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Synthesis, crystal structure and thermochemical behaviour of a barium complex [Ba(5-OH–BDC)(H_2O)$_3$] [5-OH–H_2BDC = 5-hydroxyisophtalic acid]

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Abstract

A novel complex [Ba(5-OH–BDC)(H_2O)$_3$] [5-OH–H_2BDC = 5-hydroxyisophtalic acid] was synthesized and characterized by X-ray crystallography. The complex is Monoclinic $P2_1/c$, $a = 11.1069(4)$, $b = 14.8192(6)$, $c = 6.5005(2)$ Å, $\beta = 103.465(3)^\circ$ and $Z = 4$, which exhibits a three-dimensional framework formed by linkage of adjacent two-dimensional (6, 3) layers via intermolecular hydrogen bonds. The title complex has been studied by IR spectrum and TG–DTG. The constant-volume combustion energy of the complex, $\Delta_c U$, was determined as being $(-3210.45 \pm 1.41)\,\mathrm{kJ\,mol^{-1}}$ by a precise rotating-bomb calorimeter at 298.15 K. The standard enthalpy of combustion, $\Delta_c H_m^\theta$, and the standard enthalpy of formation, $\Delta_f H_m^\theta$, were calculated as being (-3207.97 ± 1.41) and $(-1922.80 \pm 1.76)\,\mathrm{kJ\,mol^{-1}}$, respectively. A calculation model for determining the specific heat capacity of the complex with an improved RD496-III microcalorimeter is also derived. The specific heat capacity of the complex was $(6158.387 \pm 0.187)\,\mathrm{J\,mol^{-1}\,K^{-1}}$.

Keywords: [Ba(5-OH–BDC)(H_2O)$_3$]; X-ray crystallography; Constant-volume combustion energy; Standard enthalpy of formation; Specific heat capacity

1. Introduction

In recent years, self-assembled coordination polymers containing transition metal ions and organic bridging ligands have been rapidly developed because of their fascinating molecular topologies and crystal-packing motifs along with potential applications in the area of functional materials [1–3]. Substituted isophthalate derivatives have been effectively used in construction of coordination polymers because of their versatile coordination modes. Among substituted isophthalate derivatives, 5-hydroxyisophthalic acid (5-OH–H_2BDC) is C_{2v} symmetry and possesses two carboxylate groups and a hydroxy group. Two carboxylate groups may be completely deprotonated thus resulting in acidity-dependent coordination modes. It also has multiple coordination sites that may generate structures of higher dimensions [4]. Comparing with isophthalic acid ligand, hydroxy group of 5-OH–H_2BDC does not engage in coordination to metal ions, which can serve as a hydrogen bond donor or acceptor to stabilize supramolecular assemblies. A series of transition [5,6] and lanthanide elements [7] coordination polymers with 5-OH–H_2BDC have been documented, however, to the best of our knowledge, alkaline earth coordination polymer with 5-OH–H_2BDC ligand has seldom been reported [4,5,8]. Here we report the synthesis and crystal structure of one novel Ba(II) coordination polymer with the 5-OH–H_2BDC ligand and obtain the constant-volume combustion energy, $\Delta_c U$, the standard enthalpy of combustion, $\Delta_c H_m^\theta$, the standard enthalpy of formation, $\Delta_f H_m^\theta$, and the specific heat capacity, c, respectively. These thermochemical data of the complex are instructive for the thermal stability and potential application in Ba-related biochemistry.

2. Experimental

2.1. Materials and analytical methods

Reagents were purchased commercially and used without further purification. Barium content was determined with EDTA by complexometric titration. Elemental analyses (C, H and N) were

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carried out on a Vario EL III CHNOS instrument made in German. The DSC and TG–DTG experiments for the title compound were performed using a model of NETZSCH STA 449C apparatus under a nitrogen atmosphere, at a flow rate of 30 mL min^{-1}. The sample mass was about 7.963 mg. The heating rate used was 10 °C min^{-1} from ambient temperature to 1000 °C. The IR analysis was conducted on a BEQ, UZNDX-550 spectrometer (KBr discs).

