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## Research Article

# The Novel Polymorphic Form of Bis(3,5,7-triaza-1-azoniatricyclo[3.3.1.1<sup>3,7</sup>]decane) bis( $\mu_4$ -oxo)-tris( $\mu_3$ -oxo)-nonakis( $\mu_2$ -oxo)-nonaqua-decaoxo- hepta-molybdenum-di-zinc(II) dihydrate, Synthesis, and Properties

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The reaction of molybdophosphoric acid with zinc carbonate followed by addition of hmta leads to formation of a triclinic polymorph of bis(3,5,7-triaza-1-azoniatricyclo[3.3.1.1<sup>3,7</sup>]decane) bis( $\mu_4$ -oxo)-tris( $\mu_3$ -oxo)-nonakis( $\mu_2$ -oxo)-nonaqua-decaoxo-hepta-molybdenum-di-zinc(II) dihydrate in a one pot simple reaction. The obtained compound has been characterised by IR, UV-Vis spectroscopy, elemental analysis, and X-ray crystallography. A detailed comparison between both polymorphic forms: triclinic  $a = 22.758 \text{ \AA}$ ,  $b = 24.702 \text{ \AA}$ ,  $c = 31.995 \text{ \AA}$ ,  $\alpha = 101.206^\circ$ ,  $\beta = 103.256^\circ$ ,  $\gamma = 105.736^\circ$ , and  $V = 16203.8 \text{ \AA}^3$  and monoclinic  $a = 43.120 \text{ \AA}$ ,  $b = 12.399 \text{ \AA}$ ,  $c = 16.285 \text{ \AA}$ ,  $\alpha = 90.00^\circ$ ,  $\beta = 111.12^\circ$ ,  $\gamma = 90.00^\circ$ , and  $V = 8122 \text{ \AA}^3$  was performed. The influence of the synthesis procedure on polymorph formation was described.

## 1. Introduction

The coordination chemistry of zinc is a field of growing interest from various viewpoints. The attention of scientists concentrates on synthetic aspects, structural, physicochemical properties, and reactivity of zinc compounds, as well as on their potential applications such as the development of catalysts (C–C bond formation reactions [1], carbon dioxide activation [2–4], etc.). Zinc complexes compounds are widely studied as biological mimics [5–7]. Zinc is an essential element for humans and is homeostatically regulated in the body. It has an important role in protein synthesis, and it is also a cofactor for many enzymes regulating cell growth and hormone levels, including regulation of gene transcription and growth factor metabolism [8]. Moreover, the mean zinc and lead concentrations in the human body correlate with the degree of urbanization and industrialization [9, 10].

Transition metal oxides such as molybdenum oxides are used in many industrial applications and have gained an interest from both technological and scientific points of view [11–15]. The main fields of industrial applications are catalysis, sorption, energy storage, molecular electronics, optical materials, and ceramics [16, 17]. Molybdenum oxides are an interesting example of this group of compounds and have a great industrial interest due to their optical and electronic properties. In fact, these transition metal oxides can be switched between two different optical states by photochromic, thermochromic, or electrochromic means [13]. Compounds that contain molybdenum oxides substructures modified by organonitrogen ligands were classified as a fifth class of oxides in which organic materials play a significant structural role [18]. Taking the above into consideration, there is a need for synthesis and investigations of new molybdenum cluster compounds. These compounds, containing

additionally zinc cations, may possess interesting biological properties, joining in one compound the benefits of both a molybdenum cluster and zinc ions.

Hexamethylenetetraamine (hmta) is an interesting ligand forming a diversity of complex compounds. It is used in pharmaceutical and in chemical industries as an intermediate material [19]. Since the discovery of hmta, over a century ago, an enormous number of its salts, molecular adducts, and coordination complexes have been reported in the literature [20]. Hmta is a potentially tetradentate ligand, universally used for the construction of supramolecular arrays with various hmta coordination modes utilising from one to four nitrogen atoms [21]. Additionally, the hmta can be located in outer coordination sphere and influence the inner coordination sphere of metals by supramolecular bond array.

