Z. Kristallogr. Suppl. **26** (2007) 611-616

Powder diffraction studies of organoammonium polymolibdates

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Keywords: powder diffraction, molybdates, global optimisation

Abstract. Investigations of organoammonium polymolybdates, directed to synthesis and crystal structure determination of new inorganic – organic hybrid solids, have been intensively carried out. Two compounds: bis(**p**-**p**henylene**dia**mmonium) octamolybdate (compound **I** - (**ppda**2H)$_2$Mo$_8$O$_{26}$), and **m**-**x**ylylene**dia**mmonium trimolybdate (compound **II** - (**mxda**2H)$_2$Mo$_3$O$_{10}$), have been obtained by the reaction of molybdic acid with relevant amines in water solution. Their crystal structures have been determined by X-ray powder diffraction methods.

Introduction

Numerous investigations of organoammonium polymolybdates have been carried out because of their applications in photochemistry, catalysis and biomedicine [1,2,3]. Some of these compounds have photosensitive properties [4] and antitumour activity [5]. In the context of the inorganic-organic hybrid solids, polyoxomolybdates (POM) are interesting for design of new supramolecular materials by self-organisation processes between anions, organic cations and water molecules [6]. Polymolybdates are also attractive nano-building blocks, and exhibit diverse self-assembly properties, thus they can be very useful in supramolecular chemistry. Proper selection of organic cations and crystallisation conditions are the major problems in the crystal design of such materials. In the case of polyoxomolybdates strong interactions between the POM anions and organoammonium cations can lead to formation of numerous, diverse and 'unpredictable' structures; prediction of these interactions and hence new structures to be obtained is a very challenging task. For our study we selected two aromatic diamines: **mxda** (**m**-**x**ylylene**dia**mine) and **ppda** (**p**-**p**henylene**dia**mine).

There are no molybdates of **mxda** described in the literature. Very recently the crystal structure of the hexahydrated octamolybdate of **ppda** was determined [7]. In this paper the results of investigations of different anhydrous octamolybdate of **ppda** and trimolybdate of **mxda** are described.

Experimental

Synthesis

All reagents were used as received from commercial suppliers.

Compound **I**: Molybdic acid (1.8g; 0.01mol) and p-phenylenediamine (1.08g; 0.01mol) were added to 150 ml of water and heated at temperature 80°C for 24 hours. After that a white precipitate was filtered off.

Compound **II**: As before but using m-xylylenediamine (1.36g; 0.01mol) instead of p-phenylenediamine.

X-ray powder diffraction

X-ray powder diffraction patterns for both compounds were collected on a Philips X'pert Pro diffractometer (Bragg-Brentano geometry). The patterns were collected at 25ºC, Cu $K\alpha_{12}$ radiation with fixed divergence slit. Counting time was 9s/step and the 2θ range 5-70º for compound **I** and 5-80º for compound **II**.

The powder patterns were indexed using the PROSZKI [8] package. For compound **I** the best solution was obtained in the triclinic system, a = 10.5152(9) Å, b = 10.5778(9) Å, c = 7.203(5) Å, $\alpha = 98.82(1)^o$, $\beta = 109.34(2)^o$, $\gamma = 90.39(1)^o$, V=745.32(8), Z=2, F_{20} = 14.8, SG: *P-1* (2). Compound **II** crystallises in the monoclinic system, a= 10.5152(9) Å, b= 10.5991(3) Å, c= 9.0483(3) Å, β= 97.894(4)^o, V= 719.20(6), Z=2, F_{20} = 52, SG: $P2_1/m$ (11).

Initial structure models were found using the global optimisation method implemented in the FOX program [9]. The sequence of the tested structure models was based on analytical data, lattice parameters and morphology. First we tested the most probable 'Mo-O clusters'. The Rietveld refinements for the structures of compounds **I** and **II** were carried out using the JANA2000 program [10]. The initial profile was obtained by fitting the observed pattern according to the Le Bail method [11]. The refinement procedure included scale, zero-point, background, preferred orientation, lattice parameters, atomic positions, occupations and isotropic displacement. The March-Dollase function [12] was used for the preferred orientation correction. The obtained values of R_{wp} and χ^2 are: 0.114, 8.44 (for the compound **I)** and 0.163, 6.57 (for the compound **II**), respectively. The refined atomic positions have been deposited in the CSD. These atomic positions are listed in Tables 1 and 2. The most important inter-atomic distances are given in Table 3a and 3b.

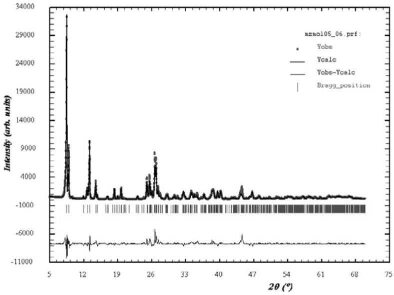

Figure 1. Rietveld refinement plot obtained for m-xylylenediammonium trimolybdate.

