CRYSTALLOGRAPHY OF AMMONIUM
MOLYBDO-DITELLURATE

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Summary

Ammonium molybdo-ditellurate, $3(NH_4)_2O \cdot 2TeO_3 \cdot 6MoO_3 \cdot 10H_2O$, is monoclinic, probably holohedral. $a:b:c = 1.8912:1:1.0731$, $\beta = 115°38'$. The crystals are usually tabular on (001) and have one distinct cleavage (100). $H = 2\frac{1}{2}$. $G = 2.22$. Biaxial negative, $\alpha = b$, $\gamma:c = 58\frac{1}{2}°$ in the acute angle. Refractive indices: $n_\alpha = 1.684$, $n_\beta = 1.727$, $n_\gamma = 1.741$. Homeomorphous with a number of substances, although with different habit. The Barker angles are given, and also the optical characters of recrystallization products on a glass slip.

Introduction

Beautiful crystals of ammonium molybdo-ditellurate can be obtained by recrystallization from an aqueous solution. They average 2 to 5 millimeters in the greatest dimension, are well developed, colorless, clear and transparent with splendent vitreous luster. The faces are plane and have good reflecting power, permitting very accurate goniometric measurements.

Hardness $= 2\frac{1}{2}$. Specific gravity $= 2.22 \pm 0.05$.

On account of the solubility of the substance in water the specific gravity was determined in ether and the value corrected accordingly.

Form

The substance crystallizes in the monoclinic system (probably prismatic class, $C_{2h} = 2/m$).

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[1] *Jour. Am. Chem. Soc.*, vol. **51**, p. 171, 1929.

[2] *Proc. Nat. Acad. Sci.*, vol. **20**, pp. 327–35, 1934.

[3] Unpublished thesis, University of Wisconsin, **1929**.

Axial elements: $\breve{a}:\bar{b}:\overset{|}{c}=1.8912:1:1.0731$; $\beta=115°38'$. These elements correctly define the Haüy-Bravais lattice, provided the unit cell is base-centered (octahedral mode of the monoclinic lattice).

Seven crystal forms were observed. They may be listed as follows: $p\{001\}$, $m\{110\}$, $h^1\{100\}$, $a^{1/2}\{20\bar{1}\}$, $b^{1/2}\{11\bar{1}\}$, $a^1\{10\bar{1}\}$, and $b^{1/4}\{22\bar{1}\}$, in the order of decreasing importance (based on their observed sizes and frequencies).

All seven forms are present on most crystals. A few did not show the form $a^1\{10\bar{1}\}$. On all crystals examined, $b^{1/4}\{22\bar{1}\}$ occurs as very narrow truncations ("line-faces"). The forms are shown on the stereographic projection (Fig. 1).
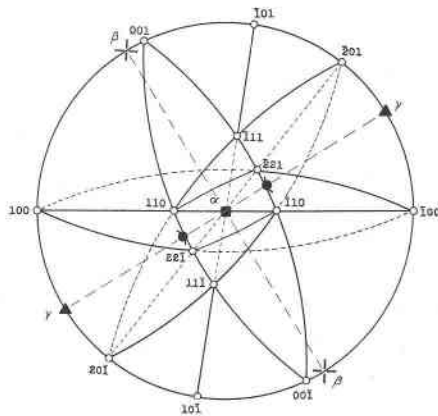

Fig. 1. Stereographic projection of ammonium molybdo-ditellurate.
Zone-circles drawn in heavy lines for edges observed on crystals with prevalent habit; dashed zone-circles for non-observed edges.

Cleavage. Only one distinct cleavage, $h^1\{100\}$, was observed. It accounts for the striae seen on $p\{001\}$, parallel to the edge $ph^1[010]$.

Habit. About 50 *per cent.* of the crystals obtained in any one crop exhibit a typical tabular habit on $p\{001\}$. The general appearance is that of thin plates, roughly rhombic in shape, with beveled edges. The "bevel" is the result of the intersection of a face of $m\{110\}$ with a face of $b^{1/2}\{11\bar{1}\}$. The acute angles of the "rhomb" are cut off by faces of $h^1\{100\}$ and $a^{1/2}\{20\bar{1}\}$. The other forms are minor truncations. This prevalent habit is illustrated in Fig. 2.