Polymorphism is a commonly known phenomenon [22–26]. Polymorphic transitions influence many properties of a compound, for example, physical stability, chemical stability, and manufacturability or in the case of drugs, can for example change the kinetics of oral absorption. Relatively small changes in crystal packing may lead to significant differences in the crystal packing density and other properties of polymorphs [27, 28].

Compounds containing many independent molecules in the unit cell of inorganic-organic compounds seem to be currently a subject of great interest both for pure science and for its industrial consequences, especially for pharmaceutical production and technical applications, as they can be considered as “locked in” compounds formed too early in crystallization processes and thus differing from the thermodynamically most stable structures [29, 30]. Such “locked in” compounds are a relatively good source of the new polymorphic forms of known compounds [29]. In the recent literature, it is observed an increasing amount of reports dedicated to the development of new compounds possessing  $Z' > 1$  and to the study of their properties [31, 32].

While searching and studying polymorphic forms of compounds possessing useful properties, a new polymorph of zinc complex compound containing hexamethylenetetraamine and a molybdenum cluster was obtained and is presented here.

## 2. Experimental

### 2.1. Synthesis

*2.1.1. Preparation of bis( $\mu_4$ -oxo)-tris( $\mu_3$ -oxo)-nonakis( $\mu_2$ -oxo)-nonaaqua-decaoxo-hepta-molybdenum-di-zinc(II).* The zinc (II) carbonate (0.003 mol, 0.3762 g) was suspended in solution of dodecamolybdophosphoric acid ( $\text{H}_3\text{PO}_4 \cdot 12\text{MoO}_3 \cdot 24\text{H}_2\text{O}$ , 0.001 mol, 2.2652 g) in  $30 \text{ cm}^3$  of water. The suspension was stirred on a magnetic stirrer until pH of mixture was 7.0 (about 3 hours). Within this time, the precipitation of non-soluble zinc (II) phosphate (V) ( $\text{Zn}_3(\text{PO}_4)_2$ ) was observed. Then, the mixture was filtered to remove unreacted excess of zinc carbonate and deposit of zinc (II) phosphate (V). The residue on the filter was washed

three times with  $5 \text{ cm}^3$  of cold water. The last filtrate showed no presence of molybdate (VI) on the basis of test with hydrogen peroxide in acidic environment [33].

*2.1.2. Preparation of the Compound I.* The solution of bis( $\mu_4$ -oxo)-tris( $\mu_3$ -oxo)-nonakis( $\mu_2$ -oxo)-nonaaqua-decaoxo-hepta-molybdenum-di-zinc(II) obtained according to Section 2.1.1. was mixed with solution of hexamethylenetetraamine (hmta, 0.001 mol, 0.1402 g in  $10 \text{ cm}^3$  of water). After six weeks of crystallization at  $21\text{--}23^\circ\text{C}$  the light green crystals were obtained and separated from the solution.

*2.2. Crystal Structure Determination.* Light green rectangular prism shape crystal was mounted on a KM-4-CCD automatic diffractometer equipped with CCD detector and used for data collection. X-ray intensity data were collected with graphite monochromated  $\text{MoK}_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at temperature  $291.0(3) \text{ K}$ , with  $\omega$  scan mode. 10 seconds exposure time was used and reflections inside Ewald sphere were collected up to  $2\theta = 50^\circ$ . The unit cell parameters were determined from least-squares refinement of the setting angles of the 5034 strongest reflections. Details concerning crystal data and refinement are given in Table 1. Examination of reflections on two reference frames monitored after each 20 frames measured showed no loss of the intensity during whole measurement. Lorentz, polarization, and numerical absorption [34] corrections were applied. The structure was solved by direct methods. All the nonhydrogen atoms were refined anisotropically using full-matrix, least-squares technique on  $F^2$ . The carbon-bonded hydrogen atoms were set in calculated position after four cycles of anisotropic refinement and refined as “riding” on the adjacent atom with individual isotropic displacement factor equal 1.2 times of the value of equivalent displacement factor of the parent carbon atoms. Due to flattening of difference Fourier syntheses, the oxygen-bonded hydrogen atoms could not be found. The hydrogen atom positions were idealised after each cycle of refinement. The SHELXS97, SHELXL97, and SHELXTL [35] programs were used for all the calculations. Atomic scattering factors were those incorporated in the computer programs.

