

Synthesis, characterization and crystal structure of zinc dimolybdate pentahydrate $\text{ZnMo}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$

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Abstract

The method of synthesis of zinc dimolybdate pentahydrate $\text{ZnMo}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$ has been elaborated. The crystal structure has been solved by X-ray powder diffraction methods. The space group of $\text{ZnMo}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$ is $\text{P}2_1/\text{c}$ (14), with lattice parameters: 6.0021(9), 18.886(3), 8.725(1) Å, $\beta = 93.85(1)^\circ$, $V = 986.8(2) \text{ \AA}^3$. The decomposition of $\text{ZnMo}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$ in air and nitrogen was studied in situ by X-ray diffraction. Results of crystal structure determination and refinement by the Rietveld method, as well as results of IR and TGA, DTA studies performed for $\text{ZnMo}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$, are presented.

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1. Introduction

Molybdenum compounds have been investigated due to their wide range of applications in industry and environment. The molybdenum complexes may be used as catalysts in the processing of petroleum products (to remove sulfur), corrosion inhibitors, smoke suppressants and lubricants [1]. On the other hand, zinc cations are very interesting as ‘inorganic nodes’ in the design of porous inorganic compounds or metal–organic framework compounds. Studying zinc molybdenum compounds, one can obtain a substance with complex architecture, also interesting for catalytic purposes [1]. In this paper the results of powder diffraction studies of zinc dimolybdate pentahydrate $\text{ZnMo}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$ are presented.

2. Experiment

2.1. Sample preparation

$\text{ZnMo}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$ was synthesized according to the procedure described in the literature [2]. To the suspension of ZnO (2.6045 g) in water (400 cm³), MoO₃ (9.2120 g) was added, to obtain a molar ratio of 1:2. The solution was stirred for one month at room temperature (a long time is essential due to the low solubility of both components; a shorter time results in an impure compound). The very fine white precipitate of $\text{ZnMo}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$ obtained was twice recrystallized from water at a temperature of about 80–85 °C. Recrystallization helped to obtain a pure phase. In all cases, however, the crystals obtained were too small for single crystal analysis.

Independently, we tried to obtain zinc dimolybdate according to a method used for successful synthesis of bismuth dimolybdate [3] which was properly modified. To a water solution of sodium molybdate, stoichiometric amounts of HNO₃ and Zn(NO₃)₂ were added. White precipitate was filtered off, washed with a small amount of

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water and dried in air. X-ray powder diffraction measurements indicated, however, that the main product obtained in this way is $\text{NaZn}_2(\text{MoO}_4)_2\text{OH} \cdot \text{H}_2\text{O}$ as described by Clearfield [4].

2.2. Chemical analysis, IR and XRD studies

Zinc was determined by EDTA titration. Molybdenum was determined by the Busiev method [5], and water by the gravimetric method. The results obtained are as follows:

Found	Calculated	
Zn (%)	14.19	14.24
Mo (%)	41.57	41.77
H_2O (%) > 300 °C	19.53	19.61
H_2O (%) 100 °C	11.60	11.77

The infrared spectra were obtained on a Bruker IFS 48 instrument (KBr pill technique) across the 4000–400 cm^{-1} region. The following bands were recorded: 467w, 564s, 698s, 843w, 893vs, 924vs, 1552w, 1625m, 3440s (abbreviations: w-weak, m-middle, s-strong, vs-very strong).

