Reversible dehydration process in a novel three-dimensional covalent network based on pyrimidine-4,6-dionato bridging ligand

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Abstract

The novel metal-organic polymer [Zn(µ-pmdt)(H₂O)]ₙ (1) (pmdt = pyrimidine-4,6-dionate) exhibits an extended three-dimensional network with two crystallographically independent pmdt bridging ligands, one zinc(II) atom and a coordinated water molecule. The Zn(II) atoms are located at the centre of a distorted ZnN₂O₂W tetrahedral chromophore. One of the pmdt ligands acts as tetradentate bridge linking four metal centers, while the other pmdt ligand shows a bidentate coordination mode bridging two metal centers. The compound shows a reversible dehydration process, involving a coordinated water molecule, to lead an amorphous anhydrous phase. This transition has been characterized by thermogravimetric and variable-temperature X-ray powder diffraction techniques.

Keywords: Pyrimidine bridge; Three-dimensional complex; Zinc complex; Crystal structure; Reversible dehydration

1. Introduction

The design and construction of high-dimensional coordination frameworks are of great interest because of their potential applications in areas such as molecular inclusion, catalysis, luminescence and magnetism [1]. In order to create such novel materials, a careful choice of the metal ion and the organic ligand is often a key issue. Zn(II) is particularly suited for the construction of coordination polymers [2], since due to the general lability and flexible coordination environment of its complexes, the formation of coordination bonds is reversible which enables metal ions and ligands to rearrange during the process of polymerization to give rise to a great variety of highly ordered network structures. The employment of a rigid multidentate organic ligand capable of bridging two or more metal ions simultaneously contributes to the development of coordination polymers [3]. In this respect, the dianion of 4,6-dihydroxypteridine [4] (dhpm), pyrimidine-4,6-dionate (pmdt), is a good candidate which provides four donor sites. The study of the biochemical properties of dhpm has aroused certain interest due to the similarities it presents with the naturally occurring oxypyrimidines such as uracil, thymine and cytosine [5]. In addition, coordination compounds of first-row transition metals are known to participate in multiple biological processes involving acid–base and redox reactions [6]. Another interesting fact is the study of gas or metal salts sorption in Zeolite analogue metal-organic frameworks based on oxypyrimidine type ligands [7]. Therefore, recently the synthesis and characterization of metal complexes based on oxypyrimidines has evolved rather rapidly [8]. In spite of this, as far as we are aware, no crystal structure of a metal-organic compound containing dhpm has been reported and the examples of structurally characterized complexes based on pmdt dianion are limited to discrete entities in which pmdt ligand bridges two Ti(IV) ions in a bis-chelated
mode [9] or acts as tetrakis-monodentate [10] bridge linking two Mo$_2^{4+}$ units by means of the two endocyclic nitrogens and two exocyclic oxygens.

As a part of our research on the design and construction of high dimensionality metal-organic complexes [11], we report here the crystal structure of a novel three-dimensional complex with formula [Zn(µ-pmdt)(H$_2$O)$_n$] (1). Thermal behaviour of compound 1 is analysed through thermogravimetric and variable-temperature X-ray powder diffraction techniques.

### 2. Experimental

#### 2.1. Synthesis of [Zn(µ-pmdt)(H$_2$O)$_n$] (1)

Colourless single crystals of 1 were prepared by the slow diffusion of an aqueous/methanolic solution of dhpm (0.0336 g, 0.3 mmol) basified with KOH up to pH 10 into an aqueous solution of ZnCl$_2$ (0.0409 g, 0.3 mmol). Crystal growth was observed after a week. Yield of ca. 70% (based on metal). Main IR features of compound 1 (cm$^{-1}$, KBr pellet): 3031(s) [m(O–H)]; 2833(w) [m(C–H)]; 1615(vs), 1490(s), 1461(s), 1417(m) [m$_{as}$(C=N) + m$_{as}$(C=C)]; 1328(w)

#### Table 1

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<thead>
<tr>
<th>Crystal data and structure refinement parameters for 1</th>
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<td>Chemical formula</td>
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<td>T (K)</td>
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<td>R$_1$, wR$_2$ $^a$</td>
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<th>Selected bond lengths (Å) and angles (°) for 1</th>
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<td>Zn–N$_{12}$</td>
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<td>N$<em>{22}$–Zn–O$</em>{1w}$</td>
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<td>O$<em>{15}$–Zn–O$</em>{1w}$</td>
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$^a$ R$_1$ = $\sum_i \left| F_i \right| - \left| \sum_i F_i \right| / \sum_i \left| F_i \right|$, wR$_2$ = $\left( \sum_i w_i \left| F_i \right| - \left| \sum_i w_i F_i \right| \right)^2 / \sum_i w_i \left| F_i \right|^2$.

