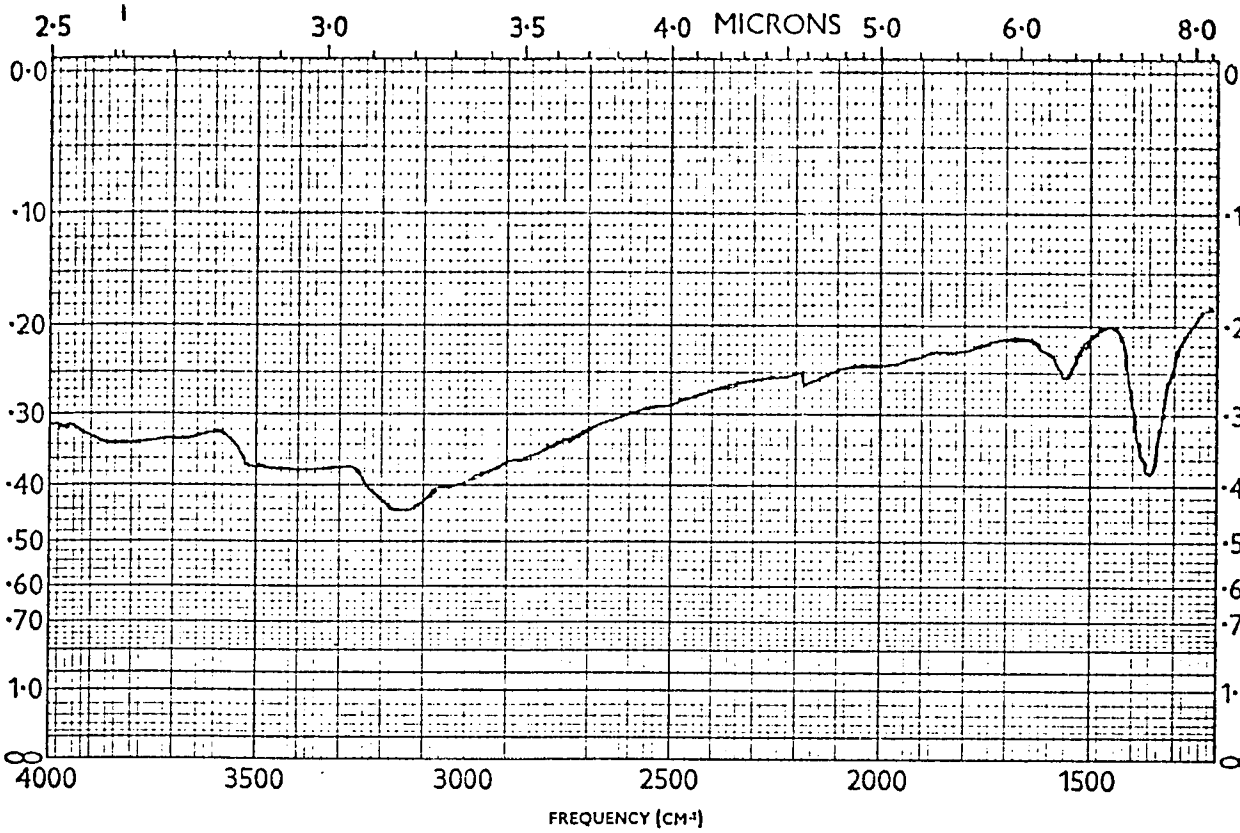
_D_. _X-ray Powder Patterns_

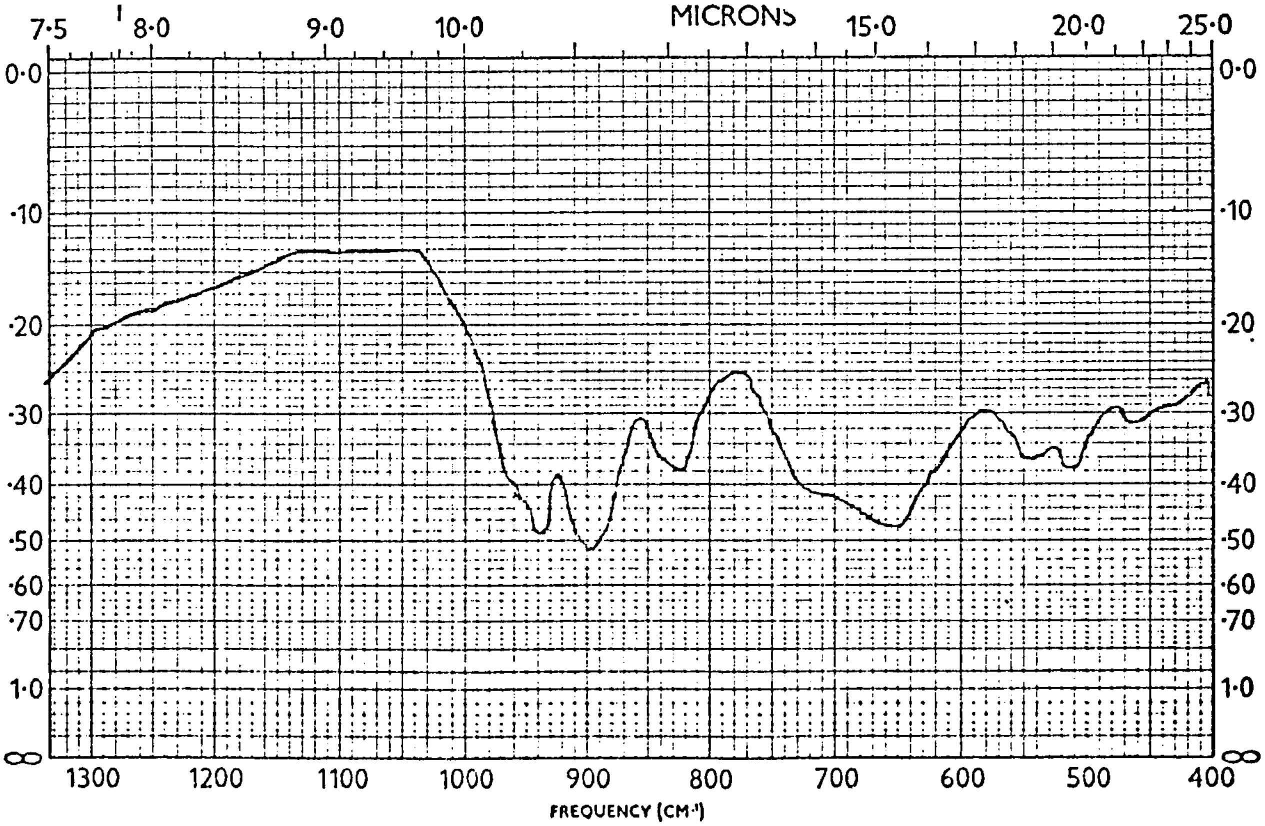
X-ray powder patterns were run as described in Chapter I page 9.

_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.


