Influence of Hydrogen Bonding Interactions on the Conformation of Ribbon-like Zn(II) Complexes Bridged by Molybdates

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The complexes [Zn(dpa)MoO_4] (**1**) and [Zn(dpa)MoO_4]·0.5H_2O (**2**·0.5H_2O) (dpa = 2,2′-dipyridylamine) were synthesized hydrothermally. Single crystal structure analyses indicate that **1** and **2** are conformational isomers. They both consist of binuclear units of edge-sharing $\{ZnN_2O_3\}$ trigonal bipyramids bridged by pairs of bidentate briding $\{MoO_4\}^{2-}$ anions into a one-dimensional ribbon, but their orientations of the terminal O atoms of the $\{MoO_4\}^{2-}$ anions are different. In **1** and **2**, the ribbon-like chains are connected into a 2D network *via* hydrogen bonding interactions between the central N–H portions of the dpa molecules and the terminal O atoms of $\{MoO_4\}$ tetrahedra. For **2**, in addition, the hydrogen bonding interactions between the crystal water molecules and the terminal O atoms of $\{MoO_4\}$ tetrahedra join the 2D layers into a 3D architecture. They play an important role not only in constructing the 3D architecture, but also in the conformational stability.

Key words: Molybdate, Zn(II) Complex, Isomer, Hydrothermal Synthesis

Introduction

There has recently been a growing interest in the synthesis of crystals assembled by polyoxometalate clusters and secondary metal-ligand subunits [1 – 5]. In crystallization processes, hydrogen bonding and/or π-π interactions play significant roles in addition to charge, size and shape matching [6 – 8]. The supramolecular interactions have been discussed in almost all crystal structures built from polyoxometalate clusters and metal-ligand units [9 – 11]. In a recent paper, we have described two isomeric complexes of [$\{Cu(dpa)_2\}_2V_4O_{12}$] in the solid state [12]. The $\{MoO_4\}^{2-}$ anion is the simplest molybdate species, but it can act as a multidentate ligand. Combined with bidentate amine ligands, it can bridge transition metal ions, constructing discrete, one-, two- or three-dimensional coordination polymers. For example, it has been found as a bidentate bridging ligand in polymers of [Ni(3,4-bipy)$_2MoO_4$] · 3H_2O [13], [VO(terpy)MoO_4] [14], [$\{Fe(terpy)\}_2Mo_3O_{12}$] · H_2O, and [Cu(terpy)MoO_4] [15], as a tridentate bridging ligand in polymers of [Cu(dpe)MoO_4] [16], [Cu(3,3′-bpy)$_{0.5}MoO_4$] [3], [Zn(*o*-phen)MoO_4] [5], [FeCl(2,2′-bpy)MoO_4] [17], and [Mn(phen)(H_2O)MoO_4] · H_2O [18], and as a tetradentate bridging ligand in the polymer of [Cu(4,4′-bpy)$_{0.5}MoO_4$] · 1.5H_2O [3]. The remaining terminal O atoms of the $\{MoO_4\}^{2-}$ anion can function as hydrogen bonding donor sites [19, 20].

In contrast to 2,2′-bpy and phen ligands, a dpa molecule (dpa = 2,2′-dipyridylamine) with one more N atom is less rigid and has a potential hydrogen bonding donor site so that more abundant hydrogen bonding interactions exist in complexes assembled from $\{MoO_4\}^{2-}$ anions and $\{M(dpa)\}^{2+}$ fragments. In this paper, we report two conformational isomers of [Zn(dpa)MoO_4] in the anhydrous crystals (**1**) and in the hydrate [Zn(dpa)MoO_4] · 0.5H_2O (**2** · 0.5H_2O). Crystal structure analyses have revealed that both **1** and **2** consist of binuclear units of edge-sharing $\{ZnN_2O_3\}$ trigonal bipyramids bridged by pairs of bidentate $\{MoO_4\}^{2-}$ anions into one-dimensional ribbons, but the orientations of the terminal O atoms of the $\{MoO_4\}^{2-}$ anions are different from each other, as a result of hydrogen bonding interactions between the crystal water molecules and the terminal oxygen atoms of the $\{MoO_4\}^{2-}$ anions in **2**.

