



Metal–organic framework (MOF) of [Co(II)(1,4-benzenedicarboxylate)₂(pyridine)₂(water)₂]: Coexistence of water cyclic hexamers through carboxylate oxygens

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ARTICLE INFO

Article history:

Received 9 July 2011

Accepted 26 September 2011

Available online 1 October 2011

Keywords:

Co(II) complex

3D supramolecular structure

Water cluster

TGA

ABSTRACT

A metal–organic framework of [Co(II)(1,4-benzenedicarboxylate)₂(pyridine)₂(water)₂] has been synthesized and characterized by IR spectra, TGA and single crystal X-ray diffraction analysis. Discrete cyclic hexameric water clusters through carboxylate oxygens and pyridine molecules are trapped inside a two-dimensional coordination channel.

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In the past several decades, considerable attention has been focused on theoretical [1] and experimental [2] studies of small water clusters to understand the structures and characteristics of liquid water and ice. A variety of water clusters including tetramer, hexamer, octamer and decamer have been structurally [3–6] characterized in crystalline hosts in one-dimensional [7] and two-dimensional [8] water morphologies. Their structural information holds considerable promise for achieving a more accurate description of the properties of bulk water at the molecular level. The cluster of ten water molecules is of particular interest because this is the smallest unit of naturally occurring cubic ice and so called molecular ice [6]. It is quite interesting to note that clusters with even numbers of water molecules appear more frequently than the odd-numbered ones. Only trimers and pentamers are common in crystal hydrates and higher nuclearity, while other odd-numbered clusters are much less known. Furthermore, it is well-known that self-assembly processes are highly affected by several factors such as the ligand's nature, medium, template, metal ligand ratio, pH value, and counter ion. The water clusters can play an important role in the stabilization of supramolecular systems both in solution and in the solid state, and there is clearly a need for a better understanding of how much water aggregations are influenced by the overall structure of their surroundings [9].

Metal–organic framework (MOF) structures with suitable organic ligands can provide void spaces where discrete water clusters can exist. Metal ions in such structures can also act as glues in holding the water clusters, interactions between the water aggregates and the surrounding often play a key role in stabilizing the unusual

water clusters in the crystal lattice. To date, chair [10] and boat [11] cyclic hexamers included in host lattices have been characterized by X-ray crystallographic analysis. While Saykally and co-workers characterized the cage form of the hexamer [12], Nauta and Miller reported [13] the detection of a quasiplanar hexamer in a helium droplet. We report here on the preparation, crystal structure of octahedral polymeric [Co(1,4-benzenedicarboxylate)₂(pyridine)₂(water)₂] and the structure of a cyclic hexamer water cluster.

The hydrothermal reaction [14] of Co(NO₃)₂·6H₂O with pyridine and 1,4-benzenedicarboxylic acid in mole ratio 1:4:2 at 180 °C leads to the formation of colored crystals. Elemental analysis confirmed the formula of polymeric complex (**1**). X-ray single crystal analysis reveals [15] that **1** contains a 1D polymeric chain through coordination of 1,4-benzenedicarboxylate ligand. Co(II) metal ion has perfect octahedral geometry. The bond distances of Co–N and Co–O (coordinated carboxylate oxygen) and Co–O (coordinated water molecule) are 2.088(6), 2.057(3) and 2.028(4), respectively. The bond angles of N–Co–N and O–Co–O are equal to perfect 180°. The crystal data together with bond lengths and angles are shown in Tables 1S and 2S. Coordinated water molecules and 1,4-benzenedicarboxylates, and pyridines are located in trans position. Each Co(II) is coordinated to two 1,4-benzenedicarboxylate, two pyridine and two water molecules. The 1,4-benzenedicarboxylate ligand helps to form a 1D polymeric chain through polycatenation.

A view of **1** and the atoms labeling scheme used are shown in Fig. 1. The structure of **1** was found as a discrete water cluster and uncoordinated pyridine, are trapped in voids (Fig. 2A). In the water cluster, the free oxygen of carboxylate are bound to water molecules by hydrogen bonding. The oxygen atoms are opposite to the cyclic hexamer (Fig. 2B). The striking feature of this cluster is that each and every oxygen atom is connected to two water molecules and every water molecule is linked by one oxygen atom and one water