Symmetry codes: (a) $-x + 3/2, y + 1/2, z$.

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Fig. 1. Zn(II) coordination environment (ellipsoids at 50% probability level).
[\delta(O-H)]; 1270(s), 1218(w) [\nu(C-O)]; 1183(w) [\delta(C-H)]; 1057(m), 998(w) [\nu_d(C==N) + \nu_s(C==C)]; 822(m) [\delta_{op}(ring)]; 705(w), 638(w) [\delta(C-H)]. Anal. Calc. for C$_4$H$_4$ZnN$_2$O$_3$: C, 25.01; H, 2.10; Zn, 33.30; N, 14.59. Found: C, 25.15; H, 2.00; Zn, 33.19; N, 14.75%.

2.2. Physical measurements

Elemental analyses (C, H, N) were performed on a LECO CHNS–932 microanalytical analyzer. Metal content was determined by absorption spectrometry. Infrared spectra were recorded on a Nicolet 740 FT-IR as KBr disks. Thermal analyses (TG/DTG/DTA) were performed on a TA Instruments SDT 2960 thermal analyzer in a synthetic air atmosphere (79%N$_2$/21%O$_2$) with heating rate of 5° min$^{-1}$. The X-ray powder diffraction patterns (XRPD) were collected on a Phillips X’PERT powder diffractometer with Cu K$\alpha$ radiation.

2.3. X-ray structure determination

A block-like crystal (0.35 × 0.10 × 0.10 mm) was mounted on a Xcalibur diffractometer equipped with graphite-monochromated Mo K$\alpha$ radiation ($\lambda = 0.71073$ Å) at 293(2) K. Data were processed and corrected for Lorentz and polarization effects. Crystallographic details for structure 1 are summarized in Table 1.

The structure was solved by direct methods using the SIR97 program [12]. Full matrix least-squares refinements were performed on $F^2$ using SHELXL97 [13]. All non-hydro-
gen atoms were refined anisotropically. All calculations were performed using the WINGX crystallographic software package [14]. Selected bond lengths and angles are listed in Table 2.

3. Results and discussion

Single-crystal X-ray diffraction analysis shows that the title compound presents an extended 3D architecture formed by Zn(II) atoms, pmdt bridging ligands (pmdt-1 and pmdt-2) and coordinated water molecules (Fig. 1). The Zn(II) atoms are located at the centre of a distorted tetrahedron formed by two pyrimidine N atoms (Zn–N12 1.986(4) Å, Zn–N22 2.004(3) Å) from crystallographically different pmdt ligands, pmdt-1 and pmdt-2, and two O atoms belonging to another crystallographically related pmdt-1 and a water molecule (Zn–O15a 1.975(4) Å, Zn–O1w 2.001(4) Å). A quantitative description of the distortion from the tetrahedral geometry has been evaluated by the Muetterties and Guggenberger method (\(\Delta D = 0\) for a regular tetrahedron and \(\Delta D = 100\) for a \(D_{4h}\) geometry) [15], obtaining a value of 13%. These two pmdt ligands show a different coordination mode. The pmdt-1 ligand is coordinated in a tetradentate fashion to four metal centres by means of two pyrimidine N atoms and two exocyclic O atoms. This coordination mode is similar to that for the previously mentioned molybdenum compound with the pmdt ligand [10]. On the other hand, pmdt-2 acts as a biden-
tate ligand linking two Zn atoms through the pyrimidine N atoms. The M···M distances through pyrimidine nitrogen atoms are 6.051 and 6.096 Å for pmddt-1 and pmddt-2, respectively. The distance between the metal centres bridged through the pyrimidine nitrogen atom and the ortho exocyclic oxygen atom of pmddt-1 is 4.433 Å, whereas for the para oxygen atom it is 7.480 Å. Finally, the distance between the two metal atoms bonded to the exocyclic oxygen atoms of the pmddt-1 ligand is 6.000 Å. Both pmddt ligands are essentially planar and the deviations from the pyrimidine ring of the Zn(II) atom are 0.134(1) and 0.196(1) Å, respectively, for pmddt-1 and pmddt-2. The dihedral angle between the two crystallographically independent pmddt ligands is 63.7(2)°.