A few crystals show less flattening on $p\{001\}$ and are thick tabular to short prismatic. Rarer still is the following development which can be termed pseudo-trigonal pyramidal. The crystal lies on $a^{1/2}(\bar{2}01)$; its apex being truncated by a small triangular face $a^{1/2}(20\bar{1})$. The combined forms $p\{001\}$, $m\{110\}$, on the one hand and $h^1\{100\}$, $b^{1/2}\{11\bar{1}\}$, on the other,

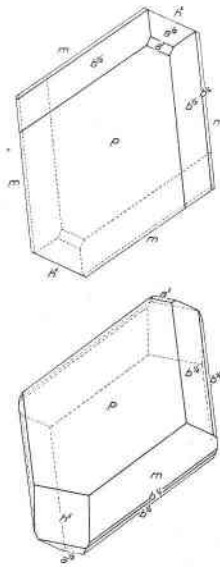very roughly resemble rhombohedra. In this unusual habit, the face $a^{1/2}(\bar{2}01)$ is the largest of all.

Fig. 2. Plan and orthographic projection (26° rotation, 25° tilt).
A common habit of ammonium molybdo-ditellurate.

Measurements and Calculations

Six crystals have been measured on the one-circle Wollaston goniometer. The signal images were good and the series of readings satisfac-

Table 1. Comparison of Measured and Calculated Angles

Number of readings	Probable error	Angle		Measured (mean)	Computed	Diff.
		Lévy	Miller			
8	7′	h^1 $a^{1/2}$	$100 \wedge 20\bar{1}$	*52° 5′	—	—
10	6′	p h^1	$001 \wedge 100$	*64°22′	—	—
12	8′	p $a^{1/2}$	$001 \wedge \bar{2}01$	63°36′	63°33′	3′
3	—	a^1 $a^{1/2}$	$\bar{1}01 \wedge \bar{2}01$	29°28′	29°25′	3′
23	7′	h^1 m	$100 \wedge 110$	59°37′	59°36′	1′
6	5′	m m	$110 \wedge \bar{1}10$	*60°47	—	—
19	15′	p m	$001 \wedge 110$	77°22	77°21′	1′
20	11′	p $b^{1/2}$	$001 \wedge \bar{1}11$	55°25′	55°25′	0′
14	6′	$b^{1/2}b^{1/4}$	$\bar{1}11 \wedge \bar{2}21$	21°31′	21°29′	2′
24	12′	$b^{1/2}m$	$\bar{1}11 \wedge \bar{1}10$	47°17′	47°13′	4′
15	23′	$a^{1/2}b^{1/2}$	$\bar{2}01 \wedge \bar{1}11$	53°38′	53°19′	19′
15	16′	$a^{1/2}m$	$\bar{2}01 \wedge \bar{1}10$	71°59′	71°53′	6′

tory. Calculations were made by means of spherical trigonometry from three angles, chosen as fundamental (see Table 1). The choice of the fundamental angles was guided by the probable error computed for each series of measurements. The agreement between mean measured angles and calculated angles is close; the difference between the two values is 4′ or less in seven cases out of ten; it is always much smaller than the computed probable error.

LAW OF BRAVAIS

The sequence of reticular planes, listed according to decreasing reticular density (or increasing reticular area), in the base-centered lattice defined by our axial elements, is given in Table 2.

Table 2

Form		S^2
p	001	22
m	110	27.5
h^1	100	
$a^{1/2}$	$20\bar{1}$	28.5
$b^{1/2}$	$11\bar{1}$	38.5
	111	60
	201	71
a^1	$10\bar{1}$	72.5
	$31\bar{1}$	73
	010	81
	310	83
	$40\bar{1}$	91
	$11\bar{2}$	93
	$02\bar{1}$	103
	$31\bar{2}$	106
$b^{1/4}$	$22\bar{1}$	109.5

List of the densest
reticular planes
(S ÷ retic. area)

The agreement with the observed importance of the various forms is quite satisfactory:

(1) $p\{001\}$ dominant, conditions the tabular habit of the crystal.

(2) $m\{110\}$ and $h^1\{100\}$ about equally important; m the one prism which is always well developed; h^1 the only cleavage.

(3) $a^{1/2}\{20\bar{1}\}$ always present, next in size.

(4) $b^{1/2}\{11\bar{1}\}$ shows fairly narrow faces, not all of which are equally developed.

(5) $a^1\{10\bar{1}\}$, small on all crystals, absent on a few.

(6) $b^{1/4}\{22\bar{1}\}$, line-faces only.

The influence of the motif and, perhaps, that of the conditions of crystallization are revealed by the gaps in the list (Table 2), where observed forms are indicated by their Lévy form-symbol next to their Miller indices. Still, this is another good illustration of the fact that the Haüy-Bravais lattice is the controlling factor in the development of crystal forms.

