

A Study of Ammonium Permolybdates

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During the investigation of the structure of polymolybdates, which is now being carried out at this institute, it seemed possible to obtain further information on the paramolybdates by studying the perparamolybdates. A study of the ammonium perparamolybdates was therefore begun.

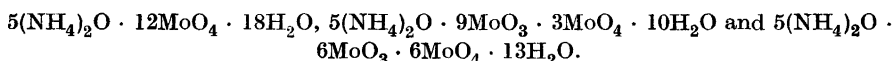
Werther¹ in 1861 noted the yellow colour obtained by the action of H_2O_2 on acid solutions of ammonium molybdate. The crystals of ammonium perparamolybdate were then investigated by Baerwald² in 1885. He dissolved ammonium paramolybdate in an excess of H_2O_2 and let the solution evaporate isothermally. From his primitive analyses he arrived at the formula $14\text{NH}_3 \cdot 18\text{MoO}_3 \cdot 3\text{H}_2\text{O}_2 \cdot 18\text{H}_2\text{O}$. The large lemon-yellow crystals were monoclinic with $a : b : c = 1.4727 : 1 : 1.0268$ and $\beta = 74^\circ 32'$ ($180^\circ - \beta = 105^\circ 28'$). Péchard³ used the same method at 100°C and undoubtedly obtained the same crystals, because Dufet⁴ who measured them crystallographically found $a : b : c = 1.4682 : 1 : 1.0259$ and $\beta = 105^\circ 41' 40''$. Péchard, however, described this compound as $(\text{NH}_4)_2\text{O} \cdot \text{Mo}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$.

Moeller⁵ claimed to have obtained a water-free compound $(\text{NH}_4)_2\text{Mo}_2\text{O}_8$ by the action of H_2O_2 on ammonium molybdate. His crystals were measured by Fock⁶ who found $a : b : c = 0.4693 : 1 : 0.2956$ and $\beta = 112^\circ 39' 30''$, so this compound was obviously not identical with that described by Baerwald and Péchard. The only analytical value, given by Moeller, is 80.89 % MoO_3 , which is possibly in agreement with 81.52 % calculated for ammonium paramolybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$. Since the crystals are bright yellow and described as easily cleaved along (010), we tried transforming the axial system given by Groth¹³ for $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ in order to show an eventual identity with Moeller's crystals. It was possible to get $a : b : c = 0.460 : 1 : 0.294$ and $\beta = 114.0^\circ$ in clear agreement with Fock's values. As is stated below Moeller obviously obtained a solid solution of small amounts of peroxide oxygen in $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$. (It is, however, interesting to note that the

habit of the crystals obtained by crystallization from an H_2O_2 solution is different from that obtained from an H_2O_2 free solution.)

The most critical analytical work in this field is surely that by Muthmann and Nagel⁷, which appeared in 1898. They found two different salts. From concentrated H_2O_2 solutions, saturated with $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ they obtained at first orange coloured crystals and then from the mother liquor lemon yellow crystals of a quite different habit. The two compounds were given the formulae $3(\text{NH}_4)_2\text{O} \cdot 7\text{MoO}_4 \cdot 12\text{H}_2\text{O}$ and $3(\text{NH}_4)_2\text{O} \cdot 5\text{MoO}_3 \cdot 2\text{MoO}_4 \cdot 6\text{H}_2\text{O}$ respectively. The latter is certainly the salt formerly described by Baerwald and Péchard.

A very confusing contribution to the knowledge of the ammonium perparamolybdates was published in 1931 by Cagliotti⁸. He gives analytical results without stating the analytical methods used and X-ray crystallographic data without any statement about the sort of radiation. He claims to have prepared the following three compounds:



(The latter was obtained from solutions of normal ammonium molybdate in 30 % H_2O_2 .) In varying the ratio $\text{MoO}_3 : \text{O}_{\text{active}}$ in the solutions of paramolybdate in H_2O_2 between 1 and 6 he obtained crystals with active oxygen contents from 1.38 % to 1.90 %. He also studied the crystallization from the solution with the ratio $\text{MoO}_3 : \text{O}_{\text{active}} = 1$ at different temperatures. The results are here given in Table 1. The colour of these crystals changes from intense yellow to very bright yellow. In his X-ray investigation, Cagliotti studied ammonium perparamolybdates with oxygen contents of 0.99, 1.42 and 2.26 % and found great similarities between the powder photographs of paramolybdate and perparamolybdates.

Finally Rosenheim, Hakki and Krause⁹ have accepted the two formulae $5(\text{NH}_4)_2\text{O} \cdot 12\text{MoO}_3 \cdot 12\text{O} \cdot 21\text{H}_2\text{O}$ and $5(\text{NH}_4)_2\text{O} \cdot 12\text{MoO}_3 \cdot 3\text{O} \cdot 12\text{H}_2\text{O}$ with-

Table 1. (From Cagliotti⁸).