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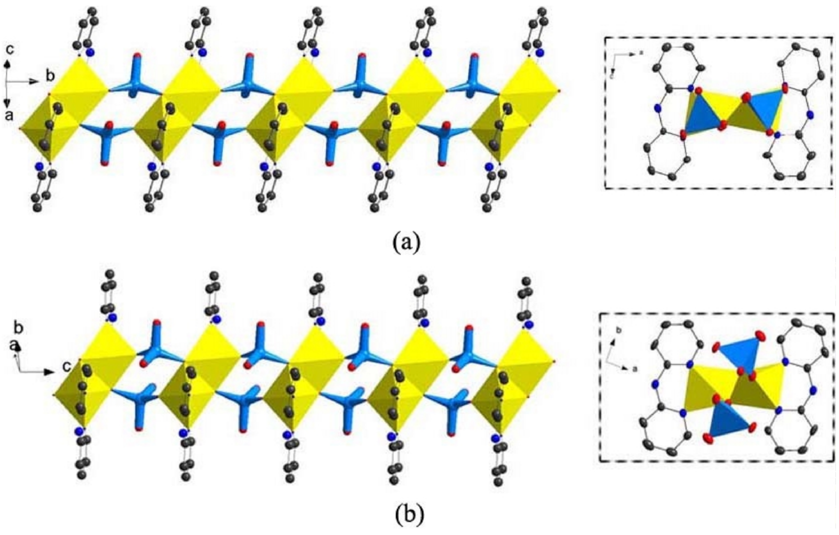

(a)

(b)

Fig. 1. The one-dimensional chain-like structures of **1** (a) and **2** (b) (H atoms omitted). Zinc-centered trigonal bipyramids are shown as yellow polyhedra, while the molybdate anions are shown as blue tetrahedra (color online).

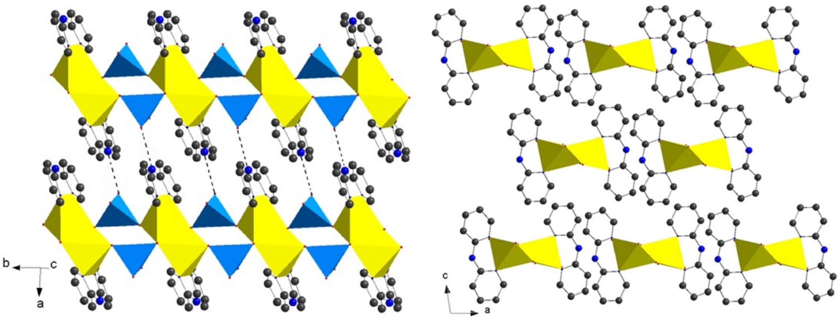

(a) **(b)**

Fig. 2. (a) View of the molecular packing of **1** onto the crystallographic *ab* plane, showing the hydrogen bonding interactions between the central N–H groups of the dpa molecules and the terminal O atoms of $\{MoO_4\}$ tetrahedra. (b) View of the stacking mode of **1** along the *b* axis.