HOMEOMORPHISM

Ammonium molybdo-tellurate with ten molecules of water is homeomorphous with a number of substances: ammonium selenate, ammonium

molybdate, potassium tungstate, etc. We have reported on this homeo-morphous series elsewhere[4] in its relation to Barker's determinative scheme.[5]

From the morphological standpoint, a curious observation can be made. These various salts are crystallographically very close to one an-other (similar values for the interfacial angles and axial elements), so much so that their stereographic projections on $g^1\{010\}$ coincide almost exactly. Yet their habits show marked divergences. The small differences which exist, from substance to substance, between the axial elements are sufficient to alter the order of density of the reticular planes, and consequently the habit, according to the Law of Bravais.

The list of planes according to decreasing density, which was:

$$p\{001\},\ m\{110\},\ h^1\{100\},\ a^{1/2}\{20\bar{1}\},\ b^{1/2}\{11\bar{1}\},\ \cdots$$

for ammonium molybdo-tellurate becomes:

$$p\{001\},\ h^1\{100\},\ a^{1/2}\{20\bar{1}\},\ m\{110\},\ b^{1/2}\{11\bar{1}\},\ \cdots$$

for potassium tungstate, and:

$$p\{001\},\ a^{1/2}\{20\bar{1}\},\ m\{110\}=h^1\{100\},\ b^{1/2}\{11\bar{1}\},\ \cdots$$

for ammonium molybdate.

The crystal habit varies accordingly. It is acicular with an elongation parallel to the edge $ph^1[010]$ in potassium tungstate, the observed forms of which[6] follow the theoretical order exactly. The same type of habit, long prismatic parallel to [010], is also found in ammonium molybdate where, however, the form $a^{1/2}\{20\bar{1}\}$ becomes much more important as can be seen on Groth's drawing.[7]

The unexpected fact that homeomorphous substances may show de-cidedly different habits is in agreement with the theory.

BARKER'S CLASSIFICATION ANGLES

The two form combinations observed lead to the same setting.
Transformation: Old to New: $102/010/\bar{1}00$. New to Old: $00\bar{2}/020/101$.

Forms: $\dfrac{\text{Old: } 001\cdot110\cdot100\cdot20\bar{1}\cdot11\bar{1}\cdot22\bar{1};\ 10\bar{1}}{\text{New: } 100\cdot11\bar{1}\cdot10\bar{1}\cdot00\bar{1}\cdot\bar{1}1\bar{1}\cdot01\bar{1};\ \bar{1}0\bar{1}}$.

Angles: cr $=29°25'$, ra $=34°8'$, **am $=62°40'$**, bq $=30°34'$.

Since the form $b^{1/4}\{\bar{2}01\}$ is very small, it may be missing on some crys-tals (although we have not found this to be the case) or, if present, it may pass unnoticed. The form $a^1\{\bar{1}01\}$ may likewise be missing. Hence

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[4] *Annales Soc. géol. Belgique*, vol. **57**, B 39–52, 1933.

[5] Barker, T. V., Systematic Crystallography, 115 pp., *London*, Thomas Murby and Co., 1930.

[6] Groth, Chemische Krystallographie, vol. **2**, p. 359, 1908.

[7] Groth, *loc. cit.*, p. 358, Fig. 637.

the combination of only the largest forms must be considered as though it were an observed combination. Another entry is thus found to be necessary. It is as follows:

Transformation: Old to New = New to Old = $\overline{1}0\overline{1}/0\overline{1}0/001$.

Forms: $\dfrac{\text{Old: } 001 \cdot 110 \cdot 100 \cdot 20\overline{1} \cdot 11\overline{1}}{\text{New: } \overline{1}01 \cdot \overline{1}10 \cdot 100 \cdot \overline{1}01 \cdot 0\overline{1}1}$.

Angles: cr = 29°25′, ra = 52°5′, **am = 59°37′**, bq = 43°18′.

Optical Properties

Biaxial negative. The refractive indices are as follows: $n_\alpha = 1.684$, $n_\beta = 1.727$, $n_\gamma = 1.741$, all ± 0.001. The above values have been obtained by the immersion method, each index liquid being checked on the refractometer as it was used.

Optical orientation: α lies along the b-axis; the plane of the optic axes is thus perpendicular to $g^1\{010\}$, its trace on g^1 coincides with the obtuse bisectrix γ and makes an angle of $58\frac{1}{2}°$ with the c-axis, in the acute angle. The optic normal β lies at an angle of 6° (toward the observer) with the normal to $p\{001\}$.
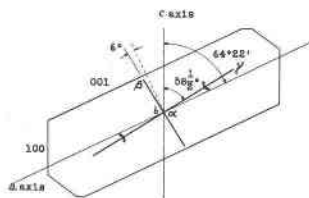

Fig. 3. Optical orientation of ammonium molybdo-ditellurate.
Cross-section parallel to (010).