	$t^\circ\text{C}$	$(\text{NH}_4)_2\text{O}$	MoO_3	O	H_2O
1	30	11.58	77.47	1.97	8.98
2	40	12.00	77.49	1.80	8.71
3	50	12.00	77.45	1.84	8.71
4	60	11.98	77.60	1.75	8.67
5	70	11.62	77.38	1.94	9.06
6	80	11.21	78.44	0.99	8.36
7	90	11.30	81.02	0.36	6.32
8	96	11.42	80.82	0.30	6.46

out giving any analytical methods. In order to get better results, however, they prepared a guanidinium perparamolybdate for which they determined the following composition:

$(\text{CN}_3\text{H}_6)_2\text{O}$	26.01; 26.35 %
MoO_3	65.20; 64.90; 65.02 %
O	1.64; 1.95; 1.51 %

These values may give weight ratios $\text{MoO}_3/(\text{CN}_3\text{H}_6)_2\text{O}$ between $65.20/26.01 = 2.51$ and $64.90/26.35 = 2.46$. The calculated values are for $12\text{MoO}_3/5(\text{CN}_3\text{H}_6)_2\text{O} = 2.54$ and for $7\text{MoO}_3/3(\text{CN}_3\text{H}_6)_2\text{O} = 2.47$. But Rosenheim, Hakki and Krause concluded that they had obtained the compound $5(\text{CN}_3\text{H}_6)_2\text{O} \cdot 12\text{MoO}_3 \cdot 3\text{O} \cdot 11\text{H}_2\text{O}$!

EXPERIMENTAL

We have investigated crystals obtained by isothermal evaporation from solutions of ammonium paramolybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}^*$, in H_2O_2 .

Analytical methods and checks

NH_3 : Kjeldahl distillation and titration to colourless solution with bromcresol green + methyl red as indicator. In a solution containing MoO_3 , H_2O_2 and a known amount of NH_3 ($\text{MoO}_3 : \text{H}_2\text{O}_2 : \text{NH}_3$ approximately as in the solutions analyzed during the investigation), we determined NH_3 . Weighed amount: 0.04669 g. Observed amount: 0.04665 g.

MoO_3 : Heating to constant weight in a furnace at 450°C . After one hour the constancy is good. The residue (MoO_3) always has a pale grey-green colour. The check was carried out as under NH_3 with a known amount of MoO_3 . Weighed amount: 0.6166 g. Observed amount: 0.6158 g.

Active oxygen: Titration in acid solution with 0.1 N KMnO_4 . Ferroine sulphate was used as indicator. To avoid catalytical decomposition of H_2O_2 we added MnSO_4 to the solution before the titration. The check was carried out as under NH_3 with a known amount of H_2O_2 . Weighed amount: 0.00440 g. Observed amount: 0.00438 g.

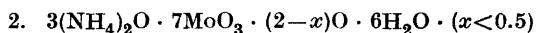
RESULTS

1. $3(\text{NH}_4)_2\text{O} \cdot 7\text{MoO}_3 \cdot x\text{O} \cdot 4\text{H}_2\text{O}$ ($x < 0.3$)

From dilute solutions we obtained paramolybdate crystals with up to 0.2 weight % O without any visible change in the powder photographs. It is

* By analyzing a commercial preparation labelled Ammonium molybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (Kemikaliebolaget Kebo, Stockholm), this was found to have the formula of the dimolybdate $(\text{NH}_4)_2\text{Mo}_2\text{O}_7$, the existence of which has been doubted (*cf.* Gmelin¹²). By recrystallization we obtained, however, the paramolybdate. The dimolybdate will be further investigated.

very strange, however, that even at these low oxygen contents the crystals may be lemon yellow. During his study of the crystallization at different temperatures, given in Table 1, Cagliotti surely has obtained this phase (nos. 7 and 8), quite as Moeller, as already has been pointed out in the historical review. We have not tried to determine the exact limit of the solid solution.

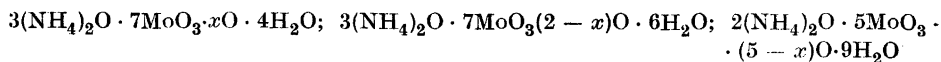


This compound was obtained by evaporation of solutions containing H_2O_2 in a mole ratio $\text{H}_2\text{O}_2 : \text{Mo}$ larger than 0.75 and is surely identical with the compound having the least oxygen, obtained by Baerwald, Péchard, Muthmann and Nagel, Cagliotti and Rosenheim *et. al.* The crystals are lemon yellow and crystallize both in needles and plates with a tendency for twinning.