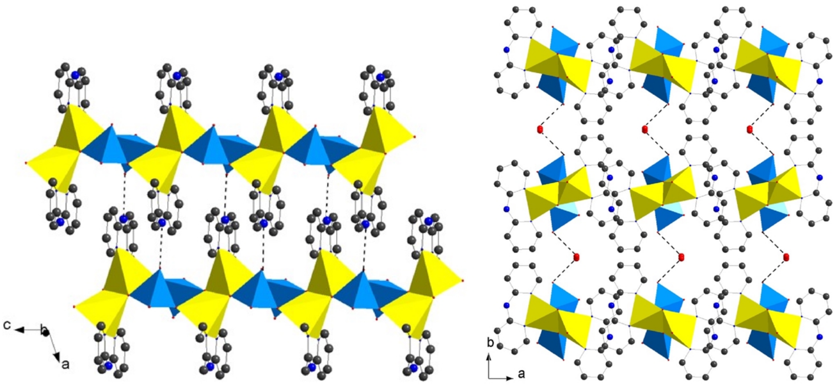
Results and Discussion

Crystal structures

As shown in Fig. 1a, the structure of **1** consists of one-dimensional chains constructed from $\{Zn(dpa)\}^{2+}$ cations bridged by $\{MoO_4\}^{2-}$ anions. Each Zn center exhibits a trigonal bipyramidal coordination environment, which is defined by two nitrogen donor atoms from a dpa ligand and three oxo groups from three $[MoO_4]^{2-}$ anions. Two $\{ZnN_2O_3\}$ trigonal bipyramids are edge-sharing to give a binuclear Zn(II) moiety which produces a $\{Zn_2O_2\}$ parallelogram with Zn–O bond lengths of 2.019(4) and 2.158(5) Å, and O–Zn–O and Zn–O–Zn bond angles of 81.6(2)° and 98.5(2)°, respectively (Fig. 2). Each $\{MoO_4\}^{2-}$ anion is bridging two binuclear Zn cations *via* one μ_3-O and one μ_2-O, leaving two terminal oxo groups. Pairs of $\{MoO_4\}^{2-}$ anions link the binuclear Zn(II) moieties into a one-dimensional ribbon along the *b* axis. The Mo–O bond lengths and O–Mo–O bond angles of each tetrahedral $\{MoO_4\}$ unit are in the range of 1.704(5) – 1.853(4) Å and 104.0(3) – 118.3(2)°, respectively.

According to the packing diagram of **1** in Fig. 2, the ribbons extending along the *b* axis are connected into a 2D network along the *a* axis *via* hydrogen bonding interactions between the central N–H groups of the dpa molecules and the terminal O atoms of $\{MoO_4\}$ tetrahedra with an N···O distance of 2.946(7) Å. The 2D networks are stacked into a 3D architecture *via* supramolecular interactions.

The basic connectivity of **2** is similar to that of **1**, as shown in Fig. 1. On comparison of **1** and **2**, it is found that the orientations of the $\{MoO_4\}$ tetrahedra are different. The uncoordinated O atoms of $\{MoO_4\}$ tetrahedra project into opposite directions within the ribbons for **1**, and up and down for **2**. Therefore the Zn–O–Mo angles are in the



(a) (b)

Fig. 3. (a) View of the molecular packing of **2** onto the *ac* plane, showing the hydrogen bonding interactions between the central N–H groups of the dpa molecules and the terminal O atoms of $\{MoO_4\}$ tetrahedra. (b) View of the stacking mode of **2** along the *c* axis, showing the hydrogen bonding interactions between the crystal water molecules and the terminal O atoms of $\{MoO_4\}$ tetrahedra.

range of 122.6(3) – 127.2(3)° in **1**, and 145.3(2) – 153.7(3)° in **2**. The ribbons of **2** extend along the *c* axis and are connected into a 2D network along the *a* axis *via* hydrogen bonding interactions (N···O, 2.878(8) Å). As shown in Fig. 3, the 2D layers are stacked in good order along the *c* axis *via* supramolecular interactions. Among them, hydrogen bonding interactions involve water molecules between the interlayers and the terminal O atoms of $\{MoO_4\}$ tetrahedra. The O–H···O distance is 2.929(1) Å. These hydrogen bonding interactions cause the above-mentioned differences in the conformations of **2** and **1**.

Thermal analyses

Thermogravimetric analysis of **1** was performed in the 100 – 900 °C temperature range in an air environment. The TG curve indicates that the material is stable up to 250 °C, while ligand loss occurs over a temperature range of 250 – 363 °C (43.9 % weight loss; 43.2 % calculated for loss of ligand). The TG curve of **2** indicates that the weight loss starts at *ca.* 100 °C up to 370 °C with loss of dpa ligands and H_2O molecules (44.5 % weight loss; 44.41 % calculated for loss of ligands and H_2O molecules).

Table 1. Crystal data and structure refinement details for **1** and **2**.