*2.3. Other Measurements.* Elemental analysis was carried out using Vario EL III CHNOS elemental analyzer (C, H, N, O). Molybdenum (VI) content was determined by polarographic analysis in presence of EDTA [36] in mineralized sample. Zinc (II) content was determined by complexometric titration with EDTA used as a complexing agent [36]. IR spectra of the samples in the form of KBr pellets were recorded on a Nicolet Magna 560 spectrophotometer in the spectral range  $4000\text{--}400 \text{ cm}^{-1}$ . The UV-VIS spectra were recorded on Jasco V-660 spectrophotometer, in transmission mode, for solid samples pressed between two quartz plates. The thermal analysis was carried out in a TG/DTA-SETSYS-16/18 thermoanalyser coupled with thermostar (Balzers) mass spectrometer. The sample was heated in corundum crucibles up to  $1000^\circ\text{C}$  at a heating rate  $2^\circ\text{C}/\text{min}$  in air atmosphere. The products of the decomposition process

TABLE 1: Details of crystal data and refinement of **1**.

Empirical formula	$C_{12}H_{48}Mo_7N_8O_{35}Zn_2$
Formula weight	1666.9
Crystal system, space group	Triclinic, $P-1$ (No. 2)
Temperature [K]	291.0(2)
Wavelength	0.71073
Unit cell dimensions [ $\text{\AA}$ , $^\circ$ ]	$a = 22.7527$ (7) $b = 24.7023$ (7) $c = 31.9954$ (9) $\alpha = 101.206$ (2) $\beta = 103.256$ (2) $\gamma = 105.736$ (2)
Volume [ $\text{\AA}^3$ ]	16203.8 (8)
$Z$ , Calculated density [ $\text{Mg/m}^3$ ]	16, 2.733
Absorption coefficient [ $\text{mm}^{-1}$ ]	2.733
$F(000)$	12960
Crystal size [mm]	$0.395 \times 0.393 \times 0.209$
$\theta$ range for data collection [ $^\circ$ ]	1.52 to 36.23
Index ranges	$-28 \leq h \leq 37$ , $-35 \leq k \leq 40$ , $-52 \leq l \leq 36$
Reflections collected/unique	267213/126216 [ $R_{\text{int}} = 0.0496$ ]
Refinement method	full-matrix least-squares on $F^2$
Completeness	100% to $\theta = 25^\circ$
Min. and max. transmission	0.340 and 0.542
Goodness-of-fit on $F^2$	1.007
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R1 = 0.0313$ , $wR2 = 0.0563$
$R$ indices (all data)	$R1 = 0.0543$ , $wR2 = 0.0607$
Largest diff. peak and hole [ $e \cdot \text{\AA}^{-3}$ ]	0.601 and $-0.722$

were calculated from TG curves, and the temperature ranges were determined by means of thermoanalyser data processing module [37]. The compound density was determined by Berman density torsion balance. Elemental analysis for **1** [Calculated/Found (%)]  $C_{12}H_{48}Mo_7N_8O_{35}Zn_2$ , C 8.61/8.58; H 2.9/3.00; O 33.61/33.01; Mo 40.32/40.58; N 6.57/6.58; Zn 7.99/7.90.