2·5
3·0
3·5
4·0
MICRONS
5·0
6·0
8·0
0·0
·10
·20
·30
·40
·50
·60
·70
1·0
∞
4000
3500
3000
2500
2000
1500
FREQUENCY (CM^{-1})


7·5
8·0
9·0
10·0
MICRONS
15·0
20·0
25·0
0·0
·10
·20
·30
·40
·50
·60
·70
1·0
∞
1300
1200
1100
1000
900
800
700
600
500
400
FREQUENCY (CM^{-1})

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 (NH_4^+ infrared absorbtion at 3200 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°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 Mo(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 #1

The method described by Killefer and Linz,[33] Kay and Mitchell,[34] Henderson et al,[35, 36] and Gopalakrishman et al.[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 1:1 mole ration was used in all cases. The solution was brought to a boil and the 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.

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

Acid	grams of acid used	grams of ammonium salt used	ml 15 M NH_4OH	grams MoO_4 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

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 #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 #1 (% Calculated for $(NH_4)_mMoO_3(Acid)_n \cdot H_2O$, m=number of ammonium ions, n=number of ligands coordinated).

Acid		%C	%H	%Mo	%N	m	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 C, 61.13; H, 5.13; 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.

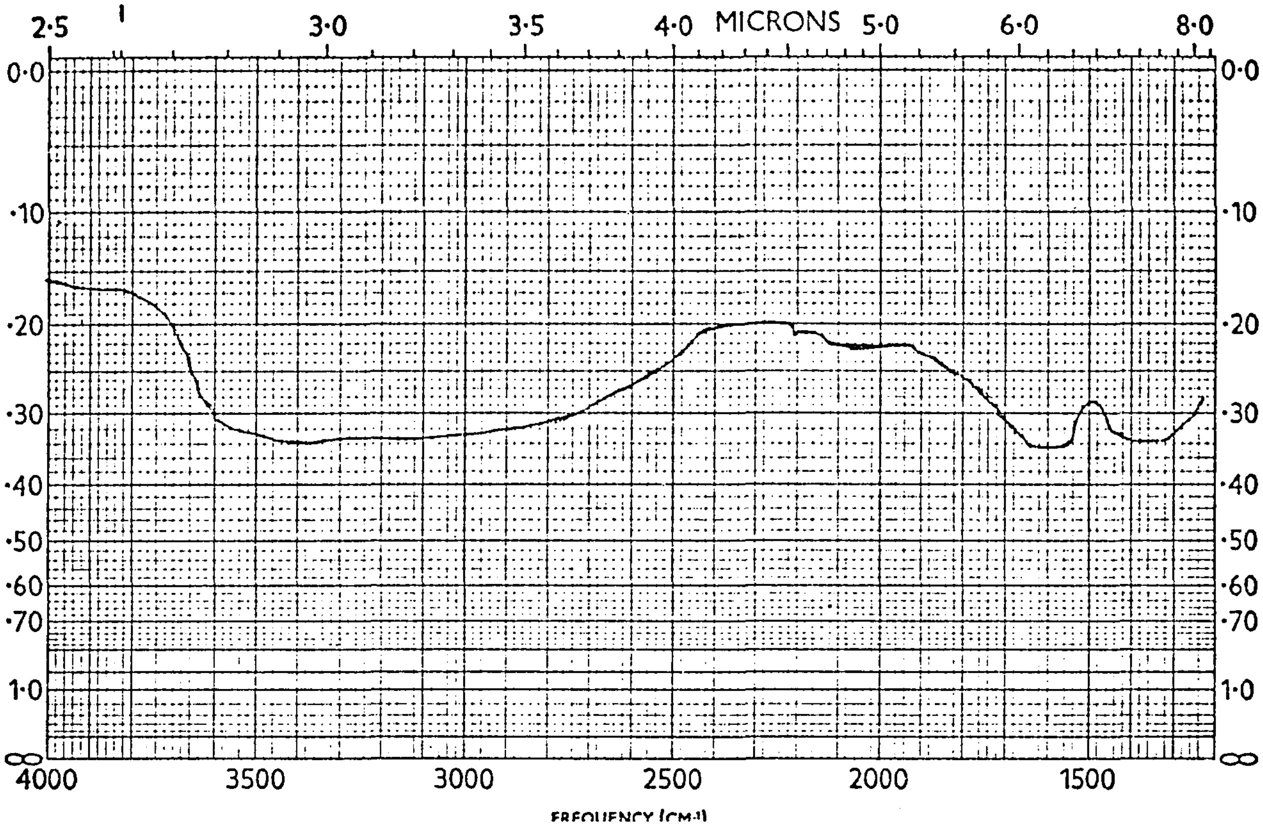
The mass spectra for the oxalate, tartrate, and phthalate complexes are given in Tables X through XII.

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.


MICRONS
2·5
3·0
3·5
4·0
5·0
6·0
8·0
0·0
·10
·20
·30
·40
·50
·60
·70
1·0
∞
4000
3500
3000
2500
2000
1500
FREQUENCY (CM⁻¹)