Compound	**1**	**2**
Empirical formula	$[(Zndpa)MoO_4]$	$[(Zndpa)MoO_4]\cdot0.5H_2O$
Formula weight	396.51	134.84
Crystal size, mm^3	$0.3 \times 0.2 \times 0.1$	$0.25 \times 0.18 \times 0.05$
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$
a, Å	10.2482(4)	9.5869(14)
b, Å	6.7907(3)	22.271(3)
c, Å	16.7406(8)	6.4182(9)
β, deg	98.316(2)	108.151(2)
Volume, Å^3	1152.77(9)	1302.2(3)
Z	4	12
Density, mg m^{-3}	2.285	2.063
Absorption coeff., mm^{-1}	3.182	2.822
$F(000)$, e	776	792
2θ range, deg	3.24 – 25.50	1.83 – 28.19
Limiting indices	$-12 \le h \le 12$ $-7 \le k \le 8$ $-13 \le l \le 20$	$-12 \le h \le 11$ $-20 \le k \le 29$ $-8 \le l \le 6$
Reflections collected	3832	8057
Refl. unique / restr.	1979 / 0	3135 / 6
Param. ref.	172	181
Goodness-of-fit on F^2	0.928	1.042
$R1/wR2^a$ $[I \ge 2\sigma(I)]$	0.034/0.109	0.046/0.118
$R1/wR2^a$ (all data)	0.057/0.163	0.078/0.133
Largest diff. peak hole, e Å^{-3}	0.85 −1.22	1.21 −0.63

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_0{}^2)^2]^{1/2}$.

Conclusion

Two new conformational isomers of $[(Zndpa)MoO_4]$ in the anhydrous crystals of **1** and in the hydrate $[(Zndpa)MoO_4] \cdot 0.5H_2O$ (**2**$\cdot0.5H_2O$) consist of binuclear cations of edge-sharing $\{ZnN_2O_3\}$ trigonal bipyramids bridged by pairs of bidentate bridging $\{MoO_4\}^{2-}$ anions into one-dimensional ribbons, but the orientation of the terminal O atoms of the $\{MoO_4\}^{2-}$ anions is different. In **1** and **2**, the crystal structures are dominated by hydrogen bonding interactions between the central N–H groups of the dpa molecules and the terminal O atoms of $\{MoO_4\}$ tetrahedra. For **2**, the hydrogen bonding interactions between the water molecules and the terminal O atoms of the $\{MoO_4\}$ tetrahedra play an important role in constructing the 3D architecture.

Table 2. Selected bond lengths (Å) and bond angles (deg) of **1** and **2**.

1[a]		**2**[a]	
Mo(1)–O(3)	1.704(5)	Mo(1)–O(2)	1.709(5)
Mo(1)–O(2)	1.723(5)	Mo(1)–O(3)	1.719(4)
Mo(1)–O(4)	1.805(5)	Mo(1)–O(4)	1.780(5)
Mo(1)–O(1)	1.853(4)	Mo(1)–O(1)	1.840(4)
Zn(1)–O(1)	2.005(4)	Zn(1)–O(1)$^{\#1}$	1.992(4)
Zn(1)–O(4)	2.019(4)	Zn(1)–O(4)$^{\#2}$	2.013(4)
Zn(1)–N(1)	2.030(6)	Zn(1)–N(3)	2.048(5)
Zn(1)–N(3)	2.084(6)	Zn(1)–N(1)	2.066(5)
Zn(1)–O(1)$^{\#2}$	2.158(5)	Zn(1)–O(1)	2.187(4)
Mo(1)–O(1)–Zn(1)	122.6(3)	Mo(1)–O(1)–Zn(1)$^{\#1}$	145.3(2)
Mo(1)–O(1)–Zn(1)$^{\#2}$	113.4(2)	Mo(1)–O(1)–Zn(1)	112.7(2)
Zn(1)–O(1)–Zn(1)$^{\#2}$	98.5(2)	Zn(1)$^{\#1}$–O(1)–Zn(1)	97.8(2)
Mo(1)–O(4)–Zn(1)$^{\#3}$	127.2(3)	Mo(1)–O(4)–Zn(1)$^{\#2}$	153.6(3)

[a] Symmetry operations for **1**: $^{\#1}$ $x, y-1, z$; $^{\#2}$ $1-x, 2-y, 2-z$; $^{\#3}$ $x, y+1, z$; symmetry operations for **2**: $^{\#1}$ $1-x, 1-y, 2-z$; $^{\#2}$ $1-x, 1-y, 1-z$.

