

Synthesis and crystal structure of layered molybdate $\text{NH}_4\text{Co}_2\text{OH}(\text{MoO}_4)_2\cdot\text{H}_2\text{O}$

Paweł Adamski ^{a)}, Aleksander Albrecht, and Dariusz Moszyński

Department of Inorganic Chemical Technology and Environment Engineering, Faculty of Chemical Technology and Engineering, West Pomeranian University of Technology in Szczecin, Piastów Ave. 42, 71-065 Szczecin, Poland

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A new compound $\text{NH}_4\text{Co}_2\text{OH}(\text{MoO}_4)_2\cdot\text{H}_2\text{O}$ was prepared by precipitation of aqueous solutions of cobalt nitrate and ammonium heptamolybdate at $\text{pH} = 7.5$. The crystal structure was identified by X-ray powder diffraction (XRPD) and Rietveld refinement as a known polymorph of layered molybdates (Φ_n) with general formula $AT_2\text{OH}(\text{MoO}_4)_2\cdot\text{H}_2\text{O}$ ($A = \text{NH}_4^+$, Na^+ , K^+ and $T = \text{Zn}^{2+}$, Co^{2+} , Cu^{2+} , Ni^{2+}) and refined from a model based on that structure. The lattice parameters were refined with $R-3$ space group (148) $a = 6.1014(2)$ Å, $b = 6.1014(2)$ Å, $c = 21.826(1)$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, and $\gamma = 120^\circ$.

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I. INTRODUCTION

Cobalt molybdates are interesting compounds, with many electrochemical (Mandal et al., 2014; Tian et al., 2017; Kim et al., 2019) and catalytical (Li et al., 2018; Xu et al., 2018) applications. Cobalt molybdates can be used as catalyst precursors to obtain cobalt molybdenum nitrides and sulfides (Kojima and Aika, 2001; Zhao et al., 2016). There are three known polymorphic forms of cobalt molybdate CoMoO_4 : the pale green low-temperature α phase (monoclinic, space group $C2/m$) (Smith and Ibers, 1965), the black high-pressure hp phase (monoclinic, space group $P2/c$) (Livage et al., 2002) and the pale violet high-temperature β phase (monoclinic, space group $C2/m$) (Courtine et al., 1968). The hydrate phases $\text{CoMoO}_4\cdot 3/4\text{H}_2\text{O}$ (triclinic, space group $P-1$) and $\text{CoMo}_4\text{O}_{13}\cdot 2\text{H}_2\text{O}$ (triclinic, space group $P-1$) are also known (Eda et al., 2005, 2009). Additionally, two more hydrates were identified in the literature: $\text{CoMoO}_4\cdot 0.9\text{H}_2\text{O}$ (PDF 00-014-0086) and $\text{CoMoO}_4\cdot 1.3\text{H}_2\text{O}$ (PDF 00-014-0087) (Liu et al., 2012; Kim et al., 2019). However, for these phases, no structural data were reported. The known structures of cobalt molybdate phases consist of cobalt atoms coordinated octahedrally with oxygen to form octahedra $[\text{CoO}_6]$. In the β -phases and $\text{CoMoO}_4\cdot 3/4\text{H}_2\text{O}$ hydrate, molybdenum is present in tetrahedra $[\text{MoO}_4]$, and in the α -, hp-phases, and $\text{CoMo}_4\text{O}_{13}\cdot 2\text{H}_2\text{O}$ hydrate in octahedra $[\text{MoO}_6]$ (Eda et al., 2005, 2009).

The hydrate was found to lose its water of crystallization at 330°C , transforming into amorphous CoMoO_4 , which then crystallizes as α - CoMoO_4 (Haber, 1974). Cobalt molybdate α - CoMoO_4 can transform into β - CoMoO_4 when cooled to 100°C or during grinding at room temperature (Haber, 1974). This transformation is reversible at 420°C (β - CoMoO_4 into α - CoMoO_4) (Haber, 1974). It was found

that when the solid-phase reaction takes place between molybdenum(VI) oxide MoO_3 and cobalt oxides, the main product is cobalt molybdate α - CoMoO_4 . Both cobalt molybdates, α - CoMoO_4 as well as β - CoMoO_4 , are reduced in hydrogen into the $\text{Co}_2\text{Mo}_3\text{O}_8$ and Co_2MoO_4 phases (Haber et al., 1976).

The most typical synthesis method of cobalt molybdates consists of precipitation from aqueous solutions of cobalt nitrate and ammonium heptamolybdate (Rodriguez et al., 1998). Also, hydrothermal synthesis (Ding et al., 2008), solid state reaction of MoO_3 with CoO (Leyzerovich et al., 2004), and other methods (Peng et al., 2008) were applied successfully. In this work, a synthesis method and crystal structure of previously unreported compound $\text{NH}_4\text{Co}_2\text{OH}(\text{MoO}_4)_2\cdot\text{H}_2\text{O}$ is presented.