2.2. *Synthesis of the complex*

A mixture of 5-OH–H_2BDC (1 mmol), NaOH (2 mmol) and distilled water (40 mL) was stirring until pH = 6, to which 20 mL 1 mmol $BaCl_2 \cdot 2H_2O$ aqueous solution was added under the condition of stirring for two hours at room temperature. After 1 week, some colorless, rectangular single crystals of the complex were cultured in the mother liquid. Anal. Calc. for the title complex: C, 25.87; H, 2.71; Ba, 36.97. Found: C, 25.84; H, 2.69; Ba, 36.97.

2.3. *Experimental conditions of calorimetric methods*

The experiment was performed using an RD496-III [9] type microcalorimeter. The calorimetric constant of the calorimeter was (63.901 ± 0.030) μV mW^{-1}, measured by the Joule effect at 298.15 K before experiment. The solution enthalpy of KCl in deionized water was determined at 298.15 K with the value of (17.238 ± 0.048) kJ mol^{-1}, which was close to the literature value of (17.241 ± 0.018) kJ mol^{-1} [10]. In the calorimetric experiment, the solid sample was loaded in a 15 mL sample cell and the reference cell with the same size was empty. When the calorimetrical system reached to the thermal equilibrium, the thermal curve was recorded.

The constant-volume combustion energy of the title complex was determined by an RBC-type II precise rotating-bomb calorimeter [11]. The main experimental procedures were described previously [9]. The initial temperature was regulated to (25.0000 ± 0.0005) °C, and the initial oxygen pressure was 2.5 MPa. The correct value of the heat exchange was calculated according to Linio–Pyfengdelel–Wsava formula [10]. The calorimeter was calibrated with benzoic acid of 99.99% purity. Its isothermal heat of combustion at 25 °C was (−26434 ± 3) J g^{-1}. The energy equivalent of calorimeter was calibrated as (17775.09 ± 7.43) J K^{-1}. The analytical methods of final products (gas, liquid and solid) were the same as those in Ref. [11]. The analytical results of the final products showed that the combustion reactions were complete.

2.4. *Derivation of formula of specific heat capacity*

The specific heat capacity of a substance can be determined according to the principle showed in Fig. 1.

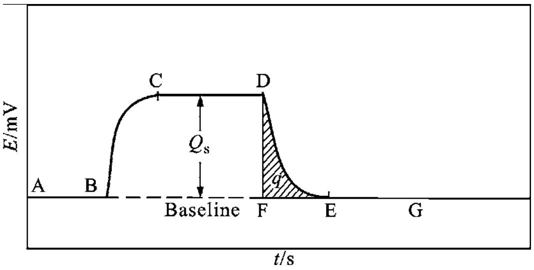

Fig. 1. Schematic thermogram of measurement of the heat capacity of solid sample.

In Fig. 1, AG is the baseline; at time B, the Peltier current is given to heat; at CD, a new homeostasis state forms (Q_s is the amount of heat flux under the steady-state condition); at the point *D*, the Peltier current is cut; at time *E*, the system comes back to the original state (that is baseline); *q* is the area integral of the shadow part in the figure representing the whole disequilibrium heat.

To measure the specific heat capacities of the samples, the empty cell (system 1), the cell containing the test sample (system 2), the cell containing the first standard substance (system 3) and the cell containing the second standard substance (system 4) are heated by the same Peltier current with the microcalorimeter, then the endothermic equations are obtained:

$$\text{to system 1}: \quad q_0 = a\theta \tag{1}$$

$$\text{to system 2}: \quad q = (a + mc)\theta \tag{2}$$

$$\text{to system 3}: \quad q_1 = (a + m_1c_1)\theta \tag{3}$$

$$\text{to system 4}: \quad q_2 = (a + m_2c_2)\theta \tag{4}$$

where q_0, q, q_1 and q_2 are the heats of thermal disequilibrium as the curve returns to baseline after the Peltier current of the above four systems are cut, respectively (J); a is the apparent heat capacity of the empty cell (J K^{-1}); θ is the equilibrium temperature of calorimeter at homeostasis state (K); m, m_1, and m_2 are the mass of the test sample, the first standard substance and the second standard one, respectively (g); c, c_1 and c_2 are the specific heat capacities of these samples, respectively (J g^{-1} K^{-1}).