For XRD studies, portions of the samples were thoroughly powdered and placed into a sample holder. The XRD patterns were taken in 2θ range from 5.0° to 105° , step size $0.02^\circ 2\theta$. Experimental details of data collection are listed in Table 1. For crystal structure study the sample was loaded into a 0.7 mm capillary (Lindeman glass, 0.02 mm wall thickness) and measurements were performed using a parallel beam (formed by the MRD mirror of an X' Pert Pro diffractometer) in DSH geometry. Taking into account the capillary parameters, the absorption

Table 1
Data collection and cell parameters for $\text{ZnMo}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$

Diffractometer	Philips X' Pert Pro
Radiation type, source	X-ray, $\text{CuK}\alpha$, 1.54178 Å
Power	40 kV, 30 mA
Filter	Secondary graphite monochromator
Crystal system	Monoclinic
Space group	$P2_1/c$ (14)
Z	4
T (°C)	20–25
a (Å)	6.0021(9)
b (Å)	18.886(3)
c (Å)	8.725(1)
β (°)	93.85(1)
V (Å ³)	986.8(2)
M_{30}	32.3
F_{30}	13.8
Number of observations	4216
Number of reflections	582
Total number of atoms/ structural parameters/restraints	15/50/16
R_F	13.3
R_{wp}	13.1

correction function was applied according to the procedure described in International Tables for Crystallography [6].

The lattice parameters and space group were determined using the PROSZKI package [7] (see Table 1). Positional parameters of molybdenum, zinc and oxygen were found using the EXPO program [8]. Final refinements were performed using the XRS-82 Rietveld system [9]. Weak geometric constraints were applied, the weight of constraints was decreasing during refinement to 3% of the weight assigned to diffraction data in the final cycles. In total 16 distances were constrained (11 Mo–O and 5 Zn–O). The background was subtracted, esd's values were calculated according to Scott [10].

The decomposition of $\text{ZnMo}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$ in air and nitrogen was studied in situ by X-ray diffraction. Measurements were performed at a temperature range from 25 to 600 °C, employing 2θ ranges from 5.0° to 55° . The heating rate was 40 °C/min. The sample was heated at each temperature for 10 min. The XRD investigations were carried out on a Philips X' Pert Pro diffractometer and reaction chamber XRK (Anton Paar). Thermal investigations were performed using a Du Pont 1090 Thermal Analyzer equipped with a 951 Thermogravimetric Analyzer and 910 Differential Scanning Calorimeter.

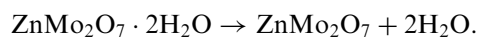
3. Obtained results

Figs. 1a and b show the evolution of the diffraction patterns measured during the decomposition of $\text{ZnMo}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$ in air and nitrogen, respectively. According to XRD investigations, the decomposition processes in air and in nitrogen are almost identical; small differences between the patterns can be attributed to different textures in both samples. The processes may be summarized by the following reaction scheme:

At 100 °C $\text{ZnMo}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ (PDF 28-1470) is obtained.



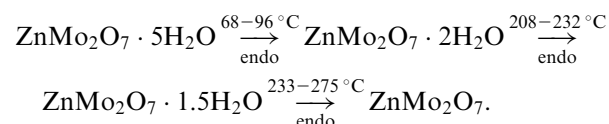
In the next step, ca. 250 °C, dihydrate decomposes to anhydrous dimolybdate (PDF 28-1469).



At the temperatures above 350 °C ZnMoO_4 (PDF 35-0765) and MoO_3 (PDF 35-0609) are obtained.



According to the results of TGA and DTA measurements, the dehydration takes place in temperature ranges 68–96, 208–232 and 233–325 °C. The occurring changes can be described as follows (small differences between XRD and DTA/TGA studies are probably caused by different heating rates):



