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A NOVEL 3D ENERGETIC COORDINATION POLYMER CONTAINING Co(II) ATOMS IN A PENTANUCLEAR CLUSTER

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A novel coordination polymer $[Co_5(OH)_2(dnbpdc)_4(H_2O)_6]\cdot 16H_2O$ (**1**) (dnbpdc = 6,6′-dinitro-4,4′-biphenyl-dicarboxylic acid) is obtained from a hydrothermal reaction. The structure of complex **1** is characterized by elemental analysis, IR spectroscopy, and single crystal X-ray diffraction analysis. The title compound ($C_{56}H_{70}Co_5N_8O_{56}$, $M_r = 2045.85$) crystallizes in the triclinic space group P-1 with $a = 11.9349(2)$ Å, $b = 12.1895(2)$ Å, $c = 15.420(2)$ Å, $\alpha = 109.390(7)°$, $\beta = 94.786(1)°$, $\gamma = 108.027(9)°$, $V = 1968.4(4)$ Å^3, $Z = 1$, $D_c = 1.726$ g/cm^3, $F(000) = 1045$, $\mu(MoK_\alpha) = 1.154$ mm^{-1}, $T = 133(2)$ K, the final $R = 0.0316$ and $wR = 0.0692$ for 7032 observed reflections with $I > 2\sigma(I)$. The coordination polymer is built of a pentanuclear Co(II) cluster, four dnbpdc ligands, two hydroxyl groups, six coordination water and sixteen crystal water molecules. Ligand oxygen atoms exhibit three types of coordination modes (monodentate, *syn-syn* bridging bidentate and bridging tridentate). Moreover, the infinite three-dimensional supra-molecular network is generated by coordination and hydrogen bonds. The thermal stability of complex **1** is evaluated by differential scanning calorimetry and thermogravimetric analysis.

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Keywords: coordination polymer, pentanuclear clusters, energetic materials.

INTRODUCTION

The interest in the rational design and synthesis of metal-organic coordination polymers (MOCPs) has been rapidly increasing in recent years due to multiform frameworks as well as potential applications of these compounds in functional materials [1—11]. Particularly, MOCPs involving carboxylic acid compounds as ligands, such as various aliphatic, aromatic, and heterocyclic acids, exhibit diverse network topologies and remarkable applicable prospect. Therefore, the construction and analysis of novel MOCPs consisting of carboxylate compounds is a hotspot in this field [12—15].

Aromatic carboxylic acids bearing coordination diversity and moderate stability, such as biphenyl acids, are a good choice in the designed synthesis of MOCPs [16—18]. In addition, the prospect of introducing the second function group into aryl rings provides further impetus. For instance, we have synthesized a series of novel MOCPs as heat-resistant energetic materials based on the bpdc ligand [19—23].

In this paper, we used dnbpdc as a ligand due to the following consideration: (*a*) the carboxylate oxygen atom of dnbpdc can adopt several coordination modes (bridging, monodentate, and chelating) which allow the construction of multidimensional systems; (*b*) in deprotonated dnbpdc, two phenyl rings are not coplanar with each other owing to the steric hindrance of nitro groups; a distortion of the

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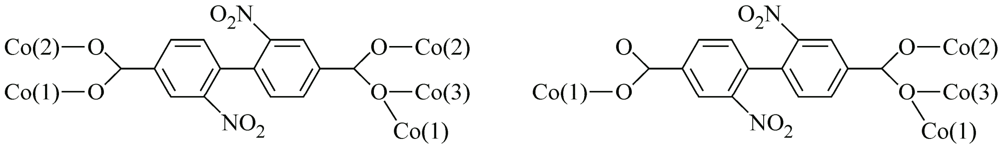
diphenyl spacer about the central bond allows dnbpdc to link metal ions or metal clusters into macrocycles or one dimensional chains; (*c*) the novel MOCP containing nitro groups can have potential applications as a heat-resistant energetic material. Herein, we report the synthesis and crystal structure of a novel energetic coordination polymer $[Co_5(OH)_2(dnbpdc)_4(H_2O)_6]\cdot 16H_2O$.