### 3. Results and Discussion

The bis(3,5,7-triaza-1-azoniatricyclo[3.3.1.1<sup>3,7</sup>]decane) bis-( $\mu_4$ -oxo)-tris( $\mu_3$ -oxo)-nonakis( $\mu_2$ -oxo)-nonaaqua-decaoxo-hepta-molybdenum-di-zinc(II) dihydrate was previously obtained in the monoclinic form (**1a**) (Herman-Maugin  $C2/c$  space group) [38], and the presented polymorph (**1**) adopts the triclinic symmetry ( $P-1$  space group) with doubled content of the unit cell ( $Z = 8$  and  $Z = 16$ , resp., for (**1a**) and (**1**)). The only structural difference between both polymorphic forms is the crystal net symmetry (Figure 1), but it must be mentioned that the overall molecules arrangement in the crystal net is similar in both polymorphs. Inspection of the crystal nets of **1a** and **1**

shows that the molecules occupy the same sites of the nets (Figure 1), but they are slightly rotated. Such rotation in **1** leads to motifs which do not reproduce the periodicity observed in **1a** (the neighbouring molecules of **1** are connected only by pseudosymmetry elements, and some atoms deviate up to about 5% from the position originating from the symmetry elements present in **1a**). The molecular geometry of the molecules is the same (in the range of experimental error) in **1** and **1a** (See Supplementary Table 1 in Supplementary Material available online at doi:10.1155/2012/516832).

The title compound was synthesized in a two-step synthesis starting from molybdophosphoric acid and zinc carbonate, with addition of hmta at the second step. The formation of molybdenum clusters originates from a protonation of molybdate anions by a strong mineral acid for example, hydrochloric acid [38]. In the case of **1**, the clustering was attained *in situ* by protons from molybdophosphoric acid. This synthesis procedure is simpler than that described earlier [38], because there is no necessity to adjust pH by adding the acid solution, but it must be noted that it leads to formation of a polymorphic form in the solid state. Formation of the bond between nonmetal and nitrogen atoms is not possible in a solution at low pH [38] and also at neutral pH (as it was found for compound **1**).

The infrared spectrum of **1** is consistent with the presence of the molybdenum oxide cluster and hmta ligand. The weak peak at  $769 \text{ cm}^{-1}$  is attributed to the vibration of MoO bonds similarly to the oscillator observed in molybdenum (VI) oxide, but it is slightly shifted to higher frequencies due to utilisation of terminal oxygen atoms lone pairs into O  $\rightarrow$  Mo interactions in molybdenum (VI) oxide and thus weakening of the oscillators in that compound [39, 40]. The sharp peak at  $896 \text{ cm}^{-1}$  is attributed to the Mo=O bonds, which is a characteristic for the symmetric and asymmetric stretches of the MoO cis-dioxo group [38, 40–42]. The very weak band at  $962 \text{ cm}^{-1}$  is assigned to the stretching vibrations of bonds of Mo–O–Mo group [43–46] as well as to the vibrations of the double bond of the Mo=O group [41]. This band can also suggest the presence of molybdenum in the lower oxidation state, that is,  $Mo^{5+}$  [39, 40] but in the studied compound, it is impossible due to stoichiometry. The absorption bands observed at  $1636$  and  $3480 \text{ cm}^{-1}$  can be attributed to the bending vibrations of O–H bonds of zinc-coordinated water molecules [38]. In **1**, all IR absorption maxima (typical for hmta molecules existing in the outer coordination sphere) are also observed (Table 2). The IR spectrum of **1** is more complex than that of **1a** [38] (Table 2), and some oscillators have different energy in each compound. The peak attributed to vibrations of OH bonds of compound **1** water molecules (at  $1636 \text{ cm}^{-1}$ ) is shifted to lower frequencies (about  $22 \text{ cm}^{-1}$ ) in comparison to **1a**, and the analogous vibrations at  $3480 \text{ cm}^{-1}$  are shifted to higher frequencies (about  $30 \text{ cm}^{-1}$ ), which originate from different intermolecular interactions in both compounds. In both polymorphic forms, bands attributed to MoO bonds and peaks assigned to hmta are present. They exist at the same wave numbers, but some vibrations observed in the IR spectrum of **1** are not reported (however, they are probably