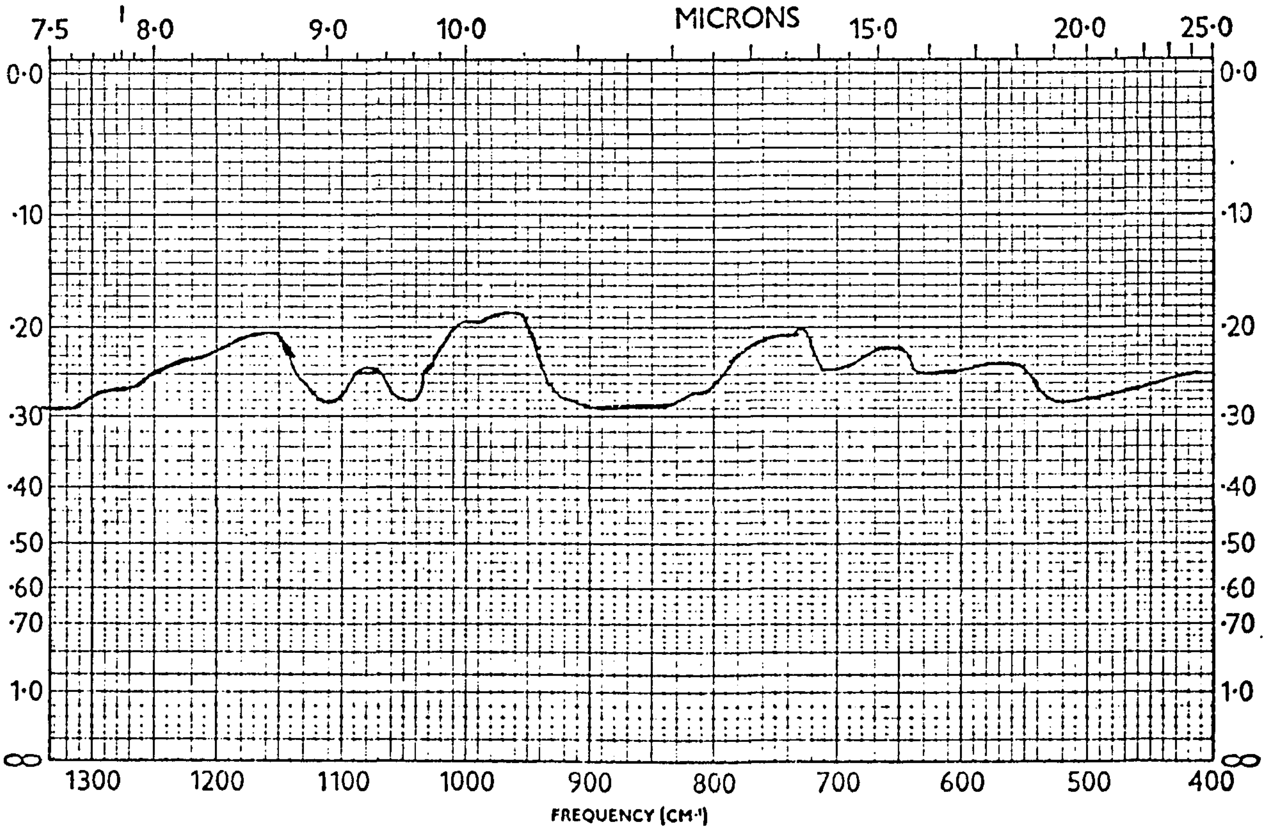
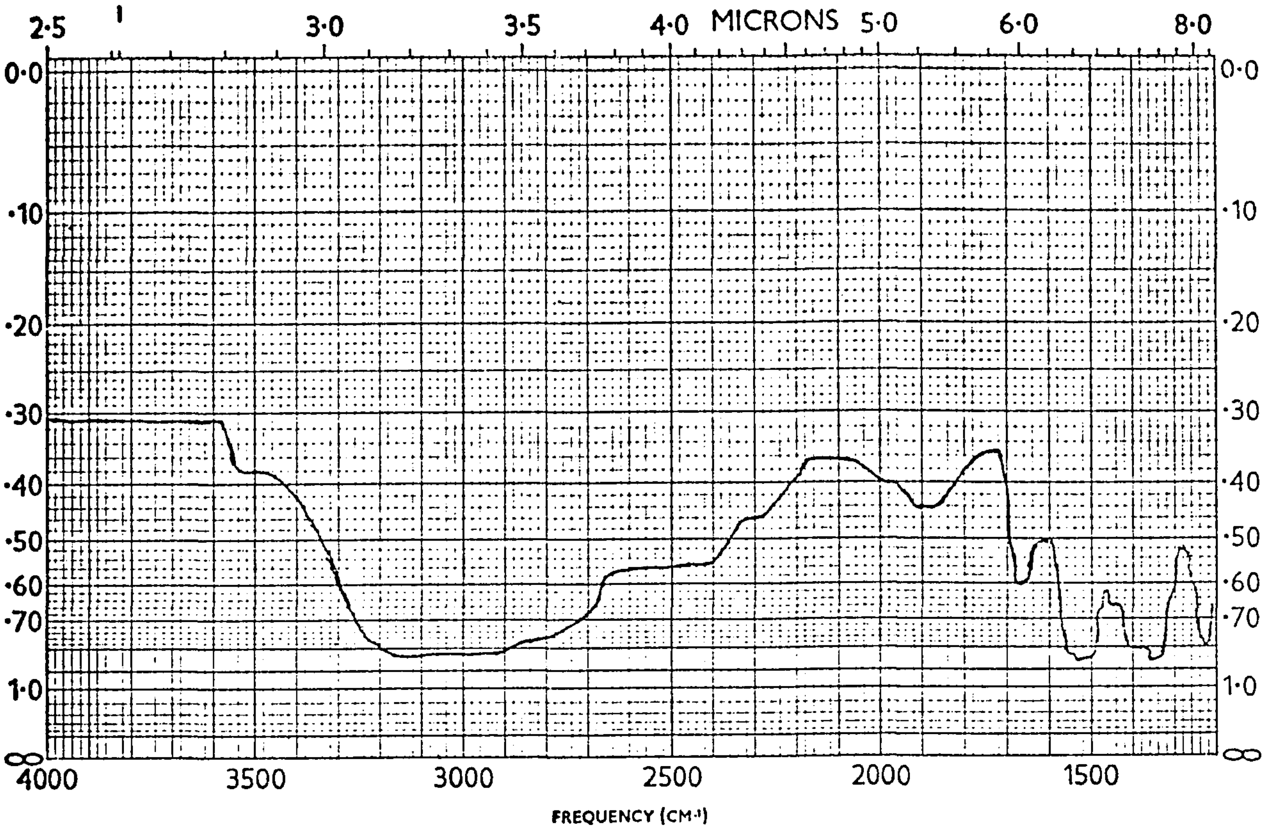

MICRONS
7·5
8·0
9·0
10·0
15·0
20·0
25·0
0·0
·10
·20
·30
·40
·50
·60
·70
1·0
∞
1300
1200
1100
1000
900
800
700
600
500
400
FREQUENCY (CM⁻¹)