EXPERIMENTAL

Material and measurements. All analytical grade chemicals and solvents were purchased commercially and used without further purification. The dnbpdc ligand was synthesized by our research group [21]. Elemental analyses were carried out on a Carlo Erba 1106 full-automatic trace organic elemental analyzer. FT-IR spectra were recorded on a Bruker Equinox 55 FT-IR spectrometer in a dry KBr pellet in the range of 400—4000 cm^{-1}. A Perkin-Elmer Pyris-1 differential scanning calorimeter (DSC) was used for DSC measurements (sample mass: about 6.0 mg, atmosphere: flowing nitrogen gas, reference sample: α-Al_2O_3, heating rate: 10°C·min^{-1}). A Perkin-Elmer Pyris-1 thermogravimeter (TG) analyzer was used for the thermogravimetric analysis (sample mass: about 6.0 mg, atmosphere: flowing dry oxygen-free nitrogen, heating rate: 10°C·min^{-1}).



a) μ_2-η^1:η^1/μ_3-η^2:η^1 *b*) μ_1-η^1:η^0/μ_3-η^2:η^1

Scheme 1. Versatile coordination modes of dnbpdc in complex **1**

Synthesis of complex **1.** A mixture of $Co(NO_3)_2\cdot 6H_2O$ (0.291 g, 1 mmol), dnbpdc (0.242 g, 1 mmol), LiOH (0.08 g, 2 mmol), and deionized H_2O (18 ml) were sealed in a 25-ml stainless-steel reactor with a Teflon liner and heated at 150 °C for 72 h. After the mixture was cooled to room temperature, pink prismatic crystals were obtained and several times washed with alcohol (yield: 42 % with respect to dnbpdc). Anal. Calcd. (%) for **1**: C 33.88, H 3.45, N 5.48. Found (%): C 33.84, H 3.47, N 5.38. IR data (KBr pellet, cm^{-1}) for **1**: 3320(br), 1610(s), 1524(s), 1396(ms), 1345(ms), 1244(w), 715(m), 550(w).

X-ray single crystal structure analysis. A pink prismatic single crystal with dimensions of 0.30×0.18×0.15 mm was selected for the diffraction analysis. The data collection was performed on a Rigaku AFC-10/Saturn 724+CCD diffractometer at 50 kV and 20 mA using MoK_α radiation ($\lambda =$ $= 0.71073$ Å) at 133(2) K by φ and ω scanning techniques. A total of 18690 reflections (8850 unique, $R_{int} = 0.0270$) were measured in the range of $3.06° < \theta < 27.48°$, out of which 7032 were observed with $I > 2\sigma(I)$. The scaled maximum and minimum transmission factors are 0.841 and 0.779, respectively. A semi-empirical absorption correction (SADABS) was applied to the raw intensities. The structure was solved by direct methods and refined by full matrix least squares techniques based on F^2 using SHELXS and SHELXTL program packages [24, 25]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were generated geometrically and treated by a mixed refinement. A full matrix least squares refinement gave final $R = 0.0306$ and $wR = 0.0692$ ($w = 1 / [\sigma^2(F_0^2) + (0.0398P)^2 + 0.0000P]$, where $P = (F_0^2 + 2F_c^2)/3$).The goodness-of-fit indicator is 0.992. The maximum peak in the final difference Fourier map is 0.444 e/Å^3 and the minimum one is –0.283 e/Å^3. In the final circle of the refinement the largest parameter shift $(\Delta/\sigma)_{max}$ is 0.002.

RESULTS AND DISCUSSION

IR spectra. The characteristic vibrational frequencies have been identified by comparing the spectra of complex **1** with their free ligands. The IR spectra of the ligand show a strong band at 1714 cm^{-1} assignable to the carbonyl group (—COOH) [20]. This band is shifted to the 1610 cm^{-1}

region in the complexes indicating the deprotonation and coordination of carboxylic acid through the carboxyl oxygen atom. The absorption of the carboxylate complex occurs at a lower wavenumber than the carbonyl absorption of free carboxyl because of the resonance of the negative charge between the two oxygen atoms. This is further supported by the appearance of a new weak bond around 550 cm^{-1} attributed to the Co—O bond. The strong absorption in 1500—1550 cm^{-1} and 1330—1350 cm^{-1} ranges was assigned to the symmetric and asymmetric stretching of two nitrogen groups. The broad absorption in the 3000—3750 cm^{-1} region is due to ν(—OH) vibrations of coordinated water molecules.