II. EXPERIMENTAL

A. Synthesis

The material was obtained by precipitation from saturated aqueous solutions of cobalt(II) nitrate hexahydrate $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (Chempur Poland, analytical grade) and ammonium heptamolybdate tetrahydrate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (Chempur Poland, analytical grade). The solutions were heated to 80°C and stirred with the use of a magnetic stirrer. In the next step, the solutions were mixed, and pH of the obtained mixture was adjusted by dropwise addition of 25 vol% aqueous ammonia to maintain at $\text{pH} 7-7.5$. The synthesis of purple precipitate was observed. The precipitation was continued at the same temperature, pH, and stirring for 25 min. Then, the precipitate was separated by vacuum filtration, rinsed with distilled water, and dried at 150°C for 12 h. The obtained powder was ground in an agate mortar.

B. XRD data collection and structure refinement

X-ray powder diffraction measurements (XRPD) were conducted with a Philips X'pert Pro MPD diffractometer.

^{a)} Author to whom correspondence should be addressed. Electronic mail: adamski_pawel@zut.edu.pl



The instrument was working in Bragg-Brentano geometry, with a goniometer radius of 240 mm, in continuous scan mode. An X-ray tube with the copper anode was used. The high voltage generator working parameters were 40 kV and 40 mA. A nickel filter was placed in the incident beam. In the diffracted beam, a graphite monochromator was mounted before the Pixel^{1D} detector. The diffraction data was collected in the angular range of 10–110° 2θ with a step size of 0.026 and ca. 230 s per step. Incident beam optics consisted of: the incident slit of 1/16°, the mask of 10 mm, and the Soller slit of 0.04 rad. Divergent beam optics used consisted of an anti-scatter slit of 7.7 mm and a 0.04 rad Soller slit.

The analysis of diffraction data was conducted with the use of PANalytical HighScore Plus v.3.0e software (Degen et al., 2014) coupled with International Centre for Diffraction Data (ICDD) Powder Diffraction File (PDF) 4+ (Gates-Rector and Blanton, 2019). Determination of the lattice parameters was conducted with the use of McMaille version 4.0 (Le Bail, 2004). Rietveld refinement method (Rietveld, 1967) was used to refine the structural parameters of the unknown phase. The following parameters were refined: scale factor, zero point error, sample displacement, unit-cell parameters, Caglioti parameters (*U*, *V*, *W*), profile coefficients, atomic coordinates, occupancies, individual isotropic thermal factors, and preferred orientation. A pseudo-Voigt type function was used. The structure imaging was performed with Crystal Impact Diamond software.

III. RESULTS AND DISCUSSION

For the obtained material, the ICDD PDF4+ database did not contain any matching patterns for a compound containing cobalt and molybdenum. It was established that the closest match to the acquired diffractogram was the PDF 04-018-0438 pattern (Wu et al., 2004). This diffraction dataset was ascribed to a compound with $\text{NH}_4\text{H}_3\text{Cu}_2\text{Mo}_2\text{O}_{10}$ formula. It is an example of layered molybdates of transition metals with the general formula $AT_2\text{OH}(\text{MoO}_4)_2\cdot\text{H}_2\text{O}$, where *A* = NH_4^+ , Na^+ , or K^+ , *T* = Co, Ni, Cu, or Zn (Mitchell et al., 2010). The mentioned above transition metal molybdates, firstly described by Pezerat (1965), occur in two distinct polymorphs designated as Φ_x and Φ_y . In the Φ_x structure, the layers consist of the edge-connected $[\text{TO}_6]$ octahedrons and $[\text{MoO}_4]$ tetrahedrons (Clearfield et al., 2002). The Φ_y structure consists of alike octahedrons and tetrahedrons, however, in the $[\text{TO}_6]$ net ordered cation vacancies are present (Levin et al., 1996). In both these polymorphs layers are stacked along the *z*-axis, they have a negative charge (balanced by cations in the interlayer positions), and hydrogen bonds are present between them.

It was assumed the as-obtained material was isostructural with that phase, and thus, its formula may be written as $\text{NH}_4\text{H}_3\text{Co}_2\text{Mo}_2\text{O}_{10}$. Applying these assumption, the Rietveld refinement was performed, where all the Cu atoms were substituted by Co. The experimental diffraction pattern with the Rietveld refinement is depicted in Figure 1. The model structure obtained from Rietveld refinement is shown in Table I. On the basis of the above, it was assumed that the obtained material was with $\text{NH}_4\text{Co}_2\text{OH}(\text{MoO}_4)_2\cdot\text{H}_2\text{O}$ formula and a Φ_y structure. Its lattice parameters are equal to $a = 6.1014(2)$ Å, $b = 6.1014(2)$ Å, $c = 21.826(1)$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, and $\gamma = 120^\circ$. The compound is in a trigonal system