Angle of the optic axes: 2V = 58° (calculated from the indices). We could not succeed in measuring the optic angle on the universal stage, the optical orientation with respect to the crystal habit being such as to make this measurement well nigh impossible.

The optical orientation is shown on Figs. 1 and 3.

Recrystallization on a Glass Slip

The substance can easily be recrystallized on a glass slip by letting a drop of saturated aqueous solution evaporate.

A large majority of the crystals formed are small plates, rhombic in outline, with the acute corner more or less truncated (Fig. 4). The acute angle of the rhomb is 55°, as measured on the rotating stage. The extinction is symmetrical, the direction of the long diagonal of the rhomb has positive elongation (length slow). The interference figure obtained in

convergent light is that of a section either nearly parallel with the plane of the optic axes or nearly perpendicular to the obtuse bisectrix. The hyperbolas flash out of the field in the direction of the small diagonal of the rhomb (Fig. 4).
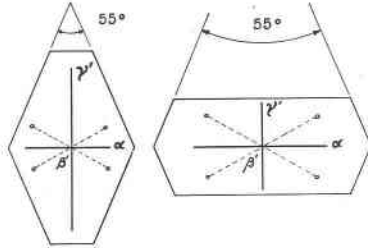

Fig. 4. Usual shape of plates obtained by recrystallization on a glass slip.

The section birefringence of such plates can be calculated from the retardation (obtained with a Berek compensator) and the thickness (measured with the micrometric focussing screw of the microscope). Six measurements gave an average of 0.055 for the section birefringence.
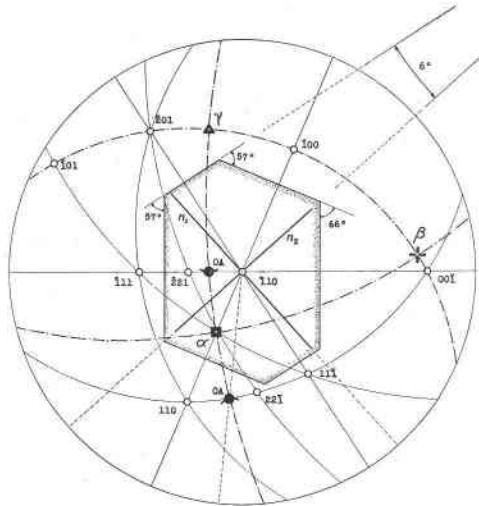

Fig. 5. Stereographic projection of ammonium molybdo-ditellurate on a plane parallel to ($\bar{1}$10).
    The stippled outline indicates the shape of plates obtained by recrystallization on a glass slip. The optical characters of the plate are derived graphically, n_1 and n_2 are the extinction directions.

These results are in agreement with our other data. The measured angle of 55° corresponds to a calculated value of 55°44'; it is the angle between the edges $pm[\bar{1}01]:[110]$ or the angle between the edges

$pb^{1/2}$ [$\bar{1}\bar{1}0$]: [$1\bar{1}0$]. The plates consequently lie on $p\{001\}$. The positive elongation is in agreement with the optical orientation. The interference figure can be accounted for by the fact that $p\{001\}$ is almost parallel to the plane of the optic axes; the hyperbolas flash out of the field in the direction of the acute bisectrix α, as is to be expected from the theory. The section birefringence of $p\{001\}$, calculated from the indices, is 0.0568, a little smaller than the maximum birefringence ($n_\gamma - n_\alpha = 0.057$).

Other crystals obtained by recrystallization show a rectangular outline, which can be identified as $h^1\{100\}$. Still others are six-sided and elongated (see Fig. 5), with external angles of 57°, 57°, and 66° (measured on the rotating stage). In convergent light they show the interference figure of a section nearly perpendicular to one of the optic axes. In parallel light a 6° extinction angle can be measured against one of the sides. The geometrical and optical characters identify the face as $m(1\bar{1}0)$, whose normal is inclined at an angle of 16° to an optic axis. The optical characters of a face ($\bar{1}10$) of the rhombic vertical prism $m\{110\}$, as derived from the orientation of the indicatrix, are shown on Fig. 5. The agreement with the experimental data is perfect. In Fig. 5, n_1 is greater than n_2.

The study of the results of recrystallization on a glass slip is of great importance from the determinative viewpoint. The present substance is a good example of the amount of information that can be gathered by such technique.