Combining Eqs. (1)–(4), we have:

$$c = [(q - q_0)/2m][m_1c_1/q_1 - q_0) + m_2c_2/(q_2 - q_0)] \tag{5}$$

Providing having the specific heat capacities c_1 and c_2 of the two standard substances, the specific heat capacity c, calibrated by these standard substances, of the test sample can be calculated according to Eq. (5).

2.5. *X-ray crystallography*

All diffraction data for the complex were collected on a Bruker SMART CCD area-detector diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 293(2) K using the program SMART and processed by SAINT-plus. Absorption corrections were applied by SADABS. The structures was solved by direct methods and refined with full-matrix least-squares technique using SHELXTL [12]. All non-hydrogen atoms were refined anisotropically. All H-atoms were located theoretically and refined. The structural plots were drawn using the SHELXTL and OLEX programs. The dimensions of the crystal used for X-ray diffraction data collection are given in

Table 1
Crystallographic data and structure refinement parameters for the title complex

Empirical formula	$C_8H_{10}BaO_8$
Formula weight	371.50
Temperature (K)	293 (2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 11.1069(4)$ Å, $\alpha = 90°$; $b = 14.8192(6)$ Å, $\beta = 103.465(3)°$; $c = 6.5005(2)$ Å, $\gamma = 90°$
Volume (Å^3)	1040.54(6)
Z	4
Calculated density (mg/m^3)	2.371
Absorption coefficient (mm^{-1})	3.847
$F(000)$	712
Crystal size (mm)	0.37 × 0.25 × 0.18
Range for data collection (°)	1.89–26.99
Limiting indices	$-14 \le h \le 13$, $-18 \le k \le 13$, $-8 \le l \le 8$
Reflections collected/unique	5652/2265 [R(int) = 0.0205]
Completeness to theta = 26.99(%)	99.7
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2265/0/179
Goodness-of-fit on F^2	1.164
Final R indices [$I > 2$ sigma (I)]	$R_1 = 0.0201$, $wR_2 = 0.0485$
R indices (all data)	$R_1 = 0.0238$, $wR_2 = 0.0555$
Largest diff. peak and hole (eÅ^{-3})	0.808 and −0.580

Table 1. Selected bond lengths and angles are listed in Table 2. The geometries of the hydrogen bonding are listed in Table 3.

3. Results and discussion

3.1. Structural description

As shown in Fig. 2, the asymmetric unit consists of one Ba(II) ion, one 5-OH–BDC and three water molecules. The metal center has a coordination number of 9, and the coordination geometry around Ba(II) ion could be described as a distorted tricapped trigonal prism arrangement (Fig. 3.) where O2, O2B and

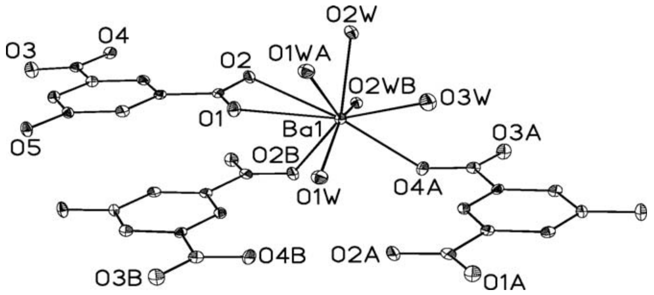

Fig. 2. Coordination environment of Ba(II) ion in the title complex. Non-hydrogen atoms are shown as 30% probability ellipsoids. The hydrogen atoms are omitted for clarity.