Figure 10. Infrared Spectrum of Ammonium Molybdenum Phthalate.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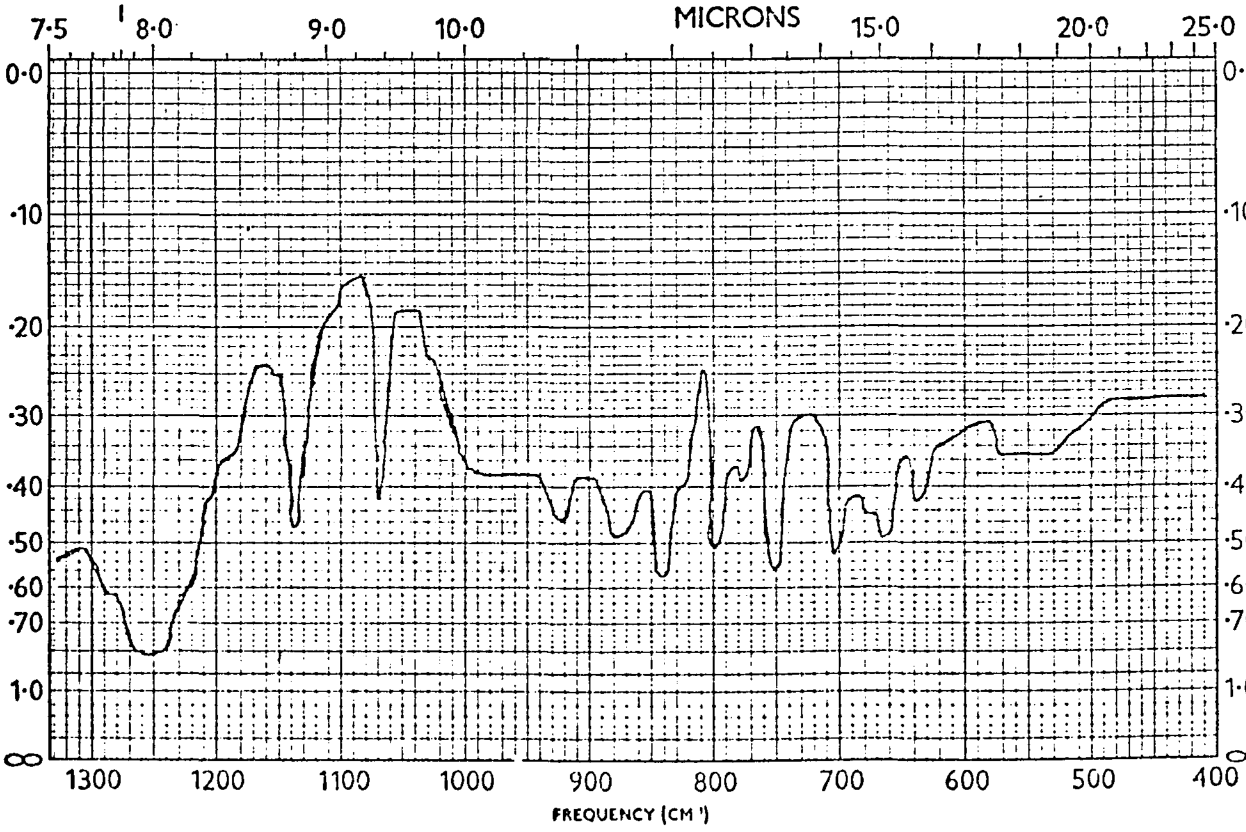
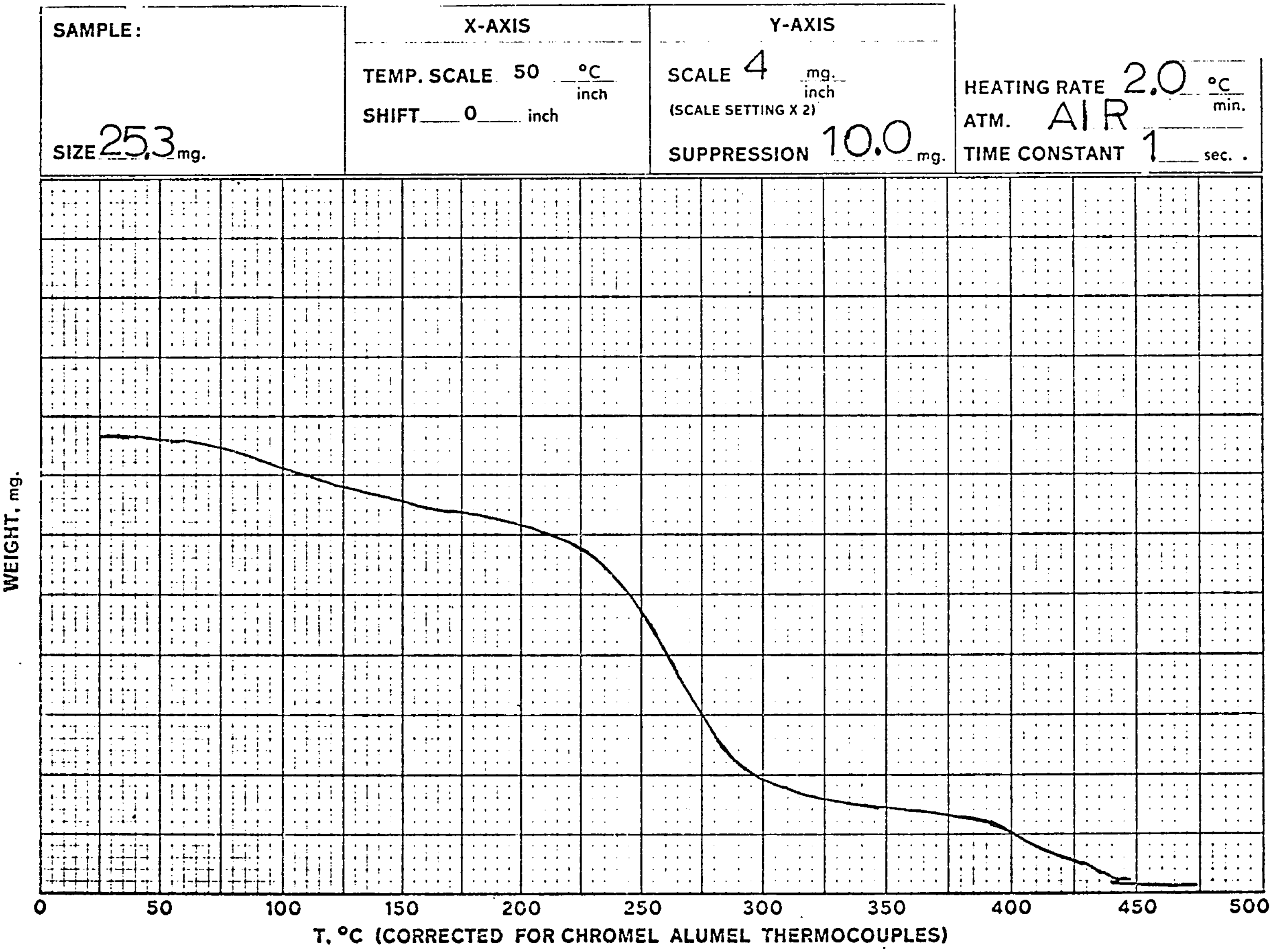
3·0
3·5
4·0
MICRONS
5·0
6·0
8·0
0·0
·10
·20
·30
·40
·50
·60
·70
1·0
∞
4000
3500
3000
2500
2000
1500
FREQUENCY (CM⁻¹)


7·5
8·0
9·0
10·0
MICRONS
15·0
20·0
25·0
0·0
·10
·20
·30
·40
·50
·60
·70
1·0
∞
1300
1200
1100
1000
900
800
700
600
500
400
FREQUENCY (CM⁻¹)



SAMPLE:

SIZE 25.3 mg.

X-AXIS

TEMP. SCALE 50 °C/inch

SHIFT 0 inch

Y-AXIS

SCALE 4 mg./inch

(SCALE SETTING X 2)

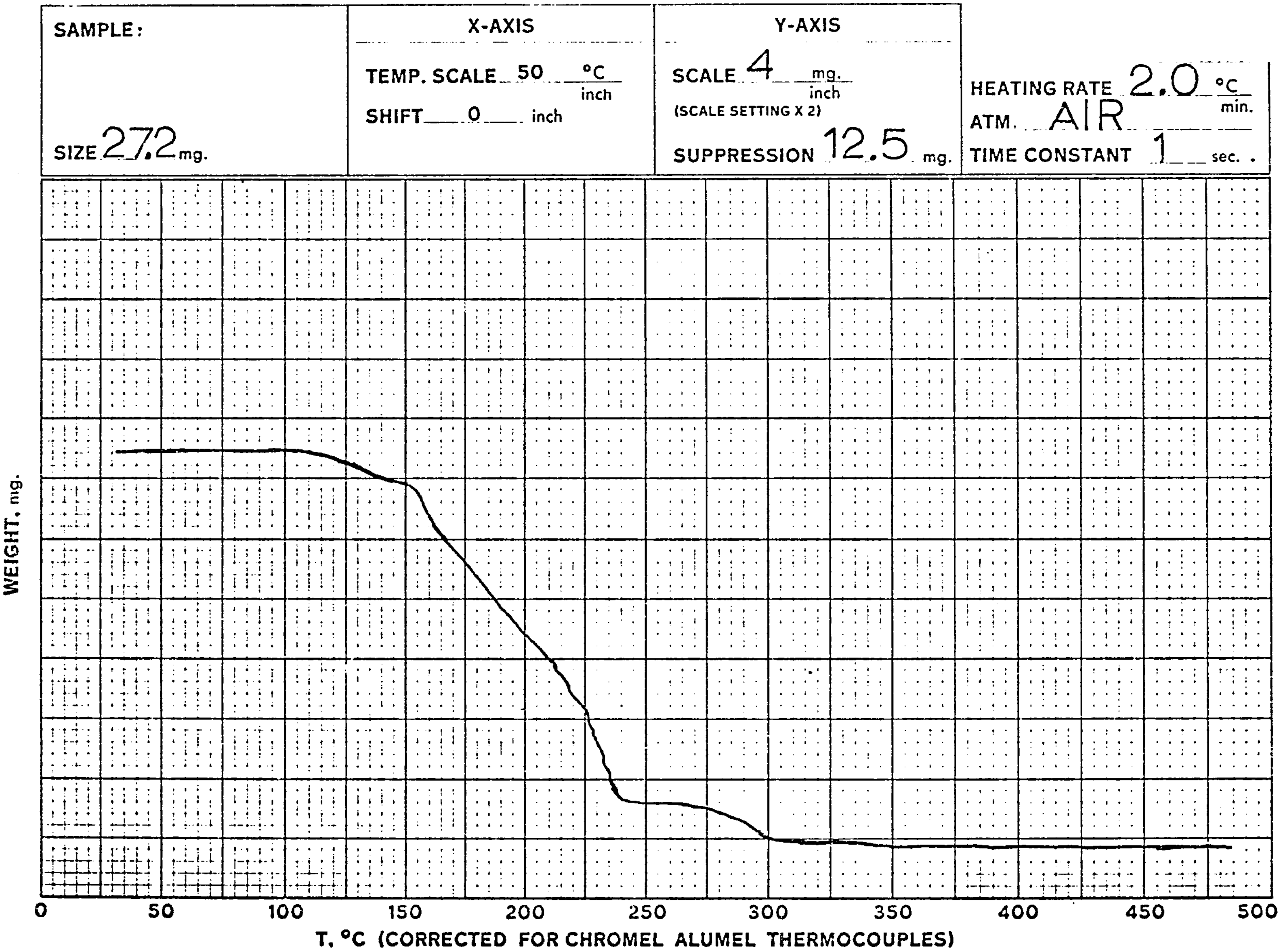
SUPPRESSION 10.0 mg.