Description of the crystal structure. The X-ray diffraction analysis reveals that complex **1** is a three-dimensional coordination polymer composed of $[Co_5(OH)_2]^{8+}$ clusters, four dnbpdc ligands, and six water molecules. In each unit, the carboxylate groups of four dnbpdc ligands [O(7), O(8), O(15), O(16), and O(7)#1, O(8)#1, O(15)#3, O(16)#2] adopt μ_2-η^1:η^1/μ_3-η^2:η^1 and μ_1-η^1:η^0/μ_3-η^2:η^1 coordination mode linking five Co(II) centers [Co(3), Co(2), Co(1)#1, Co(2)#1, Co(1)] (Scheme 1). Two symmetrical μ_3-hydroxyl groups [O(18), O(18)#1] act as a bridge, linking three atoms [Co(1), Co(2), Co(3); Co(1)#1, Co(2)#1, Co(3)] by a tri (monodentate) bridging mode, respectively. Moreover, oxygen atoms of six coordination water molecules link Co(1) and Co(2) in a μ_1-bridging coordination mode, in which O(17) links Co(1) and O(19) and O(20) links Co(2) (Fig. 1).

All of Co(II) ions are located in a slightly distorted octahedral coordination environment. The Co(1) ion is coordinated by four oxygen atoms of carboxyl groups from four different dnbpdc ligands and two oxygen atoms from water molecules and a hydroxyl group. The adjacent Co(2) ion is coordinated by six oxygen atoms from three different dnbpdc ligands and two water molecules and a hydroxyl group. The Co(3) ion is centrosymmetric in the metal cluster bridged by six oxygen atoms from four dnbpdc ligands and two hydroxyl groups. The Co—O bond lengths range from 2.0225(1) Å to 2.2132(1) Å (Table 1).

Similar to dnbpdc [19], two aryl rings of biphenyl are not coplanar with the C(4)—C(5)—C(10)—C(11) torsion angle of 109.65° and C(18)—C(19)—C(24)—C(25) of –77.98° because of the steric hindrance effect. However, the defect of complex **1** is more severe than that of dnbpdc because

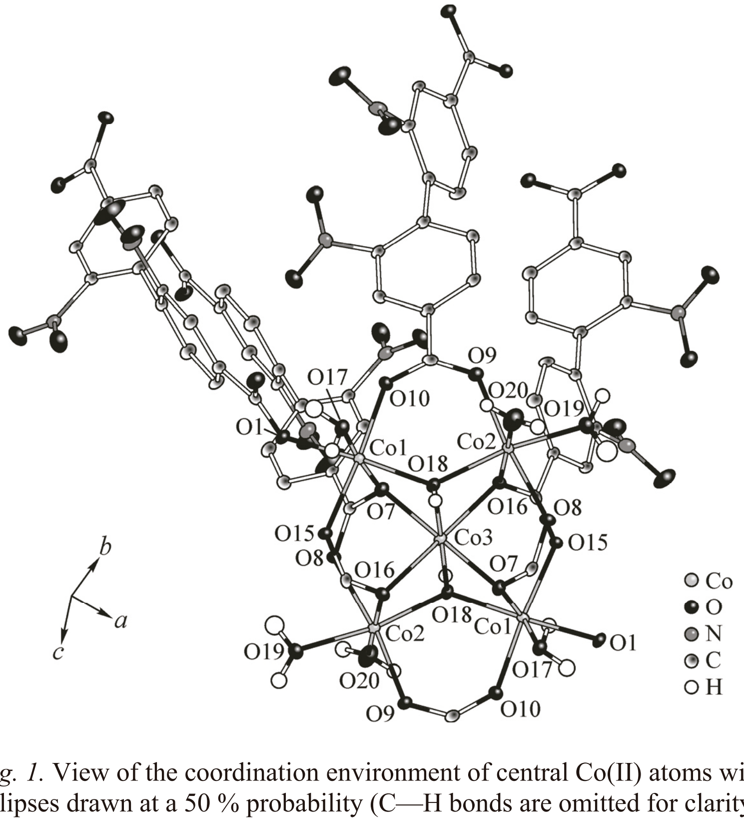


Fig. 1. View of the coordination environment of central Co(II) atoms with ellipses drawn at a 50 % probability (C—H bonds are omitted for clarity)

Table 1

Selected Bond Lengths (Å) *and Angles* (deg.)