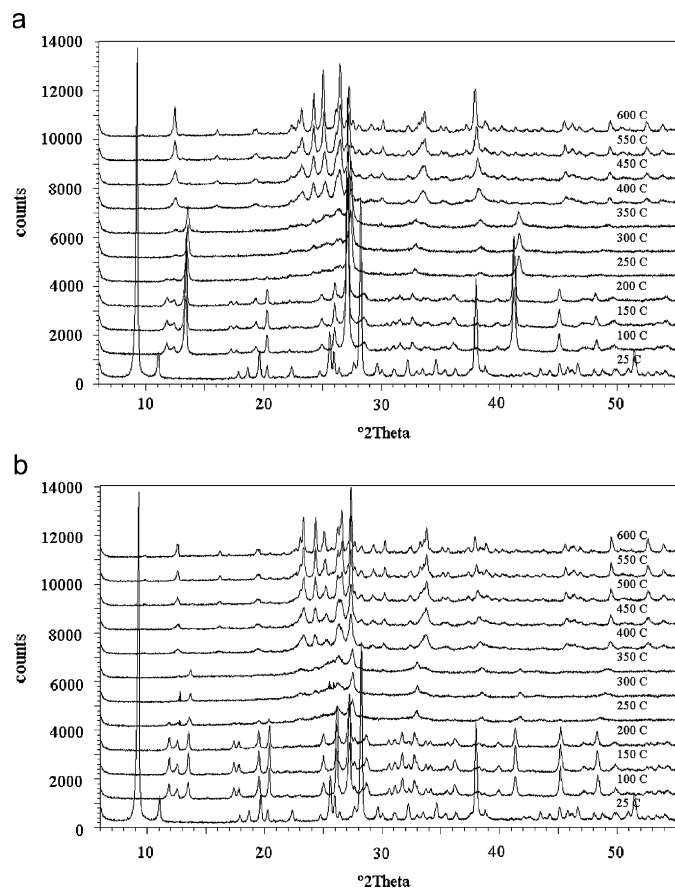
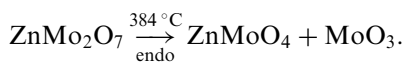


Fig. 1. (a) Evolution of the X-ray diffraction pattern during decomposition of $\text{ZnMo}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$ in air. (b) Evolution of the X-ray diffraction pattern during decomposition of $\text{ZnMo}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$ in nitrogen.

The very weak endothermic effect detected at 208–232 °C by the DTA/DTG method indicates that $\text{ZnMo}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ dehydrates in two steps; however, this observation is not accompanied by noticeable changes in X-ray powder patterns. The last stage of thermal decomposition is weak and exothermic:



In contradiction to the thermal decomposition of zinc trimolybdate we studied recently [11] there were no temperature ranges in which only amorphous phases were observed. We tried to index zinc dimolybdate dihydrate (using the diffraction pattern recorded during thermal study). Unfortunately, all attempts, using the most popular indexing programs (ITO, TREOR, DICVOL [7]), were unsuccessful. In addition, we tried to index the diffraction pattern of zinc dimolybdate listed in PDF (PDF 28-1470) file using modern indexing programs. Unfortunately, all our attempts were unsuccessful. Taking into account the rather good quality of our diffraction patterns, it is very probable that the sample of $\text{ZnMo}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ we obtained, and described by PDF 28-1470 card, is not a pure phase.

4. Crystal structure study and discussion

Crystal structure investigations were performed using the EXPO package [8]. The structure model obtained, consisting of almost all atoms (without oxygens from water molecules), was refined and completed using the XRS-82 Rietveld refinement package [9]. To test the crystal structure model independently, all atoms but Mo and Zn atoms were deleted; next on difference Fourier maps missing atoms were sought and refined by the Rietveld method. In both cases the same crystal structure was obtained. The atomic positions and selected distances in $\text{ZnMo}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$ are presented in Table 2. The Rietveld refinement plots for $\text{ZnMo}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$ are shown in Fig. 2.

The crystal structure of zinc dimolybdate consists of layers perpendicular to the y -axis. Layers are built of infinite Mo_2O_7 chains, running along [100], linked together by Zn^{2+} cations. In Mo_2O_7 chains there are dimers built of two edge-sharing MoO_6 octahedra. From both sides each dimer is connected to analogue dimers by two square pyramids (where Mo is coordinated by five oxygens). In each MoO_6 octahedron there are two terminal Mo–O bonds in cis position to each other. In octahedra Mo–O distances span a range of 1.76–2.49 Å; in square pyramids, 1.91–2.07 Å.