HEATING RATE 2.0 °C/min.

ATM. AIR

TIME CONSTANT 1 sec.

Figure 11. TGA of Ammonium Molybdenum Tartrate



SAMPLE:

SIZE 27.2 mg.

X-AXIS

TEMP. SCALE 50 °C/inch

SHIFT 0 inch

Y-AXIS

SCALE 4 mg./inch

(SCALE SETTING X 2)

SUPPRESSION 12.5 mg.

HEATING RATE 2.0 °C/min.

ATM. AIR

TIME CONSTANT 1 sec.

Figure 12. TGA of Ammonium Molybdenum Phthalate

Table X. The Mass Spectrum of Ammonium Molybdenum Oxalate

m/e	%
144	30
45	36
44	42
43	67
42	3
37	8
35	23
29	11
28	14
27	6
19	100
18	73
17	42
1	27

Table XI. The Mass Spectrum of Ammonium Molybdenum Tartrate.

m/e	%	m/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)

d_{obsd}, A$^{\circ}$	d_{calc}, A$^{\circ}$	I/I_o	hkl^a
12.6090	12.51362	m	110
7.5122	7.51316; 7.46826	m	200; 001
6.7071	6.73534; 6.63950	s	130; 11$\bar{1}$
6.2623	6.25681; 6.23081; 6.20818	m	220; 021; 111
5.1022	5.10697; 5.06979	vw	13$\bar{1}$; 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	3.78895; 3.77369; 3.76733	s	15$\bar{1}$; 241; 060
3.5297	3.54562; 3.52901	vw	022; 331
3.3240	3.33154; 3.32414; 3.31975	s	42$\bar{1}$; 13$\bar{2}$; 22$\bar{2}$
3.1523	3.15706	vw	170
3.0228	3.02386	w	261
2.9280	2.92817	w	171
2.8550	2.86518; 2.85767; 2.84764	w	$\bar{1}$52; 51$\bar{1}$; 312
2.7849	2.79142; 2.79141	m	152; 530
2.6602	2.66009; 2.65209	m	460; 062
2.5865	2.59239	w	37$\bar{1}$
2.5183	2.51862	w	28$\bar{1}$
2.4346	2.43911; 2.43406; 2.43114; 2.43041; 2.42945	w	51$\bar{2}$; $\bar{1}$72; 023; $\bar{2}$03; 55$\bar{1}$

continued -

Table XIII. Continued

d_{obsd}, A^o	d_{calc}, A^o	I/I_o	hkl^a
2.3642	2.36681	w	$\bar{1}33$
2.2464	2.24907; 2.24511; 2.24224	w	$37\bar{2}$; 390; $64\bar{1}$
2.2090	2.21317	vw	$33\bar{3}$
2.1734	2.17480; 2.17397	w	$39\bar{1}$; $60\bar{2}$
2.1337	2.13700; 2.13484; 2.13388; 2.13114; 2.21966	vw	710; $62\bar{2}$; 153; 243; $42\bar{3}$
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	1.87942; 1.87940; 1.87829; 1.87807	w	443; $46\bar{3}$; 800; $73\bar{2}$
1.8268	1.82794; 1.82768; 1.82642	m	$62\bar{3}$; $22\bar{4}$; 114
1.7751	1.77435; 1.77281	vw	204; 044
1.7229	1.72299; 1.72285	w	$68\bar{2}$; $82\bar{2}$
1.6922	1.69286	vw	244
1.6551	1.65519	vw	$2,10,\bar{3}$
1.6208	1.62077; 1.61954; 1.61908	vw	$\bar{1}74$; 802; 643
1.5728	1.57156	vw	791
1.5399	1.53844	vw	2,14,1
1.5027	1.50380; 1.50263; 1.50263; 1.50211; 1.50193	vw	374; 284; 10,0,0; 0,12,3; $\bar{1}94$
1.3960	1.39678; 1.39576; 1.39571; 1.39571; 1.39541	w	$\bar{3}55$; $10,4,\bar{2}$; 2,10,4; 10,6,0; 245

continued -

Table XIII. Continued

d_{obsd}, A°	d_{calcd}, A°	I/I_o	hkl[a]
1.3516	1.35182; 1.35137	w	10,0,2; 10,6,1
1.3020	1.30261; 1.30258; 1.30182	w	11,3,$\bar{2}$; 11,3,1; $64\bar{5}$
1.2640	1.26412; 1.26411	vw	$73\bar{5}$; 10,6,$\bar{3}$
1.2499	1.24978	vw	10,10,$\bar{1}$
1.1749	1.17555; 1.17502; 1.17466; 1.17455	vw	10,6,3; 715; 10,12,0; $53\bar{6}$
1.1523	1.15242; 1.15237; 1.15225; 1.15221; 1.15162	vw	11,1,4; 11,1,3; 266; 954; $62\bar{6}$
1.1308	1.13093; 1.13046	vw	685; $95\bar{5}$
1.1198	1.12020	vw	805
1.0122	1.01228; 1.01209	vw	$88\bar{6}$; 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	$\bar{2}$,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)