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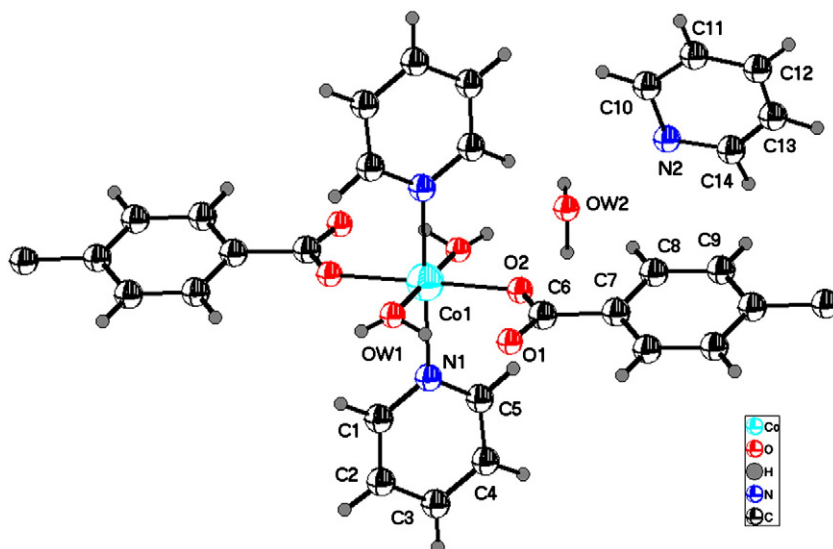


Fig. 1. ORTEP diagram of compound **1** with partial atom labeling and 40% thermal ellipsoids. Selected bond lengths (Å) and bond angles (deg): Co1–O2 = 2.058(3), Co1–N1 = 2.089(6), Co1–OW1 = 2.028(4), N1–Co1–N1 = 180.0, OW1–Co1–OW1 = 180.0, OW1–Co1–O2 = 91.69(15), O2–Co1–O2 = 180.0.

molecule via hydrogen bonds. One hydrogen atom is along each edge of the hexamer, so each oxygen is bound to two hydrogen atoms of two water molecules. Each oxygen atom has two hydrogen bonds to an oxygen atom of water and an oxygen atom of carboxylate and one hydrogen bond from an adjacent oxygen atom on the same site. There are two kinds of O–H–O hydrogen bonds in this water cluster. This hydrogen bond O–O separations are in the range of 2.599–2.759 Å, which is shorter than the reported [16], 2.85 Å for liquid water. Bond lengths and bond angles of hydrogen bonds are given in Table 1. The strengths of hydrogen bonding are confirmed by thermal analysis. The angles of O2W–O1W–O1, O1W–O1–O2W and O1–O2W–O1W are 128.7(2), 112.8(1) and 108.7(2), respectively. The cyclic hexamer bound through carboxylate oxygen atoms to water molecules is like a cyclohexane molecule. The packing diagram of compound **1** is shown in Fig. 3. The two 1D chains are connected by π – π interactions with a distance of 4.364 Å in *c*-direction to form a regular 3D channel. Water clusters and pyridine molecules are well trapped in isolated cavities surrounded by liner polymeric chains of the Co(II) complex (Fig. 1S). The uncoordinated pyridine hangs in the voids of the polymeric channels by C–H– π interaction between the

Table 1

Hydrogen bonds for (1) [Å and °].

D–H...A	d(D–H)	d(H...A)	d(D...A)	<(DHA)
OW1–H(04)...O(1)	0.83(8)	1.82(8)	2.597(6)	154(7)
OW1–H(07)...OW2	0.77(10)	1.82(11)	2.590(7)	170(11)
OW2–H(06)...O(1) ^{#1}	0.89(11)	2.02(11)	2.760(7)	139(10)

Symmetry transformations used to generate equivalent atoms: ^{#1} –*x*, –*y*, –*z* – 1.

C–H of uncoordinated pyridine and the π system of 1,4-benzenedicarboxylate with a distance of 2.7495(8) Å.

The IR spectrum of **1** shows disappearance of the broad band at 1710 cm^{-1} and the appearance of a band at 1589 cm^{-1} (antisymmetric COO^- stretch) and 1416 cm^{-1} (symmetric COO^- stretch) corresponding to a coordinated carboxylate group. A sharper band at 1545 cm^{-1} is due to the aromatic ring stretch. Other prominent bands are at 766, 715 and 684 cm^{-1} . The compound shows O–H stretching vibrations at 3440 and 3260 cm^{-1} and these are more analogous to those of liquid water than those of ice [16,17].