Table 1. Atomic coordinates and equivalent isotropic displacement parameters for I.

Atom	*x/a*	*y/b*	*z/c*	Uiso
Mo1	-0.0298(7)	0.2821(5)	0.6401(10)	0.014(5)
Mo2	0.1652(7)	0.2192(4)	0.3720(9)	0.006(5)
Mo3	0.2815(6)	0.5182(5)	0.5008(11)	0.022(5)
Mo4	0.0806(7)	0.5778(5)	0.7537(8)	0.007(4)
O1	0.0945(16)	0.2652(15)	0.8556(16)	0.07(3)
O2	0.2522(18)	0.3630(8)	0.3151(18)	0.07(2)
O3	0.3732(12)	0.6111(7)	0.415(2)	0.38(7)
O4	-0.1668(14)	0.2003(8)	0.652(2)	0.10(4)
O5	-0.0718(11)	0.4611(6)	0.724(3)	0.01(2)
O6	0.195(2)	0.6558(4)	0.631(3)	0.08(3)
O7	0.0174(15)	0.1661(10)	0.448(2)	0.094(18)
O8	0.1069(12)	0.4150(6)	0.5453(14)	0.091(3)
O9	0.1979(16)	0.5458(15)	0.9635(12)	0.11(2)
O10	0.0139(14)	0.7204(5)	0.830(2)	0.10(5)
O11	0.2962(15)	0.1838(13)	0.566(2)	0.04(2)
O12	0.1576(14)	0.1024(7)	0.1765(18)	0.02(2)
O13	0.3934(11)	0.4786(16)	0.7135(18)	0.027(17)
N1	0.480(10)	0.353(12)	0.714(8)	0.0127
N2	0.542(7)	0.081(3)	1.357(3)	0.0127
C1	0.495(9)	0.284(13)	0.877(12)	0.0127
C2	0.439(9)	0.328(7)	1.024(11)	0.0127
C3	0.455(13)	0.261(7)	1.183(10)	0.0127
C4	0.526(8)	0.150(12)	1.194(3)	0.0127
C5	0.582(9)	0.105(8)	1.047(1)	0.0127
C6	0.567(4)	0.172(8)	0.888(4)	0.0127

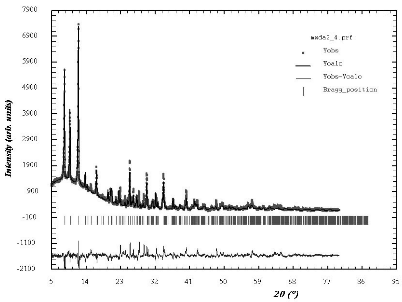

Figure2. Rietveld refinement plot obtained for bis(p-phenylenediammonium) octamolybdate.

Table 2. Atomic coordinates and equivalent isotropic displacement parameters for II.

Atom	x/a	y/b	z/c	Uiso
Mo1	0.3889(8)	0.25	0.1621(5)	0.025(5)
Mo2	0.3553(7)	0.4883(6)	-0.1382(7)	0.006(2)
O1	0.396(4)	0.4998(5)	0.1325(14)	0.064(13)
O2	0.6262(4)	0.25	0.161(6)	0.027(7)
O3	0.373(4)	0.25	-0.1150(6)	0.04(3)
O4	0.451(8)	0.25	0.384(3)	0.072(8)
O5	0.2064(10)	0.25	0.214(9)	0.055(2)
O6	0.297(4)	0.4368(4)	-0.3249(15)	0.0278(12)
N1	0.928(6)	0.25	0.199(7)	0.0127
N2	0.640(3)	0.25	0.502(4)	0.0127
C1	0.963(5)	0.25	0.706(6)	0.0127
C2	0.872(6)	0.25	0.597(6)	0.0127
C3	0.898(7)	0.25	0.462(8)	0.0127
C4	1.015(6)	0.25	0.437(3)	0.0127
C5	1.105(5)	0.25	0.545(6)	0.0127
C6	1.079(6)	0.25	0.681(7)	0.0127
C7	0.760(5)	0.25	0.621(5)	0.0127
C8	1.042(7)	0.25	0.297(8)	0.0127

Results and discussion

Crystal Structure

The octamolybdate anion (Figure 3, Table 3) consists of eight sharing edges and corners octahedra. These octahedra are highly distorted, but the symmetry of the anion is close to *mm2* (C_{2v}). According to the literature [10] the Mo – O distances (Table 5) can be divided into four groups: short (1.65 Å – 1.74 Å), intermediate (1.90 Å – 2.00 Å), long (2.14 Å – 2.17 Å) and very long (2.25 Å – 2.50 Å), The p-phenylenediammonium cations are placed between octamolybdate anions and are connected to them by a network of hydrogen bonds (suggested by distances between nitrogen and oxygens from **ppda** and $Mo_8O_{26}^{4-}$ anions).