d_{obsd}, A^{o}	d_{calcd}, A^{o}	I/I_o	hkl[a]
13.3310	13.38858; 12.88992	s	110, 200
7.7958	7.89440; 7.8331; 7.76423	m	201, 020, 111
6.7324	6.69429	m	220
6.4168	6.44496	vw	400
6.1253	6.12577	vw	311
5.5876	5.57924; 5.56151	w	401, 221
4.9607	4.97706	vw	420
4.5314	4.54502; 4.52926; 4.50969	vw	421, 511, 131
3.8900	3.88212	w	222
3.6731	3.66962; 3.66911	w	$\bar{2}22$, 530
3.5325	3.53972; 3.53568; 3.52551	vw	512, $\bar{4}02$, 422
3.3572	3.36357	w	$62\bar{1}$
3.2249	3.22228	w	$42\bar{2}$
3.0675	3.06288	w	622
2.7790	2.78076	w	442
2.5894	2.58961; 2.58808; 2.58768	vw	$\bar{1}33$, 333, 152
2.4188	2.42008	vw	460
2.1704	2.17126	w	171
2.0808	2.08299	vw	$3\bar{3}4$

a. Based on the Powder pattern given in Table XVI

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

d_{obsd}, A^{o}	d_{calcd}, A^{o}	I/I_o	hkl^{a}
12.9790	12.93828	vw	001
8.9161	8.96874	s	110
8.1018	8.28243; 8.13140; 8.12566	vw	201, 200, 111
7.0923		s	
6.8046	6.79380	w	$11\bar{1}$
6.4917	6.46914	w	002
6.0177	6.01732	w	$\bar{2}01$
5.7909	5.79220	s	112
5.3434	5.37577	m	020
5.0220	5.07194	m	311
4.6225	4.61196	m	312
4.3239	4.32623; 4.31276	vw	401, 003
4.1907	4.21019	w	113
4.0167	4.00894	w	$22\bar{1}$
3.7792		w	
3.6362	3.64812; 3.62795	s	403, $11\bar{3}$
3.5463	3.54640	w	$\bar{4}01$
3.4755		w	
3.3847	3.39690; 3.37037	w	$22\bar{2}$, 421
3.2855	3.28179; 3.28065	s	511, 422
3.0924	3.10215	vw	404
3.0419	3.04237; 3.04177	w	513, 331
2.9921	2.98958; 2.98735	vw	330, $13\bar{2}$

continued -

Table XV. Continued

d_{obsd}, A^{o}	d_{calcd}, A^{o}	I/I_{o}	hkl^{a}
2.8965	2.89610	s	224
2.7942	2.79901	vw	$33\bar{1}$
2.7385	2.73635	w	514
2.7095	2.70855; 2.70384	vw	333, $\bar{2}04$
2.6442	2.64331	vw	315
2.5865	2.58766	vw	005
2.5349	2.53720; 2.53597	vw	$33\bar{2}$, 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

d_{obsd}, A^o	d_{calcd}, A^o	I/I_o	hkl[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 $(NH_4)_2MoO_3(Acid)\cdot H_2O$. The oxalate complex was studied by Gopalskrishman et al.[37] Henderson and Barr[35] made the complex $MoO_2(NaC_4H_4O_6)_2\cdot 3H_2O$ by dissolving 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. All three complexes have the infrared absorptions for the ammonium ion (about 3100 cm^{-1}) and for the carbonyl group (about 1600 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 $C_6H_4^+$ fragment (m/e=76), but does not have a significant peak at m/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 cm^{-1}, 875 cm^{-1}, and 750 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 cm^{-1} and 710 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°C, while the phthalate complex starts to lose the ligand at about 160°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 Å, β 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
β	69.941	83.324	95.250
Cell Type	Monoclinic	Monoclinic	Monoclinic
Centering	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 Mo(VI) to Mo(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.[80-83]

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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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 three 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 m/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.