Co(1)—O(18)	2.0225(1)	O(18)#1—Co(3)—O(18)	179.999(2)	O(18)—Co(2)—O(16)#2	81.63(5)
Co(1)—O(10)	2.0390(1)	O(18)#1—Co(3)—O(16)#2	95.44(5)	O(19)—Co(2)—O(9)	92.64(6)
Co(1)—O(1)	2.0598(1)	O(18)#1—Co(3)—O(16)#3	84.56(5)	O(19)—Co(2)—O(8)#1	81.93(6)
Co(1)—O(15)#3	2.1155(1)	O(18)#1—Co(3)—O(7)	94.65(5)	O(19)—Co(2)—O(16)#2	88.57(6)
Co(1)—O(17)	2.1452(1)	O(18)#1—Co(3)—O(7)#1	85.35(5)	O(9)—Co(2)—O(8)#1	173.82(6)
Co(1)—O(7)	2.2132(1)	O(18)—Co(3)—O(16)#2	84.55(5)	O(9)—Co(2)—O(16)#2	92.08(56)
Co(2)—O(9)	2.0741(1)	O(18)—Co(3)—O(16)#3	95.44(5)	O(8)#1—Co(2)—O(16)#2	89.84(5)
Co(2)—O(8)#1	2.1147(1)	O(18)—Co(3)—O(7)	85.35(5)	O(18)—Co(1)—O(10)	93.69(5)
Co(2)—O(16)#2	2.2082(1)	O(16)#3—Co(3)—O(16)#2	180.00(4)	O(18)—Co(1)—O(1)	173.69(5)
Co(2)—O(20)	2.0267(2)	O(16)#1—Co(3)—O(7)#1	85.35(5)	O(18)—Co(1)—O(15)#3	89.35(5)
Co(2)—O(18)	2.0411(1)	O(16)#2—Co(3)—O(7)	86.22(5)	O(18)—Co(1)—O(17)	93.14(5)
Co(2)—O(19)	2.0607(2)	O(16)#3—Co(3)—O(7)	93.78(5)	O(18)—Co(1)—O(7)	82.71(5)
Co(3)—O(18)	2.0248(1)	O(16)#3—Co(3)—O(7)#1	86.22(5)	O(10)—Co(1)—O(1)	88.25(5)
Co(3)—O(18)#1	2.0247(1)	O(7)—Co(3)—O(7)#1	180.00(6)	O(10)Co(1)—O(15)#3	176.66(5)
Co(3)—O(16)#2	2.1070(1)	O(20)—Co(2)—O(18)	95.50(6)	O(10)—Co(1)—O(17)	92.83(5)
Co(3)—O(16)#3	2.1070(1)	O(20)—Co(2)—O—(19)	94.04(7)	O(10)—Co(1)—O(7)	87.78(5)
Co(3)—O(7)	2.1080(1)	O(20)—Co(2)—O(9)	90.02(6)	O(1)—Co(1)—O(15)#3	88.91(5)
Co(3)—O(7)#1	2.1080(1)	O(20)—Co(2)—O(8)#1	88.34(6)	O(1)—Co(1)—O(17)	92.83(5)
		O(20)—Co(2)—O(16)#1	176.59(6)	O(1)—Co(1)—O(7)	91.37(5)
		O(18)—Co(2)—O(19)	167.67(6)	O(15)#3—Co(1)—O(17)	87.23(5)
		O(18)—Co(2)—O(9)	95.54(5)	O(15)#3—Co(1)—O(7)	93.99(5)
		O(18)—Co(2)—O(8)#1	90.54(5)	O(17)—Co(1)—O(7)	175.65(5)

Symmetry code for complex **1**: #1: 2–*x*, 1–*y*, 2–*z*; #2: 2–*x*, 1–*y*, 1–*z*; #3: *x*, *y*, 1+*z*.

of coordination. Four nitro groups have a slight torsion at different levels and the carboxyl groups are also not coplanar with the aryl rings. In addition, two carboxyl groups of the ligands are deprotonated, in agreement with the IR data, in which no strong absorption peaks around 1700 cm^{-1} for —COOH are observed.

Pentanuclear Co(II) clusters are slightly distorted rectangles (Co(1)—Co(2)—Co(1)#1 89.24°), formed by two Co(1), two Co(2), and one Co(3) atoms. Two Co(1) and Co(2) atoms are located in two diagonal positions respectively, and Co(3) is located in the center of the rectangle. Five cobalt atoms compose a parallelogram with the plane equation: $-0.3212x + 0.087y + 0.943z = 10.602(7)$, in which Co(1)—Co(2) and Co(2)—Co(1)#1 lengths are 3.6765(6) Å and 4.7957(6) Å respectively.