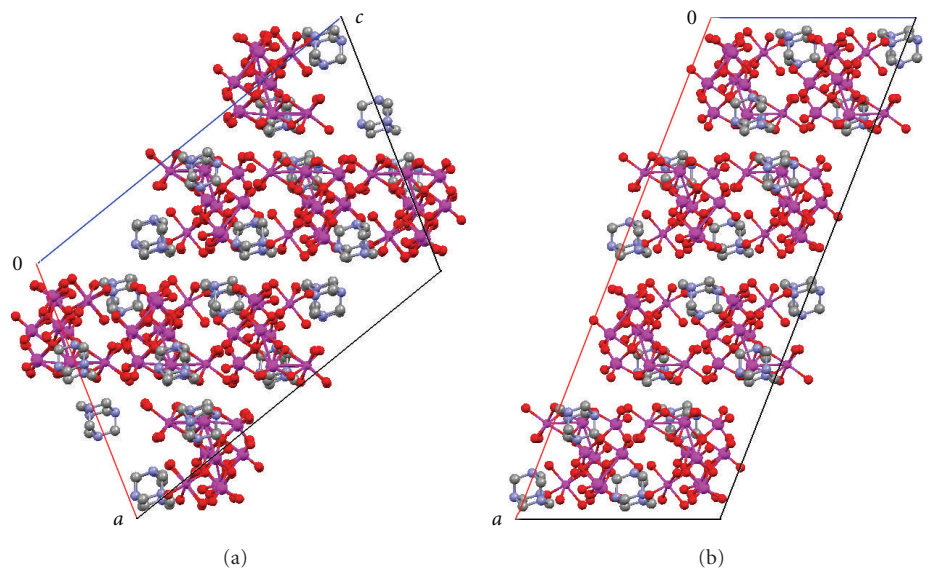


FIGURE 1: The part of the crystal packing of **1** (a) and **1a** (b) showing the differences in the unit cell symmetry and similarity of the placement of the molecules in the unit cell.

observed) in case of compound **1a** (including strong bands at 664.3, 831.8, 2993.7, and 3005.8  $\text{cm}^{-1}$ ).

The solid state UV-Vis spectrum of compound **1** shows maxima at 243, 299, 536, 590, and 749 nm. The first two bands are also detected in the UV-Vis diffuse reflectance spectrum of molybdate clusters [47, 48]. The band at 243 nm is attributed to electronic transitions in tetrahedral molybdate, while the band at 299 nm is assigned to electronic transitions in Mo–O–Mo bridge bond existing between two octahedral metal atoms of molybdate [47]. Both these absorption maxima exist in electronic spectra of molybdenum (VI) oxide (this oxide possesses a total of four absorption maxima in UV-VIS spectrum at 217, 245, 326, and 620 nm), but it is worth noticing that in **1**, the second one is distinctly blue shifted (about 27 nm) in comparison to molybdenum (VI) oxide [48]. The first broad band (243 nm) is assigned to  $\pi \rightarrow \pi^*$  transitions, and its shape and position are the consequence of the presence of many double Mo=O bonds in the compound **1**. The second band (299 nm) can be attributed to the  $n \rightarrow \pi^*$  transitions and it is a characteristic of oxygen atoms bonded to metal atoms by a double bond [49]. The above-mentioned blue shift originates from enlarged energy gap between  $n$  and  $\pi^*$  orbitals caused by localising of  $n$  orbitals on oxygen atoms of **1** (in molybdenum (VI) oxide, these  $n$  orbitals are partially utilised for creation of O  $\rightarrow$  Mo interactions, thus they have larger energy). The two absorption maxima (at 217 and 620 nm) existing in the UV-VIS spectrum of molybdenum (VI) oxide are not observed in **1**. The absorption maximum at 217 nm (assigned to  $\pi \rightarrow \pi^*$  electron transitions) is blue shifted to the vacuum ultraviolet region (because the M=O bonds in molybdenum (VI) oxide are longer and thus weaker than those ones existing in compound **1**, this increases the energy gap between the  $\pi$  and  $\pi^*$  orbitals). Due to the impossibility of total removing of atmospheric nitrogen from

solid samples, such shifted absorption maxima could not be identified in the case of the current compound. The visible region absorption of molybdenum (VI) oxide with absorption maximum at 620 nm (responsible for the yellow-green colour of the compound) is absent in **1**, and it is replaced by three absorption maxima (two strong at 536, 590 nm and one medium strength at 749 nm) responsible for the green colour of crystals of **1**.