Table 3. Hydrogen bonds for **1** and **2** (Å, deg).

	D–H···A	d(H···A)	∠(DHA)	d(D···A)
1	N(2)–H(2B)···O(2)$^{\#4}$	2.13	159.2	2.946(7)
2	N(2)–H(2B)···O(3)$^{\#3}$	2.01	172.9	2.864(7)

Symm. operations: $^{\#4}$ $-x, 2-y, 2-z$; $^{\#3}$ $-x, 1-y, 1-z$.

Experimental Section

General methods and materials

All chemicals were used as purchased commercially. The hydrothermal reactions were carried out in a 20 mL Teflon-lined stainless steal autoclave under autogenous pressure with a filling capacity of ∼75 %. The reactants were stirred briefly before heating. Elemental analysis (C, H and N) was performed on a Perkin-Elmer 2400 CHN elemental analyzer. The content of metal elements (Mo and Zn) was determined by ICP-AES analysis. Infrared spectra were recorded from KBr pellets on a Bruker AXS Tensor 27 FT-IR spectrometer. TG analyses were carried out with a Pyris Diamond TG/DTA instrument using platinum crucibles under an immobile atmosphere in air with a temperature increasing rate of 10 °C min^{-1}.

Synthesis

*[Zn(dpa)MoO$_4$] (**1**)*

Complex **1** was prepared from a mixture of Zn(NO$_3$) · 6H$_2$O, Na$_2$MoO$_4$ · 2H$_2$O, 2,2′-dipyridylamine, and H$_2$O in the molar ratio 2: 3: 2: 5550. After stirring for 20 min, the mixture was heated in a Teflon-lined stainless steel container at 170 °C for 4 d. After cooling to r. t., it contained block-shaped crystals. Yield: 45 % based on Na$_2$MoO$_4$. – Anal. for $C_{10}H_9N_3O_4ZnMo$: calcd. C 30.28, H 2.27, N 10.60, Zn 16.50, Mo 24.21; found C 30.41, H 2.36, N 10.25, Zn 16.78, Mo 24.01. – IR: ν = 1000 – 1650 [ν(C = C), ν(C = N)], 932 [ν(Mo = O)], 790 – 885 [ν(Zn – O – Mo)] cm^{-1}.

*[Zn(dpa)MoO$_4$]·0.5H$_2$O (**2**·0.5H$_2$O)*

The procedure for complex **2** was similar to that of **1**, except that NaN$_3$ was added. A mixture of Zn(NO$_3$)·6H$_2$O, Na$_2$MoO$_4$ · 2H$_2$O, NaN$_3$, 2,2′-dipyridylamine, and H$_2$O in the molar ratio 2: 3: 5: 2: 5550 was heated in a Teflon-lined stainless steel container at 170 °C for 4 d. After the mixture was cooled to r. t., the plate-like crystals were manually isolated from the mixture in *ca.* 5 % yield based on Na$_2$MoO$_4$. – Anal. for $C_{10}H_{10}N_3O_{4.5}ZnMo$: calcd. C 29.60, H 2.47, N 10.36, Zn 16.13, Mo 23.67; found C 29.46, H 2.63, N 10.09, Zn 16.42, Mo 23.31. – IR: ν = 1000 – 1650, 927, 775 – 880 cm^{-1}.

X-Ray crystallography

A suitable single crystal was selected under a microscope. The diffraction data were collected on a SMART APEX II-CCD single crystal diffractometer at 293 ± 1 K with graphite-monochromated MoK_α radiation (λ = 0.71073 Å) using the ω-2θ scan mode. An empirical absorption correction was applied. The structures were solved by Direct Methods and refined by full-matrix least-squares on F^2 using SHELXL-97 [21]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in calculated positions. Some relevant crystallographic data and structure determination parameters are summarized in Table 1. Selected bond lengths and angles are given in Table 2, and hydrogen bonds are given in Table 3.

CCDC 666398 and 666399 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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