The dnbpdc ligands connected to pentanuclear Co(II) clusters form a zigzag chain in the *a* direction (Fig. 2, *a*) and a 2D layer in the *b* direction (Fig. 2, *b*). The pentanuclear clusters built by Co(II) and dnbpdc links stack over each other to generate an infinitude 3D network. There is no face-to-face π—π interaction in the benzene rings owing to the steric hindrance of nitro groups. However, there are intramolecular hydrogen bonds between oxygen atoms of the carboxyl group and coordination water molecules (Table 2). Meanwhile, crystal water molecules fill efficiently the pore and consolidate the whole architecture by intermolecular hydrogen bonds between the carboxyl groups and crystal water molecules as well as between crystal water molecules themselves.

Thermal behavior. The DSC curve of complex **1** observed in the 50—600 °C range indicates that the decomposition consists of an endothermic process in the range 90—150 °C with peaks at 125 °C and an aculeate exothermic process in the range 360—430 °C with a peak at 380 °C (Fig. 3).

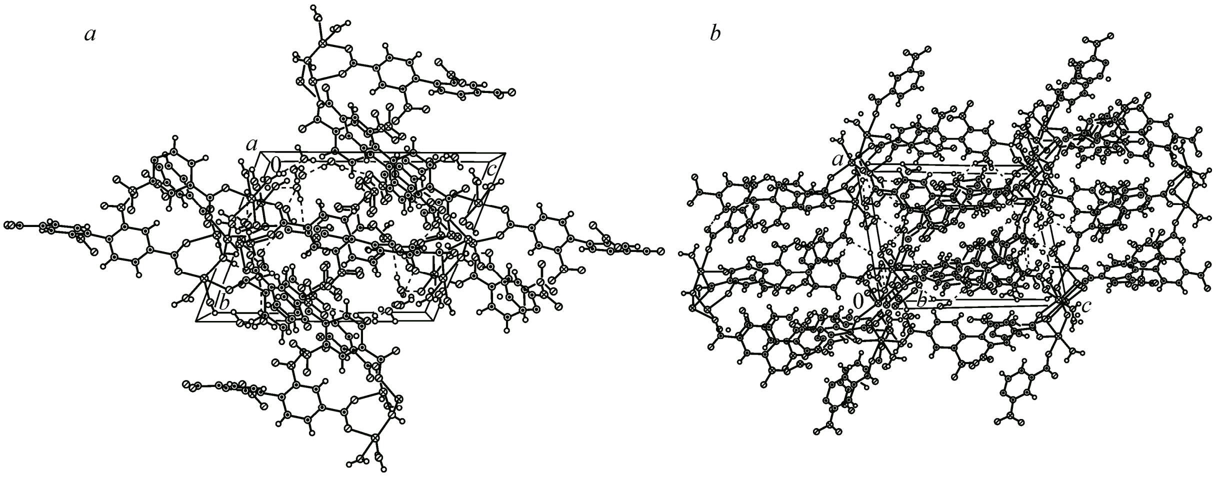


Fig. 2. View of the zigzag chain in the complex **1** from *a* direction (*a*); view of the layer structure of the complex **1** from *b* direction (*b*)

Table 2

Hydrogen Bond Lengths (Å) *and Bond Angles* (deg.)

Nr	D—H···A	*d*(D—H)	*d*(H···A)	*d*(D···A)	∠DHA
1	O(17)—H(17A)···O(2)#1	0.84	1.96	2.770(2)	163
2	O(17)—H(17B)···O(2)	0.84	1.80	2.623(2)	164
3	O(18)—H(18)···O(22)#2	0.82	1.96	2.779(2)	176
4	O(19)—H(19A)···O(23)#3	0.84	1.92	2.744(2)	166
5	O(19)—H(19B)···O(28)#4	0.83	1.97	2.802(2)	172
6	O(20)—H(20A)···O(25)	0.82	1.92	2.735(2)	176
7	O(20)—H(20B)···O(21)#5	0.82	1.94	2.758(2)	169
8	O(21)—H(21B)···O(26)#6	0.84	2.06	2.873(2)	161
9	O(22)—H(22B)···O(24)#7	0.84	2.03	2.872(2)	174
10	O(23)—H(23B)···O(25)#8	0.84	2.00	2.810(2)	163
11	O(24)—H(24A)···O(21)#9	0.84	1.94	2.767(2)	168
12	O(25)—H(25B)···O(17)	0.84	1.90	2.745(2)	173
13	O(26)—H(26A)···O(14)	0.84	2.13	2.967(2)	170
14	O(27)—H(27B)···O(23)	0.84	2.08	2.843(2)	150
15	O(28)—H(28A)···O(27)#10	0.85	1.97	2.777(2)	159
16	O(28)—H(28B)···O(15)#11	0.85	2.20	2.945(2)	148