The thermal decomposition of the investigated complexes is a gradual process. According to TG and DTG curves, compound **1** decomposes by the same scheme as observed for **1a** [38], but the DTA curve obtained for compound **1** shows a distinctly smaller endothermic peak during the water evolution process accompanied by a very small exothermic peak, not observed in **1a**. Thus, it can be supposed that during the first step of thermal degradation, the differences between the polymorph disappear, and the resulting anhydrous compounds have the same structure.

## 4. Conclusions

The reaction of molybdophosphoric acid with zinc carbonate followed by addition of hmta leads to formation of a triclinic polymorph of bis(3,5,7-triaza-1-azoniatricyclo[3.3.1.1<sup>3,7</sup>]decane) bis( $\mu_4$ -oxo)-tris( $\mu_3$ -oxo)-nonakis( $\mu_2$ -oxo)-nonaqua-decaoxo-hepta-molybdenum-di-zinc(II) dihydrate in a one pot simple reaction. Some differences were observed between the properties of the two polymorph, for example, some IR spectral bands observed in **1** are shifted in comparison to **1a**, and some bands are unreported or absent in the spectrum of **1**. During thermal decomposition, different effects were observed. In addition, **1** is slightly denser than **1a** (about 0.01  $\text{Mg/m}^3$ ).

TABLE 2: Vibrational frequencies [ $\text{cm}^{-1}$ ] and their assignment.

Compound 1	Compound 1a [38]	hmta [50, 51]	MoO	Assignment
3480.2bb	3449bb			$\nu$ OH ( $\text{H}_2\text{O}$ ) [47]
3005.8s			2955	$\nu_{\text{as}}$ $\text{CH}_2$
2993.7s		2934		$\nu$ CH
2954.3wv		2955		$\nu_{\text{as}}$ CH
2822.6wv				$\nu_{\text{s}}$ $\text{CH}_2$
2785.9wv				$\nu_{\text{s}}$ $\text{CH}_2$
2705.4w				$\nu_{\text{s}}$ $\text{CH}_2$
1636.4w	1655m			$\delta$ OH ( $\text{H}_2\text{O}$ ) [47]
1465.7w	1462s	1489		$\sigma$ $\text{CH}_2$
1450.1vw		1456		$\sigma$ $\text{CH}_2$
1374.6w	1369s	1370		$\tau$ $\text{CH}_2$
1298.4w	1300s	1306		$\omega$ $\text{CH}_2$
1256.5m	1253s	1269		$\rho$ $\text{CH}_2$
1245.9w		1240		$\rho$ $\text{CH}_2$
1217.9vw	1211s	1238		$\rho$ $\text{CH}_2$
1148.5vw		1128		$\delta$ CNC
1042.9vw		1042		$\delta$ NCN
1019.2w	1024s	1024		$\nu$ NC
978.4w	979s	974.4		$\nu$ NC
962.3vw			960 [39, 40] 950 [41] 945–970 [43–46]	$\text{Mo}^{5+}$ $\nu$ MoO $\nu$ Mo–O–Mo
931.1m		925		$\nu$ NC
896.9vs	893s		880–920 [38, 40–42]	$\nu_{\text{s}}$ and $\nu_{\text{as}}$ Mo=O
852.2m				$\nu$ NC
831.8s		812		$\nu$ NC
786.6vw		779		$\nu$ NC
769.5w			740–760 [39, 42]	$\text{Mo}^{6+}$ - $\text{MoO}_3$
676.9s	671 s	673		$\delta$ NCN
664.3s		670.9		$\delta$ CNC

Vibrations symbols: vw: very weak, w: weak, m: medium strength, s: strong, vs: very strong, bb: broad band,  $\nu$ : stretching,  $\delta$ : bending,  $\tau$ : wagging,  $\omega$ : twisting,  $\rho$ : rocking,  $\sigma$ : scissoring, s: symmetric, and as: asymmetric.

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