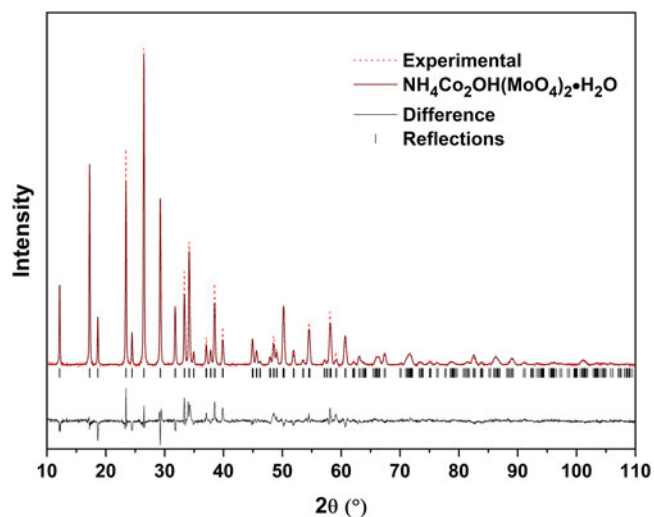


Figure 1. Diffraction pattern of the material with the Rietveld refinement indicated.

TABLE I. Atomic positions and occupancy obtained with Rietveld refinement.

Atom	Position	X	Y	Z	SOF	<i>B</i> _{iso} (Å ²)
Mo1	6c	0	0	0.4093(1)	1	2.7872
Co1	9d	0.5	0	0.5	0.63	1.8099
N1	6c	0	0	0.0150(8)	1	2.4915
O1	18f	0.186(5)	0.334(1)	0.0982(3)	1	4.6497
O2	6c	0	0	0.3210(8)	1	7.8167
O3	6c	0	0	0.2105(5)	1	2.4705

with an *R*-3 space group (148). The atomic positions are given in Table I. In Rietveld refinement, a March-Dollase (Dollase, 1986) preferred orientation model was included; the 1st preferred orientation parameter alongside $[001]$ direction was refined as 0.974(3). The *R* factors were: $R_{\text{exp}} = 3.54\%$, $R_{\text{wp}} = 7.82\%$, $R_p = 5.80\%$, and $\text{GOF} = 4.88$. The structural model of the material is depicted in Figure 2. The refined structure was deposited with the ICDD PDF4+ database with the 00-071-0747 number.

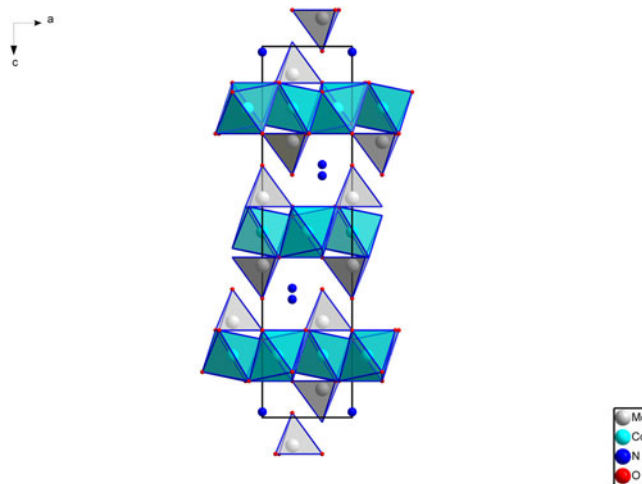


Figure 2. Crystal structure of $\text{NH}_4\text{Co}_2\text{OH}(\text{MoO}_4)_2\cdot\text{H}_2\text{O}$. The vacancies in Co positions are omitted for clarity.

IV. CONCLUSION

It was established that the precipitation of cobalt molybdate from aqueous solutions of cobalt nitrate and ammonium heptamolybdate at pH 7.5, modified with aqueous ammonia resulted in the synthesis of previously unpublished compound $\text{NH}_4\text{Co}_2\text{OH}(\text{MoO}_4)_2 \cdot \text{H}_2\text{O}$. Its structure is a polymorph of layered molybdates (Φ_y) $A\text{T}_2\text{OH}(\text{MoO}_4)_2 \cdot \text{H}_2\text{O}$ ($A = \text{NH}_4^+$, Na^+ , K^+ and $T = \text{Zn}^{2+}$, Co^{2+} , Cu^{2+} , Ni^{2+}), and consist of the layers of the edge-connected $[\text{CoO}_6]$ octahedrons and $[\text{MoO}_4]$ tetrahedrons.

V. DEPOSITED DATA

Files containing the raw diffraction data of material along with a file containing the refined structural parameters were deposited with the ICDD. The data can be requested at pdj@icdd.com. As observed powder diffraction pattern is included in the .cif file.

Supplementary material

The supplementary material for this article can be found at <https://doi.org/10.1017/S0885715623000350>.

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CONFLICT OF INTEREST

The authors have no conflicts of interest to declare.

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