Analyses:	Found		Calc. (for the comp. $x = 0$)
$(\text{NH}_4)_2\text{O}$	11.98 %	12.11 %	11.98 %
MoO_3	77.30 »	77.80 »	77.27 »
O	2.11 »	1.88 »	2.45 »
H_2O (by difference)	8.61 »	8.21 »	8.30 »
$(\text{NH}_4)_2\text{O} : \text{MoO}_3$	3.00 : 7	3.01 : 7	3 : 7

The mole ratio $(\text{NH}_4)_2\text{O}/\text{MoO}_3$ is constant = 3.0 : 7, but the oxygen content varies (*cf.* Muthmann and Nagel, Cagliotti). It is not easy to decide definitely if the compound loses part of its oxygen due to instability in the air, or if we have a solid solution range. Nor have we tried to determine any limits for the oxygen content exactly. We prefer to give the formula $3(\text{NH}_4)_2\text{O} \cdot 7\text{MoO}_3 \cdot (2-x)\text{O} \cdot 6\text{H}_2\text{O}$ ($x < 0.5$). A crystal structure determination will possibly yield a definite answer to this question.

A single crystal has been investigated. Weissenberg photographs (CuK-radiation) around [100] were taken. The absence of $(h \ 0 \ l)$ with l odd and of $(0 \ k \ 0)$ with k odd indicate the spacegroup to be $C_{2h}^5 - P2_1/c$. The monoclinic cell dimensions are $a = 10.7 \text{ \AA}$, $b = 10.2 \text{ \AA}$, $c = 30.0 \text{ \AA}$ and $\beta = 106^\circ \pm 0.5^\circ$ which give $a : b : c = 1.05 : 1 : 2.94$. (We have interchanged the a and c axes in order to conform to the space group notation $P2_1/c$.) The value 1.05 for $a : b$ instead of 1.03 as found by Baerwald² may be attributed partly to difficulties in the crystallographic measurements, partly to inaccuracy in the determination of a solely from rotation photographs. The density has been determined by the swimming method to 2.71 (Baerwald gives without description of his method the value 2.975). These data give 3.94 units of $3(\text{NH}_4)_2\text{O} \cdot 7\text{MoO}_3 \cdot 2\text{O} \cdot 6\text{H}_2\text{O}$ and 2.3 units of $5(\text{NH}_4)_2\text{O} \cdot 12\text{MoO}_3 \cdot 3\text{O} \cdot 12\text{H}_2\text{O}$ in the

Table 2. Powder photographs taken with monochromatized $CuK\alpha$ -radiation.

<i>I</i>	$\sin^2\Theta$	<i>I</i>	$\sin^2\Theta$	<i>I</i>	$\sin^2\Theta$
v st	0.0071	v st	0.0063	v w	0.0036
m	0.0084	v st	0.0083	w	0.0044
st	0.0104	st	0.0106	v w	0.0059
st	0.0110	st	0.0110	v st	0.0068
v st	0.0117	st	0.0113	v st	0.0074
m	0.0139	st	0.0120	m	0.0085
st	0.0145	v w	0.0126	m	0.0089
m	0.0171	w	0.0130	st	0.0111
m	0.0176	st	0.0144	st	0.0130
m	0.0211	st	0.0168	v w	0.0134
w	0.0217	st	0.0208	m	0.0142
m	0.0231	m	0.0228	v w	0.0149
w	0.0244	v w	0.0244	v w	0.0171
v w	0.0250	m	0.0253	w	0.0193
v w	0.0269	m	0.0266	v w	0.0206
m	0.0284	st	0.0277	v w	0.0250
st	0.0297	v w	0.0281	w	0.0268
v w	0.0308	w	0.0288	w	0.0279
v w	0.0317	st	0.0297	m	0.0302
m	0.0341	w	0.0329	w	0.0361
m	0.0358	w	0.0353	w	0.0398
m	0.0383	w	0.0371	w	0.0425
m	0.0398	m	0.0405	w	0.0449
st	0.0409	m	0.0423	st	0.0469
st	0.0434	m	0.0438	w	0.0501
st	0.0460	v st	0.0451	m	0.0526
w	0.0467	v st	0.0478	w	0.0543
v st	0.0493	m	0.0532	w	0.0576
st	0.0519	w	0.0551	v w	0.0591
st	0.0531	v st	0.0562	v w	0.0605
m	0.0558	v w	0.0568	w	0.0653
v w	0.0580	w	0.0583	v w	0.0690
st	0.0593	st	0.0603	v w	0.0712
v st	0.0625	m	0.0619	v w	0.0741
v w	0.0640	m	0.0632	m	0.0789
m	0.0655	v w	0.0643	w	0.0833

cell. We have thus obtained a final confirmation of the formula $3(NH_4)_2O \cdot 7MoO_3 \cdot (2-x)O \cdot 6H_2O$ quite in the same way as the formula $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ was established by Sturdivant¹⁰ and Lindqvist¹¹. As it seemed very strange that $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ with $a = 8.38 \text{ \AA}$, $b = 36.12 \text{ \AA}$,