The thermal stability of the oxygen–water cluster in [Co(II) (1,4-benzenedicarboxylate)₂(pyridine)₂(water)₂] (**1**) was studied

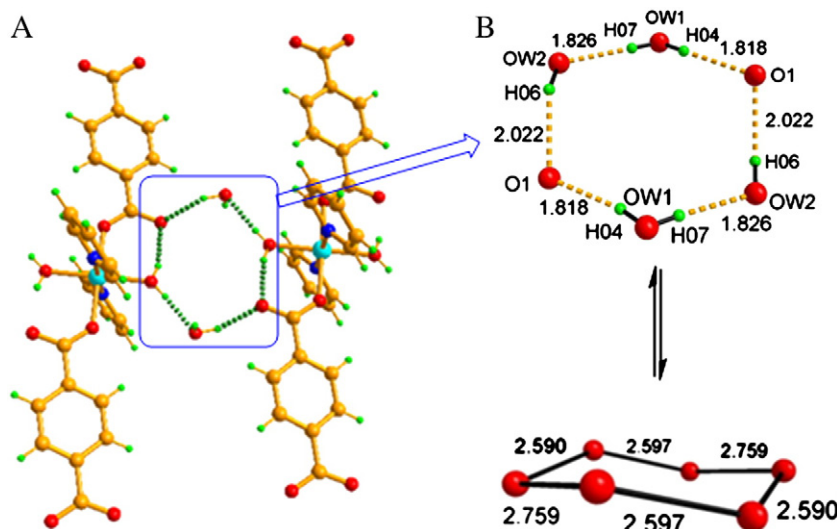


Fig. 2. (A). Two chains are connected by a cyclic hexamer. (B). Six oxygen atoms are bound through hydrogen bonding with the range of bond distances 1.826–2.022 Å and through bound oxygen (four of these oxygens are part of a water molecule and two of them pertain to carboxylate moieties).

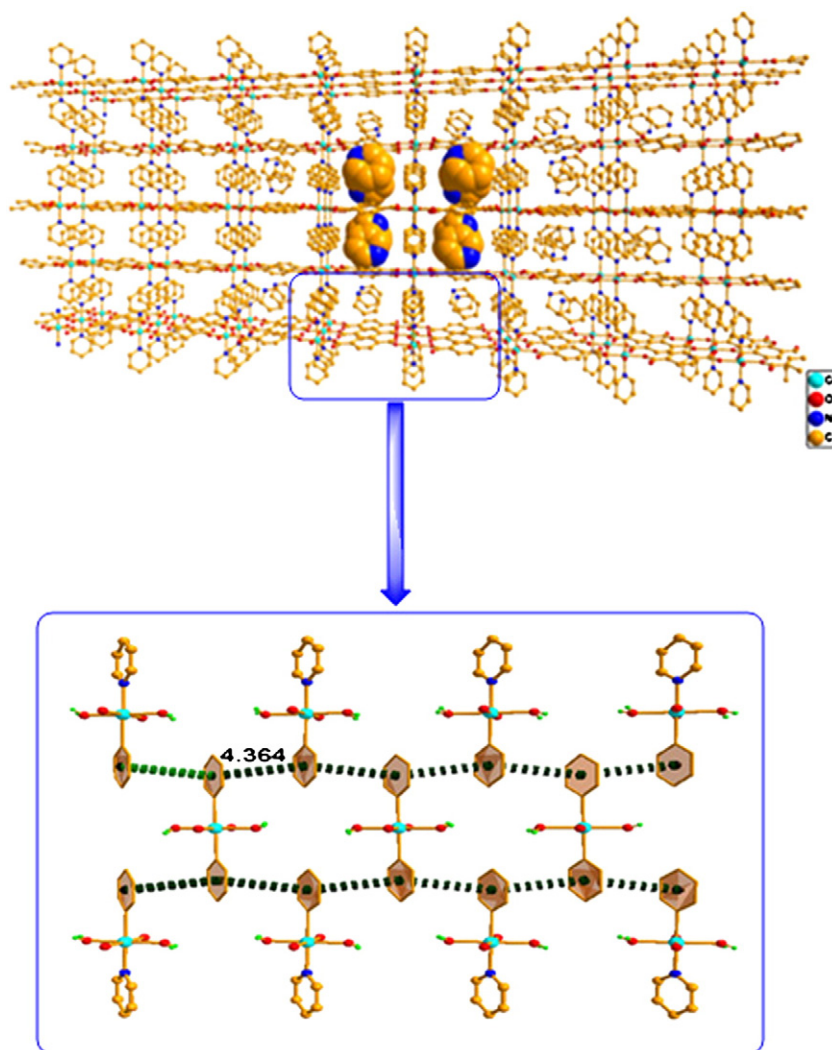


Fig. 3. 3D building block of the chains of compound **1**, connected to each other by hydrogen bonding and π - π interactions at a distance of 4.364 Å (in *c*-direction is shown). Uncoordinated pyridine molecules (spacefill style) are trapped between the two layers.