U.N.H. Program No. 39

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
ER = maximum allowable difference between calculated and observed masses for any fragment.
H1 = maximum number of hetero atoms of type 1 in any fragment
H2 = maximum number of hetero atoms of type 2 in any fragment
H3 = maximum number of hetero atoms of type 3 in any fragment
Note: LN + LO + H1 + H2 + H3 = LH
ATOM1, ATOM2, ATOM3 = name of each hetero atom, of type 1,2, or 3
WH1, WH2, WH3 = corresponding atomic weight
EXPM = experimental m/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 m/e, XXXX.XXXXX
(3) Hetero atoms, FORMAT(3I5)
Columns 1-5 H1 = 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 ATOM1 = name of hetero atom of type 1
25-34 WH1 = atomic weight, as XXXX.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 XXXX.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.

```
C     PROGRAM UNH-39 (REVISED)  MASS SPECTRUM FRAGMENT FORMULAS.          39R-0010
C     COMPUTES POSSIBLE FRAGMENT FORMULAS FROM THE MASS SPECTRUM PEAKS    39R-0020
C     ADAPTED FROM STEPHEN R. SHRADER, "INTRODUCTORY MASS SPECTROMETRY",39R-0030
C        APPENDIX C, NOVEMBER, 1974, BY HAENDLER AND ESTES                39R-0040
C     INPUT                                                               39R-0050
C       CARD #1 IS A TITLE CARD (FORMAT 20A4)                             39R-0060
C       CARD #2 - LN, LO, AND LH ARE THE MAXIMUM NUMBERS OF NITROGENS,    39R-0070
C          OXYGENS, AND ALL HETEROATOMS RESPECTIVELY; ER IS THE MAXIMUM  39R-0080
C          ALLOWED DIFFERENCE BETWEEN THE CALCULATED FRAGMENT WEIGHT AND39R-0090
C          THE EXPERIMENTAL M/E VALUE (FORMAT 3I5,F10.5)                 39R-0100
C       CARD #3 - H1, H2, AND H3 ARE THE MAXIMUM NUMBERS OF THREE TYPES 39R-0110
C          OF HETEROATOMS OTHER THAN C, H, N, OR O (FORMAT 3I5)          39R-0120
C       ONE CARD IS INCLUDED NEXT FOR EACH HETEROATOM (H1, H2, H3), OF   39R-0130
C          WHICH THERE IS AT LEAST ONE IN THE MOLECULE. THIS CARD        39R-0140
C          CONTAINS THE NAME (COLUMNS 1-24 FORMAT 6A4) AND ATOMIC WEIGHT39R-0150
C          (COLUMNS 25-35 FORMAT F10.5) OF THE HETEROATOM.               39R-0160
C       THE EXPERIMENTAL M/E VALUES ARE ENTERED NEXT, 1 PER CARD IN      39R-0170
C          COLUMNS 1-10 (FORMAT F10.5)                                   39R-0180
C       THE LAST DATA CARD IS BLANK IN COLUMNS 1 THROUGH 10.             39R-0190
C     OUTPUT - THE TITLE, NAME AND ATOMIC WEIRHT OF EACH HETEROATOM, AND39R-0200
C       THE POSSIBLE FRAGMENT FORMULAS (WITH THE EXPERIMENTAL AND        39R-0210
C       CALCULATED M/E VALUES AND THE DIFFERENCE) ARE LISTED IN THE      39R-0220
C       OUTPUT                                                           39R-0230
C                                                                        39R-0240
      INTEGER READR,PRINTR,H1,H2,H3                                      39R-0250
      DIMENSION TITLE(20),ATOM1(6),ATOM2(6),ATOM3(6)                      39R-0260
      READR=5                                                            39R-0270
      PRINTR=6                                                           39R-0280
      READ(READR,206)(TITLE(I),I=1,20)                                   39R-0290
      WRITE(PRINTR,208)(TITLE(I),I=1,20)                                 39R-0300
   20 N1=0                                                               39R-0310
      N2=0                                                               39R-0320
      N3=0                                                               39R-0330
      WH1=0.0                                                            39R-0340
      WH2=0.0                                                            39R-0350
      WH3=0.0                                                            39R-0360
      L1=0                                                               39R-0370
      L2=0                                                               39R-0380
      L3=0                                                               39R-0390
      READ(READR,201)LN,LO,LH,ER                                         39R-0400
      READ(READR,202)H1,H2,H3                                            39R-0410
      LN=LN+1                                                            39R-0420
      LO=LO+1                                                            39R-0430
      IF(H1)40,40,31                                                     39R-0440
   31 READ(READR,207)((ATOM1(I),I=1,6),WH1)                              39R-0450
      WRITE(PRINTR,209)(ATOM1(I),I=1,6)                                  39R-0460
      WRITE(PRINTR,210)WH1                                               39R-0470
      L1=H1+1                                                            39R-0480
```

```
      IF(H2)40,40,32                                                    39R-0490
   32 READ(READR,207)((ATOM2(I),I=1,6),WH2)                             39R-0500
      WRITE(PRINTR,211)(ATOM2(I),I=1,6)                                 39R-0510
      WRITE(PRINTR,210)WH2                                              39R-0520
      L2=H2+1                                                           39R-0530
      IF(H3)40,40,33                                                    39R-0540
   33 READ(READR,207)((ATOM3(I),I=1,6),WH3)                             39R-0550
      WRITE(PRINTR,212)(ATOM3(I),I=1,6)                                 39R-0560
      WRITE(PRINTR,210)WH3                                              39R-0570
      L3=H3+1                                                           39R-0580
   40 WRITE(PRINTR,204)                                                 39R-0590
   50 READ(READR,203)EXPM                                               39R-0600
      IF(EXPM)101,101,60                                                39R-0610
   60 C=EXPM                                                            39R-0620
      D=ROUND(C)                                                        39R-0630
      NM=IFIX(D)                                                        39R-0640
      NN=0                                                              39R-0650
      NC=0                                                              39R-0660
      N1=0                                                              39R-0670
      N2=0                                                              39R-0680
      N3=0                                                              39R-0690
      C=WH1                                                             39R-0700
      D=ROUND(C)                                                        39R-0710
      NH1=IFIX(D)                                                       39R-0720
      C=WH2                                                             39R-0730
      D=ROUND(C)                                                        39R-0740
      NH2=IFIX(D)                                                       39R-0750
      C=WH3                                                             39R-0760
      D=ROUND(C)                                                        39R-0770
      NH3=IFIX(D)                                                       39R-0780
      DO 99 J=1,L3                                                      39R-0790
      N3=J-1                                                            39R-0800
      DO 98 K=1,L2                                                      39R-0810
      N2=K-1                                                            39R-0820
      DO 97 L=1,L1                                                      39R-0830
      N1=L-1                                                            39R-0840
      DO 96 M=1,LN                                                      39R-0850
      NN=M-1                                                            39R-0860
      DO 95 N=1,LC                                                      39R-0870
      NC=N-1                                                            39R-0880
      IH=NN+NC+N1+N2+N3                                                 39R-0890
      IF(IH-LH)51,51,95                                                 39R-0900
   51 NMS=NM-16*NO-14*NN-NH1*N1-NH2*N2-NH3*N3                           39R-0910
      NC=NMS/12                                                         39R-0920
      IF(NC)95,52,52                                                    39R-0930
   52 NH=NMS-12*NC                                                      39R-0940
      IF(NH)95,53,53                                                    39R-0950
   53 NHC=2*NC+NN+3                                                     39R-0960
```

```
      IF(NHC-NH)95,54,54
   54 DNH=FLOAT(NH)
      DNN=FLOAT(NN)
      DNC=FLOAT(NC)
      DNO=FLOAT(NO)
      DN1=FLOAT(N1)
      DN2=FLOAT(N2)
      DN3=FLOAT(N3)
      CALC=12.00*DNC+1.007825*DNH+14.003074*DNN+15.99491*DNO+WH1*DN1+
     1WH2*DN2+WH3*DN3
      DIFF=CALC-EXPM
      IF(ER+DIFF)80,55,55
   55 IF(ER-DIFF)80,56,56
   56 DIFF=DIFF*1000.0
      Y=ROUND(DIFF)
      IFF=IFIX(Y)
      WRITE(PRINTR,205)EXPM,NC,NH,NN,NO,N1,N2,N3,CALC,IFF
   80 NC=NC-1
      NH=NH+12
      GO TO 53
   95 CONTINUE
   96 CONTINUE
   97 CONTINUE
   98 CONTINUE
   99 CONTINUE
  100 GO TO 50
  101 STOP
  201 FORMAT(3I5,F10.5)
  202 FORMAT(3I5)
  203 FORMAT(F10.5)
  204 FORMAT(1H ,3X,'EXPM',5X,'C',5X,'H',5X,'N',5X,'O',5X,'H1',4X,'H2',
     14X,'H3',7X,'CALC',4X,'DIFFERENCE*1000.0')
  205 FORMAT(1H ,1X,F8.4,7(2X,I4),2X,F8.4,2X,I8)
  206 FORMAT(20A4)
  207 FORMAT(6A4,F10.5)
  208 FORMAT(1H1,20A4)
  209 FORMAT(1H ,6X,'HETEROATOM #1 IS',2X,6A4)
  210 FORMAT(1H ,6X,'ATOMIC WEIGHT =',2X,F10.5)
  211 FORMAT(1H ,6X,'HETEROATOM #2 IS',2X,6A4)
  212 FORMAT(1H ,6X,'HETEROATOM #3 IS',2X,6A4)
      END

      FUNCTION ROUND(B)
      X=AINT(B)
      IF(B-X-0.5)300,301,301
  301 X=X+1.0
  300 ROUND = X
      RETURN
      END
```