Table 2

Atomic positions (a) and selected distances (b) in $\text{ZnMo}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$

Atom	x	y	z	U^a	
(a)					
Mo1	0.930(3)	0.076(2)	0.367(2)	0.014(6)	
Mo2	0.394(3)	0.074(2)	0.565(2)	0.023(6)	
Zn	0.637(6)	0.070(2)	0.976(3)	0.033(8)	
O1	0.81(2)	0.07(1)	0.182(7)	0.03(1)	
O2	0.66(1)	0.098(5)	0.46(1)	0.03	
O3	1.07(1)	0.054(4)	0.610(9)	0.03	
O4	1.261(9)	0.07(1)	0.343(7)	0.3	
O5	0.88(2)	0.171(4)	0.39(1)	0.03	
O6	0.39(2)	0.179(4)	0.60(1)	0.03	
O7	0.48(2)	0.058(9)	0.775(6)	0.03	
O8	0.61(2)	0.184(3)	0.99(2)	0.00(2)	
O9	0.32(1)	0.048(5)	1.07(1)	0.00	
O10	0.95(1)	0.081(9)	0.87(1)	0.00	
O11	0.41(2)	0.274(7)	0.76(1)	0.00(2)	
O12	-0.05(2)	0.219(6)	0.71(1)	0.00	
(b)					
Mo1–O1	1.76(7)	Mo2–O2	2.0(1)	Zn–O1 ^b	2.03(7)
Mo1–O2	1.9(1)	Mo2–O3	2.05(7)	Zn–O9	2.16(9)
Mo1–O3	2.30(7)	Mo2–O4	2.07(6)	Zn–O9 ^c	2.3(1)
Mo1–O4	2.03(6)	Mo2–O6	2.02(7)	Zn–O8	2.17(8)
Mo1–O5	1.85(8)	Mo2–O7	1.91(6)	Zn–O7	1.98(7)
Mo1–O3 ^d	2.49(8)			Zn–O10	2.17(9)

^aTemperature factors of oxygen atoms were divided into group of atoms: from Mo–O chains, Zn–O group and water molecules. In each group U values were constrained to be equal to each other, esd value was listed only for first atom of each group.

^b $[x, y, z + 1]$.

^c $[-x + 1, -y, -z + 2]$.

^d $[-x + 2, -y, -z + 1]$.

The dimolybdate chain is presented in Fig. 3, while the crystal structure packing along the x -axis is presented in Fig. 4.

Zinc in the presented structure is coordinated by six O atoms; the coordination polyhedron is a distorted octahedron. Zn–O distances span a range of 2.0–2.35 Å. By sharing an edge zinc–oxygen octahedra form dimers, with a Zn–Zn distance of about 3.17 Å. Interestingly, in sodium–zinc monomolybdate edges-sharing ZnO_6 octahedra form straight infinite chains [4].

In general all dimolybdates can be divided into two groups. To the first group belong compounds built of

discrete $Mo_2O_7^{2-}$ ions, created by a pair of corner-sharing tetrahedra. Such compounds are obtained both from water solutions and from melt [12,13].

To the second group belong infinite chain $[Mo_2O_7]^{2-}$ anions. These infinite dimolybdate chains can adopt a number of structures. They can be:

- built of MoO_6 octahedra exclusively: $Ag_2Mo_2O_7$ [14], $BiMo_2O_7 \cdot OH \cdot 2H_2O$ [3],
- formed by MoO_6 octahedra and MoO_4 tetrahedra: $K_2Mo_2O_7$ [15], $Na_2Mo_2O_7$ [16], $NH_4Mo_2O_7$ [17] and
- created by MoO_6 octahedra and MoO_5 trigonal bipyramids: $K_2Mo_2O_7 \cdot H_2O$ [18].