Symmetry codes: #1: $-x+1, -y+1, -z+2$; #2: $x, y, z+1$; #3: $x+1, y, z$; #4: $x+1, y, z+1$; #5: $-x+2, -y+2, -z+2$; #6: $-x+1, -y+1, -z+1$; #7: $x, y+1, z$; #8: $-x+1, -y+2, -z+2$; #9: $-x+2, -y+1, -z+1$; #10: $-x+1, -y+2, -z+1$; #11: $-x+1, -y+1, -z$.

The TG-DTG curve reveals that the first weight loss of 13.7 % (calcd. 14.1 %) in the range 90—150 °C corresponds to the loss of sixteen crystal water molecules (Fig. 4). Further decomposition begins at 352 °C and ends at 430 °C with the DTG peak at 380 °C, which is an intense exothermic peak accompanied by an explosion. Corresponding to this exothermic process, a very fast mass loss process occurs in this temperature range and mass loss calculations indicate that the decomposition is incom-

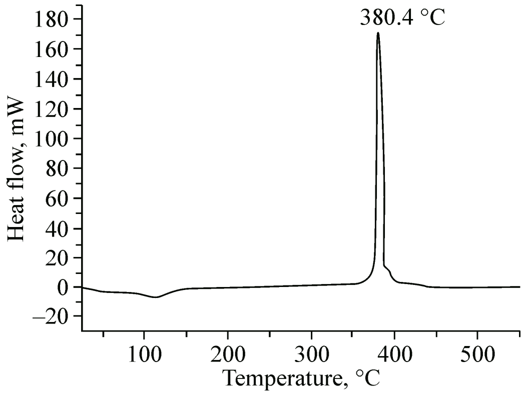


Fig. 3. DSC curve of complex **1**

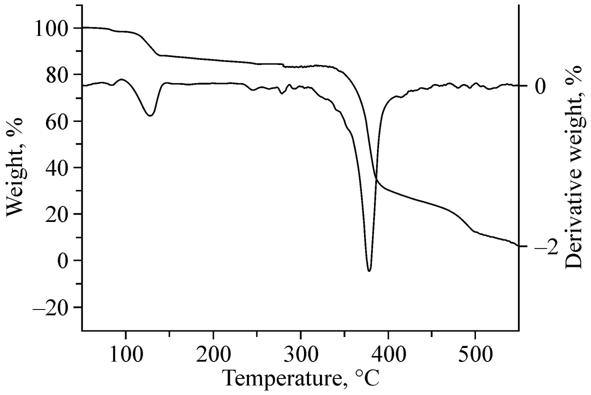


Fig. 4. TG-DTG curve of complex **1**

plete. However, the final residues are not found because the decomposition is fast and releases much heat, so the decomposition residues were blown away. As compared with the DNBPDC compound [20], the title compound decomposes directly and there is no melting process in this temperature range of the decomposition. The number of nitro groups of dnbpdc is halved as compared to that in tnbpdc, so the thermal stability of complex **1** is higher than that of the tnbpdc complexes [22, 23].

CONCLUSIONS

A novel $[Co_5(OH)_2(dnbpdc)_4(H_2O)_6]\cdot 16H_2O$ complex is prepared and characterized. The complex consists of the five-nuclear metal clusters, four dnbpdc ligands, six water molecules, and two hydroxyl groups, then generated into a complicated three-dimensional netted structure through coordination bonds and inter- and intramolecular hydrogen bonds. The carboxyl groups of the dnbpdc ligands are deprotonated and the coordination modes are monodentate, *syn-syn* bridging bidentate, and bridging tridentate. Thermal analysis of complex **1** indicates intensely exothermic decomposition occurring at appoximately 360—430 °C, which indicates a higher thermal stability and potential application as a heat-resistant energetic material.

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