The structure of m-xylylenediamine trimolybdate consists of zigzag anionic chains $[Mo_3O_{10}^{2-}]_\infty$, built of edge sharing octahedra, running parallel to the b axis, (see Figure 4). The **mxda** molecules are perpendicular to this axis, and are placed exactly on the mirror planes (Sg. $P2_1/m$). As one can see from Figure 4, there are no π–π interactions between the **mxda** molecules. The Mo_3O_{10} chains are surrounded by **mxda** molecules joined to them by hydrogen bonds.

Table 3. Selected bond lengths L *in Å for a) octamolybdate anion, b). trimolybdate anion.*

a).

Atoms	L	Atoms	L
Mo1-O1	1.702(14)	Mo3-O2	1.904(11)
Mo1-O4	1.706(17)	Mo3-O3	1.687(16)
Mo1-O5	1.996(10)	Mo3-O5	2.266(15)
Mo1-O6	2.481(19)	Mo3-O6	2.00(2)
Mo1-O7	1.90(2)	Mo3-O8	2.259(16)
Mo1-O8	2.345(15)	Mo3-O13	1.708(15)
Mo2-O2	1.932(16)	Mo4-O5	1.947(15)
Mo2-O7	1.92(2)	Mo4-O6	1.96(3)
Mo2-O8	2.437(11)	Mo4-O8	2.188(10)
Mo2-O10	2.219(13)	Mo4-O8	2.456(11)
Mo2-O11	1.697(16)	Mo4-O9	1.687(13)
Mo2-O12	1.705(13)	Mo4-O10	1.757(11)

b).

Atoms	L
Mo1-O1	1.950(5)
Mo1-O1	1.950(5)
Mo1-O2	2.51(2)
Mo1-O3	2.327(5)
Mo1-O4	1.795(5)
Mo1-O5	1.696(8)
Mo2-O1	2.451(13)
Mo2-O1	2.376(11)
Mo2-O2	2.010(11)
Mo2-O3	1.853(5)
Mo2-O6	1.755(5)
Mo2-O7	1.685(6)

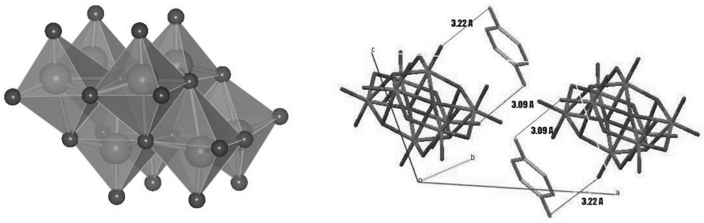

*Figure 3. View of the octamolybdate anion with O atoms at the corners of the octahedra and Mo atoms in the centres (left); and unit cell of compound **I** (right) with hydrogen bonds indicated by dashed lines.*

Concluding remarks

In the investigation of the compounds Bis(**p**-**p**henylene**dia**mmonium) octamolybdate (compound **I**) and **m**-**x**ylylene**dia**mmonium tri molybdate **(**compound **II)** by X-ray powder diffraction methods the well known and very popular in chemistry of molybdenum $Mo_8O_{26}^{4-}$ and $Mo_3O_{10}^{2-}$ anions were found. It is interesting to note that in very similar conditions (the same molar ratio of Mo/amine, the same concentrations) two different molybdates (tri- and octa-) were obtained. A possible explanation can be the different alkaline character of both amines. Synthesis with more alkaline amine (pK_a(**mxda**) = 9.19) leads to trimolybdate, whereas less alkaline amines like **ppda (**pK_a(**ppda**) = 5.11**)** favour octamolybdates which are typical for more acidic solutions.

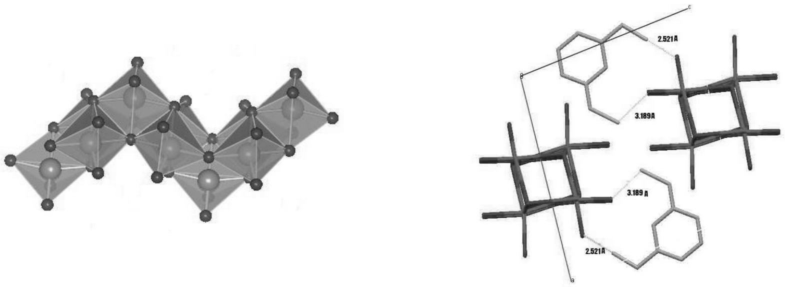

*Figure 4. View of the trimolybdate anion with O atoms at the corners of the octahedra and Mo atoms in the centres (left); and unit cell of compound **II** (right) with hydrogen bonds indicated by dashed lines.*

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Acknowledgements. Financial support of Polish Ministry of Science and Higher Education (1T09A07730) is kindly acknowledged.