The compound investigated by us belongs to a new family of chain dimolybdates. Its infinite $[Mo_2O_7]^{2-}$ anions are similar to both potassium dimolybdate hydrate [18] and sodium dimolybdate [16]. Similarly to both compounds, each octahedra-based dimer is connected to the next dimer by two linking groups. In the potassium salt, Mo_2O_{10} dimers are linked with each other by five coordinated molybdenum atoms (trigonal bipyramids), whereas in sodium dimolybdate, MoO_4 tetrahedra are the linking elements. In our case, however, linking Mo atoms have a tendency toward square pyramid coordination. Such coordination is observed, e.g. in potassium trimolybdate obtained from melt [19].

5. Conclusions

Zinc dimolybdate was synthesized and investigated by X-ray powder diffraction methods. Using direct methods ‘package EXPO’, its crystal structure model was built and refined by the Rietveld method. Infinite Mo_2O_7 chains parallel to [100] direction are built up of edge-sharing MoO_6 octahedra and MoO_5 distorted square pyramids. Chains are connected to each other by zinc cations, forming layers perpendicular to [010]. Heated either in air or nitrogen, zinc dimolybdate decomposes in three steps. First, dimolybdate dihydrate is formed; in the next step anhydrous zinc dimolybdate appears; in the last step zinc monomolybdate and MoO_3 are formed.

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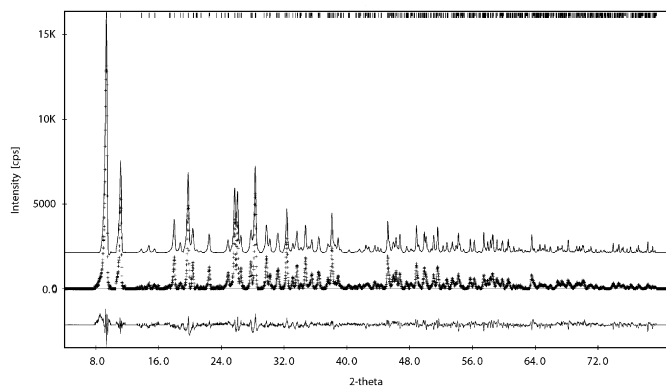


Fig. 2. Rietveld refinement plots for $ZnMo_2O_7 \cdot 5H_2O$, curves from top to bottom are: calculated, observed and difference patterns, respectively.

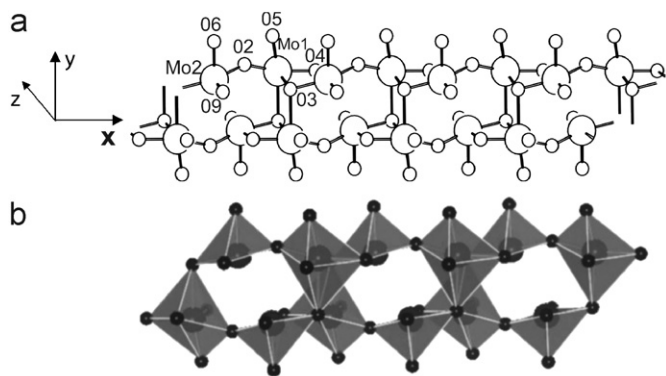


Fig. 3. Molybdenum–oxygen chains in $ZnMo_2O_7 \cdot 5H_2O$.

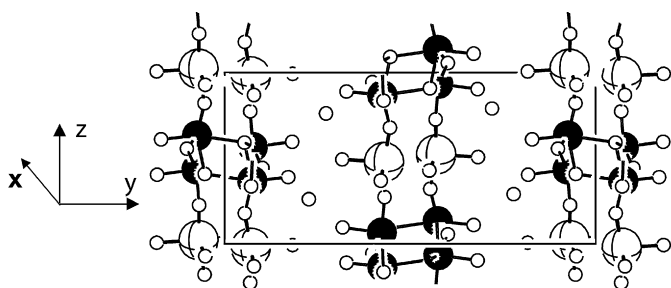


Fig. 4. Projection of the unit cell along x -axis. Big empty spheres—Zn, big black spheres—Mo, small empty spheres—O.

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