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
H = number of hydrogen atoms in the formula
N = number of nitrogen atoms in the formula
O = 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 C = number of carbons, as XXXX
6-9 H = number of hydrogens, as XXXX
11-14 N = number of nitrogens, as XXXX
16-19 O = number of oxygens, as XXXX
21-24 H1 = 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 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.

```
C     PROGRAM UNH-40  PREDICTED MASS SPECTRUM.                          40-00010
C     CALCULATES ALL POSSIBLE M/E PEAKS FROM THE EMPIRICAL FORMULA.     40-00020
C     INPUT                                                             40-00030
C       CARD #1 - TITLE - ANY INFORMATION (FORMAT 20A4)                 40-00040
C       CARD #2 - C = # CARBONS, H = # HYDROGENS, N = # NITROGENS, O =  40-00050
C       # OXYGENS; H1, H2, H3 = THE NUMBERS OF 3 OTHER TYPES OF ATOMS;  40-00060
C       A = 0 FOR THE LAST DATA SET, A = 1 FOR ALL OTHER DATA SETS      40-00070
C       (FORMAT 7F5.1,I2)                                               40-00080
C       ONE CARD IS INCLUDED FOR EACH HETEROATOM (H1, H2, OR H3) OF     40-00090
C       WHICH THERE IS ONE OR MORE. THIS CARD CONTAINS ITS NAME AND     40-00100
C       ATOMIC WEIGHT (FORMAT 6A4,F10.5).  H1, H2, H3 ARE USED IN ORDER.40-00110
C     OUTPUT INCLUDES THE TITLE, NAME AND ATOMIC WEIGHT OF HETEROATOMS, 40-00120
C       THE FORMULA AND M/E VALUE OF ALL POSSIBLE FRAGMENTS, AND THE M/E40-00130
C       VALUE OF THE MOLECULAR ION PEAK                                 40-00140
      DIMENSION TITLE(20),ATOM1(6),ATOM2(6),ATOM3(6)                    40-00150
      DIMENSION DM(500),MC(500),MH(500),MN(500),MO(500),MH1(500)        40-00160
      DIMENSION MH2(500),MH3(500)                                       40-00170
      INTEGER READR,PRINTR,A                                            40-00180
      REAL C,H,N,O,H1,H2,H3                                             40-00190
      READR=5                                                           40-00200
      PRINTR=6                                                          40-00210
    7 WH1=0.0                                                           40-00220
      WH2=0.0                                                           40-00230
      WH3=0.0                                                           40-00240
      READ(READR,101)(TITLE(I),I=1,20)                                  40-00250
      WRITE(PRINTR,102)(TITLE(I),I=1,20)                                40-00260
      READ(READR,103)C,H,N,O,H1,H2,H3,A                                 40-00270
      IF(H1)4,4,1                                                       40-00280
    1 READ(READR,104)((ATOM1(I),I=1,6),WH1)                             40-00290
      WRITE(PRINTR,105)(ATOM1(I),I=1,6)                                 40-00300
      WRITE(PRINTR,106)WH1                                              40-00310
      IF(H2)4,4,2                                                       40-00320
    2 READ(READR,104)((ATOM2(I),I=1,6),WH2)                             40-00330
      WRITE(PRINTR,107)(ATOM2(I),I=1,6)                                 40-00340
      WRITE(PRINTR,106)WH2                                              40-00350
      IF(H3)4,4,3                                                       40-00360
    3 READ(READR,104)((ATOM3(I),I=1,6),WH3)                             40-00370
      WRITE(PRINTR,108)(ATOM3(I),I=1,6)                                 40-00380
      WRITE(PRINTR,106)WH3                                              40-00390
    4 WRITE(PRINTR,109)                                                 40-00400
      LC=1+IFIX(C)                                                      40-00410
      LH=1+IFIX(H)                                                      40-00420
      LN=1+IFIX(N)                                                      40-00430
      LO=1+IFIX(O)                                                      40-00440
      LH1=1+IFIX(H1)                                                    40-00450
      LH2=1+IFIX(H2)                                                    40-00460
      LH3=1+IFIX(H3)                                                    40-00470
      NC=1                                                              40-00480
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```
      DO 99 IH3=1,LH3                                                   40-00490
      NH3=IH3-1                                                         40-00500
      DO 98 IH2=1,LH2                                                   40-00510
      NH2=IH2-1                                                         40-00520
      DO 97 IH1=1,LH1                                                   40-00530
      NH1=IH1-1                                                         40-00540
      DO 96 IO=1,LO                                                     40-00550
      NO=IO-1                                                           40-00560
      DO 95 IN=1,LN                                                     40-00570
      NN=IN-1                                                           40-00580
      DO 94 IH=1,LH                                                     40-00590
      NH=IH-1                                                           40-00600
      DO 93 IC=1,LC                                                     40-00610
      NC=IC-1                                                           40-00620
      NHC=2*NC+NN+3                                                     40-00630
      IF(NH-NHC)6,6,93                                                  40-00640
    6 DNC=FLOAT(NC)                                                     40-00650
      DNH=FLOAT(NH)                                                     40-00660
      DNN=FLOAT(NN)                                                     40-00670
      DNO=FLOAT(NO)                                                     40-00680
      DNH1=FLOAT(NH1)                                                   40-00690
      DNH2=FLOAT(NH2)                                                   40-00700
      DNH3=FLOAT(NH3)                                                   40-00710
      CALC=12.0*DNC+1.007825*DNH+14.003074*DNN+15.99491*DNO+WH1*DNH1+   40-00720
     1WH2*DNH2+WH3*DNH3                                                 40-00730
      DM(NQ)=CALC                                                       40-00740
      MC(NQ)=NC                                                         40-00750
      MH(NQ)=NH                                                         40-00760
      MN(NQ)=NN                                                         40-00770
      MO(NQ)=NO                                                         40-00780
      MH1(NQ)=NH1                                                       40-00790
      MH2(NQ)=NH2                                                       40-00800
      MH3(NQ)=NH3                                                       40-00810
      NQ=NQ+1                                                           40-00820
   93 CONTINUE                                                          40-00830
   94 CONTINUE                                                          40-00840
   95 CONTINUE                                                          40-00850
   96 CONTINUE                                                          40-00860
   97 CONTINUE                                                          40-00870
   98 CONTINUE                                                          40-00880
   99 CONTINUE                                                          40-00890
      NQ=NQ-1                                                           40-00900
      DO 80 I=2,NQ                                                      40-00910
      MQ=I-1                                                            40-00920
      DO 81 J=1,MQ                                                      40-00930
      IF(DM(I)-DM(J))21,81,81                                           40-00940
   21 Z=DM(J)                                                           40-00950
      DM(J)=DM(I)                                                       40-00960
```

```
      DM(I)=Z
      K=MC(J)
      MC(J)=MC(I)
      MC(I)=K
      K=MH(J)
      MH(J)=MH(I)
      MH(I)=K
      K=MN(J)
      MN(J)=MN(I)
      MN(I)=K
      K=MO(J)
      MC(J)=MC(I)
      MO(I)=K
      K=MH1(J)
      MH1(J)=MH1(I)
      MH1(I)=K
      K=MH2(J)
      MH2(J)=MH2(I)
      MH2(I)=K
      K=MH3(J)
      MH3(J)=MH3(I)
      MH3(I)=K
   81 CONTINUE
   80 CONTINUE
      DO 82 I=1,NQ
      WRITE(PRINTR,110)MC(I),MH(I),MN(I),MC(I),MH1(I),MH2(I),MH3(I),
     1CM(I)
   82 CONTINUE
      CALC=12.0*C+1.007825*H+14.003074*N+15.99491*O+WH1*H1+WH2*H2+WH3*H3
      WRITE(PRINTR,111)CALC
      IF(A)8,8,7
    8 STOP
  101 FORMAT(20A4)
  102 FORMAT(1H1,20A4)
  103 FORMAT(7F5.1,I2)
  104 FORMAT(6A4,F10.5)
  105 FORMAT(1H ,6X,'HETEROATOM #1 IS ',6A4)
  106 FORMAT(1H ,6X,'ATOMIC WEIGHT IS ',F10.5)
  107 FORMAT(1H ,6X,'HETEROATOM #2 IS ',6A4)
  108 FORMAT(1H ,6X,'HETEROATOM #3 IS ',6A4)
  109 FORMAT(1H ,5X,'C',8X,'H',6X,'N',8X,'O',7X,'H1',7X,'H2',7X,'H3',
     110X,'M/E')
  110 FORMAT(1H ,3X,7(I5,4X),F10.5)
  111 FORMAT(1H ,'MOLECULAR ION PEAK HAS M/E = ',F10.5)
      END
```