The compound shows a relatively complex overall crystal structure, so in order to provide an affordable look insight into the structure we have chosen a somewhat arbitrary description. Zn(II) centres and pmddt-1 bridging ligands form puckered sheets parallel to the crystallographic ab-plane (Fig. 2a). These sheets are cross-linked by the pmddt-2 ligands to build up a pillared-layer covalent three-dimensional network (Fig. 2b). The coordinated water molecule establishes two hydrogen bonds with the non-coordinated oxygen atoms of two pmddt-2 ligands (O1w··O25b 2.695(5) Å, O1w··H1··O25b 165°; O1w··O25c 2.732(6) Å, O1w··H2··O25c 169°). These molecules are placed in channels running along the c axis and the distance between the adjacent water molecules within the channels is ca. 5.19 Å.

The thermal degradation under synthetic air atmosphere shows (Fig. 3) that the compound is stable up to 300 °C, after which it undergoes an endothermic process due to the loss of coordinated water molecules (exp. 9.2%, calc. 9.3%). Then, it remains stable up to 490 °C where a last exothermic process occurs leading to ZnO as the final product. In order to obtain a deeper insight of the anhydrous intermediate, thermodiffractometry measurements were run under ambient atmosphere in the range 5° < 2θ < 38° with a step size of 0.03° and an acquisition time of 2 s per step (Fig. 4). The compound was heated to 80 °C with a heating rate of 10 °C min⁻¹ and after that diagrams were collected every 12 °C with a heating rate of 1 °C min⁻¹ up to 500 °C. The XRPD profile at 80 °C matches the simulated pattern generated from the crystal structure of 1 and remains crystalline up to 250 °C, after which a decrease in crystallinity was observed. The dehydration process leads to an amorphous phase above 300 °C. It seems that the release of the water molecule from the tetrahedral coordination environment of the Zn(II) ion implies a structural rearrangement, which does not allow a long range order. Taking into account the crystal structure, the vacant coordination site might be occupied by a free oxygen atom of the pmddt-2 ligand; a plausible dehydration mechanism is proposed in Scheme 1. The IR spectrum of the anhydrous phase shows the absence of the ν(O–H) peak and that the characteristic bands of the pmddt ligand are slightly displaced. This may be indicative of a change in the coordination modes of the pmddt ligands (see Supplementary Material). Finally, when a temperature of 450 °C is reached peaks corresponding to ZnO began to appear.

In order to analyse a possible reversibility of the dehydration process, the anhydrous and insoluble residue was left suspended in a water solution for 6 days. The resulting compound was filtered out and analysed by X-ray powder diffractometry, thermoanalytical gravimetry and IR spectrometry; all techniques confirm the rehydration process from the amorphous anhydrous phase to the initial crystalline compound 1. Most of the reported reversible dehydration processes are related to the loss of crystallization water molecules with accessible channels in open framework compounds [16]. However, the reversible release of coordinated water molecules is more unusual [17]. In addition, reported examples of crystalline to amorphous reversible dehydration of coordinated water molecules are scarce [18] and, as far as we know, the title compound represents the first example implying a 3D covalent network.

4. Conclusions

In conclusion, we have synthesized and characterized a novel three-dimensional covalent structure based on pmddt ligand and Zn(II) ion, which shows an interesting reversible dehydration process to an amorphous anhydrous phase. In addition, this work proves that the pmddt dianion is a well
suited bridging ligand for the construction of high dimensionality covalent networks.

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Appendix A. Supplementary material

IR spectrometry plots of compound 1 and of its dehydrated phase. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 279029. Copies of this information can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK, fax: +44 1223 366 033, e-mail: deposit@ccdc.ac.uk or on the web www: http://www.ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2006.02.004.

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