$c = 10.46 \text{ \AA}$ and $\beta = 116^\circ 0'$ ¹⁰ should give the same powder photographs as $3(\text{NH}_4)_2\text{O} \cdot 7\text{MoO}_3 \cdot (2-x)\text{O} \cdot 6\text{H}_2\text{O}$, as Cagliotti⁸ states, we compared the powder photographs of the two compounds. They were quite different. As Cagliotti does not state the radiation used by him we have not been able to compare his values with ours which are given in Table 2.

3. $2(\text{NH}_4)_2\text{O} \cdot 5\text{MoO}_3 \cdot (5-x)\text{O} \cdot 9\text{H}_2\text{O}$ ($x < 1.5$)

All efforts to get the compound richest in oxygen described by Muthmann and Nagel have been in vain. The solutions are very unstable and give in most cases $3(\text{NH}_4)_2\text{O} \cdot 7\text{MoO}_3 \cdot (2-x)\text{O} \cdot 6\text{H}_2\text{O}$. In a few preparations, however, we have obtained another compound with high but varying oxygen content. Plate-shaped and orangecoloured hexagons were formed by room temperature (lowest oxygen content) or low temperature ($+ 4^\circ \text{C}$) (highest oxygen content) evaporation of paramolybdate solutions in H_2O_2 , saturated at low temperature ($+ 4^\circ \text{C}$). Some of the crystals showed signs of efflorescence while others proved to be stable. Some of the latter were picked out and analyzed:

Analyses:	Found	Calc. for the comp. $x = 0.63$
$(\text{NH}_4)_2\text{O}$	9.86 %	9.87 %
MoO_3	68.08 »	68.17 »
O_{active}	6.62 »	6.62 »
H_2O	15.47 »	15.35 »
$(\text{NH}_4)_2\text{O} : \text{MoO}_3$	2.00 : 5	

The mole ratio is thus surprisingly not 3 : 7 but 2 : 5 which would correspond to a formula $2(\text{NH}_4)_2\text{O} \cdot 5\text{MoO}_3 \cdot (5-x)\text{O} \cdot 9\text{H}_2\text{O}$. Such a type of molybdate has not been described before.

A single crystal investigation with CuK radiation indicates that the compound is monoclinic with $a = 12.9 \text{ \AA}$, $b = 18.6 \text{ \AA}$, $c = 10.7 \text{ \AA}$, $\beta = 109^\circ$. The density was determined by the swimming method to be 2.50. The number of Mo atoms in the cell will then be 19.6. This gives a further support to the formula $2(\text{NH}_4)_2\text{O} \cdot 5\text{MoO}_3 \cdot (5-x)\text{O} \cdot 9\text{H}_2\text{O}$.

This compound gives powder photographs (Table 2) with weak lines, which are difficult to detect together with the lines of other phases. We have not tried to determine the limits of the oxygen content.

SUMMARY

The existence of a solid solution of peroxide oxygen in ammonium paramolybdate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ has been proved. These crystals have been shown to be identical with those described by Moeller and Fock as $(\text{NH}_4)_2\text{Mo}_2\text{O}_8$. The lemon yellow ammonium permolybdate first obtained by Baerwald has been found to possess the formula $3(\text{NH}_4)_2\text{O} \cdot 7\text{MoO}_3 \cdot (2-x)\text{O} \cdot 6\text{H}_2\text{O}$ ($x < 0.5$). It is monoclinic with $a = 10.7 \text{ \AA}$, $b = 10.2 \text{ \AA}$, $c = 30.0 \text{ \AA}$ and $\beta = 106^\circ$. The unit cell contains 4 units of the above formula. Space-group $C_{2h}^5 - P2_1/c$.

We have also found an orange-coloured compound of a new type and with the formula $2(\text{NH}_4)_2\text{O} \cdot 5\text{MoO}_3 \cdot (5-x)\text{O} \cdot 9\text{H}_2\text{O}$ ($x < 1.5$). This is monoclinic with $a = 12.9 \text{ \AA}$, $b = 18.6 \text{ \AA}$, $c = 10.7 \text{ \AA}$, $\beta = 109^\circ$. The unit cell contains 4 formula units.

An effort will be made to determine the crystal structures of these compounds.

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