by thermogravimetric analysis (TGA). The TGA curve shows that the compound exhibits a first weight loss of 5.80% in the temperature range 215–308 °C corresponding to the loss of water molecules in the cluster (calculated weight loss 5.88%) (Fig. 4). This analysis confirms that there are two water molecules per formula unit, as expected from X-ray diffraction and elemental analysis data. The temperature required for water molecule removal is

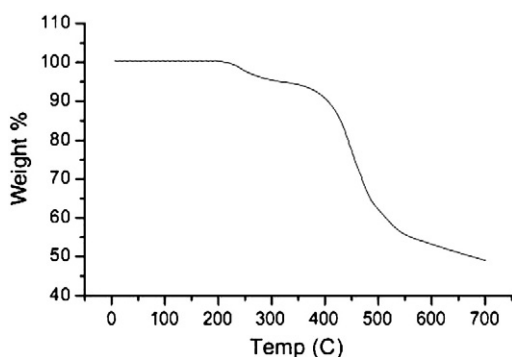


Fig. 4. TGA spectrum of compound **1**.

well above 100 °C (more than 215 °C), suggesting that the hydrogen bonding that builds the oxygen–water cluster must be of significant strength and that water molecules are strongly incorporated as a part of this cluster. Such observation of retaining very volatile liquids in the crystal packing has been reported [18] previously.

In conclusion, a discrete dioxygen-tetrahydrate water cluster has been trapped in the solid state structure. This water cluster has a chair like structure in which the oxygen atoms occupy opposite corners. From thermal analysis, the temperature required for water molecule removal is more than 215 °C, which shows that the hydrogen bonding that builds the oxygen atom of water cluster is strongly incorporated as a part of this cluster.

Acknowledgment

SK is thankful to TWAS and CONICET for Postdoc fellowship.

Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.inoche.2011.09.032.

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- [14] A mixture of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.1 mmol), pyridine (0.4 mmol), 1,4-benzenedicarboxylic acid (0.2 mmol) and NaOH (0.2 mmol) was stirred for 20 min in air (the pH value of the mixture was 7.2), then sealed in a 25 mL Teflon lined stainless steel container, which was heated to 180 °C for 24 h. After the sample was cooled to room temperature at a rate of 5 °C per h, colored crystals were obtained in ca. 52% yield. Elemental analysis, observed (calculated), %: C, 54.92 (54.99); H, 5.31 (5.27); N, 9.18 (9.16). IR (KBr pellet)/ cm^{-1} : 3440 (m), 3260(m), 1618 (w), 1602 (w), 1555 (s), 1445 (m), 1201 (m), 780(m), 446 (w).
- [15] Crystal data for compound **1**: $\text{C}_{28}\text{H}_{32}\text{CoN}_4\text{O}_8$, monoclinic, space group, $P2(1)/c$, $a = 11.392$ (5), $b = 15.232$ (5), $c = 8.634$ (5) Å, $\beta = 104.852$ (5)°, volume = 1448.1 (12) Å³, $Z = 2$, $D_c = 1.402$ Mg m⁻³, $F(000) = 638$, Mo–K α radiation ($\lambda = 0.71069$ Å), $T = 100$ (2) K, 9556 reflections collected, 3580 unique ($R_{int} = 0.0512$), $R1 = 0.0968$, $wR2 = 0.2110$ [$I > 2\sigma(I)$], $GOF = 1.079$. Single-crystal X-ray data were collected using graphite-monochromated Mo–K α radiation ($\lambda = 0.71073$ Å) on “Bruker SMART APEX CCD” diffractometer at 100 K. The linear absorption coefficients, scattering factors for the atoms and the anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography. The data integration and reduction were processed with SAINT software. An empirical absorption correction was applied to the collected reflections with SADABS using XPREP. All the structures were solved by the direct method using SIR-97 and were refined on F^2 by the full-matrix least-squares technique using the SHELXL-97 program package. All non-hydrogen atoms were refined anisotropically in the structure.
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