Table 2
Selected bond lengths (Å) and angles (°) for the title complex

Ba1–O1	2.706(2)	Ba1–O4#1	2.777(2)	Ba1–O3W	2.794(3)
Ba1–O2#2	2.810(2)	Ba1–O2W	2.849(2)	Ba1–O2W#2	2.865(3)
Ba1–O1W	2.957(3)	Ba1–O2	2.985(2)	Ba1–O1W#3	3.146(3)
O1–Ba1–O4#1	149.14(6)	O1–Ba1–O3W	121.61(8)	O4#1–Ba1–O3W	74.99(7)
O1–Ba1–O2#2	78.66(7)	O4#1–Ba1–O2#2	76.08(6)	O3W–Ba1–O2#2	146.78(7)
O1–Ba1–O2W	89.46(7)	O4#1–Ba1–O2W	120.79(7)	O3W–Ba1–O2W	77.49(7)
O2#2–Ba1–O2W	132.42(7)	O1–Ba1–O2W#2	111.42(7)	O4#1–Ba1–O2W#2	74.45(7)
O3W–Ba1–O2W#2	119.04(8)	O2#2–Ba1–O2W#2	67.32(6)	O2W–Ba1–O2W#2	75.06(5)
O1–Ba1–O1W	73.51(7)	O4#1–Ba1–O1W	88.41(7)	O3W–Ba1–O1W	74.54(9)
O2#2–Ba1–O1W	88.71(7)	O2W–Ba1–O1W	131.88(8)	O2W#2–Ba1–O1W	153.06(7)
O2–Ba1–O1W#3	86.05(7)	O4#1–Ba1–O2	139.13(6)	O3W–Ba1–O2	138.85(7)
O2#2–Ba1–O2	74.36(4)	O2W–Ba1–O2	65.21(6)	O2W#2–Ba1–O2	68.43(7)
O1W–Ba1–O2	118.26(7)	O1W–Ba1–O1W#3	65.36(8)	O4#1–Ba1–O1W#3	134.68(7)
O3W–Ba1–O1W#3	63.04(8)	O2#2–Ba1–O1W#3	134.98(7)	O2W–Ba1–O1W#3	67.20(8)

Symmetry transformations used to generate equivalent atoms – #1: $-x+2$, $y+1/2$, $-z+5/2$; #2: x, $-y+3/2$, $z+1/2$; #3: $-x+2$, $-y+2$, $-z+2$; #4: x, $-y+3/2$, $z-1/2$; #5: $-x+2$, $y-1/2$, $-z+5/2$.

Table 3
Hydrogen bonding geometry (Å, °) of the title complex

D–H···A (Å)	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
O2W–H2WA···O5	0.75(4)	1.95(4)	2.692(4)	169(4)
O1W–H1WA···O4	0.80(5)	2.15(5)	2.950(3)	173(5)
O2W–H2WB···O4	0.68(4)	2.13(5)	2.797(4)	171(5)
O3W–H3WA···O1	0.81(4)	2.04(4)	2.835(4)	170(3)
O1W–H1WB···O1	0.71(7)	2.60(7)	2.92(8)	109(7)
O3W–H3WB···O3	0.82(6)	2.30(6)	3.108(4)	167(6)
O5–H5A···O3	0.82(0)	1.77(0)	2.582(3)	172(9)

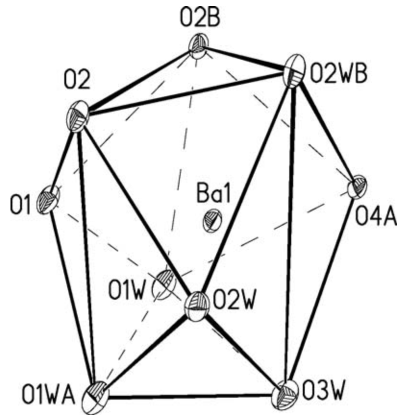

Fig. 3. Coordination polyhedron for Ba(II) ion in the title complex.

O2WB form the top plane of the trigonal prism, and the bottom plane is completed by O1WA, O1W, and O3W, while O1, O2W and O4A capped quadrilateral face formed by O2, O2B, O1W, O1WA; O2, OWB, O3W, O1WA and O1W, O2B, O2WB, O3W, respectively. Among all the nine coordinated oxygen atoms, two oxygen atoms (O1 and O2) come from one carboxylate group, two oxygen atoms (O2B and O4A) come from two different carboxylate groups, and five oxygen atoms (O1W, O1WA, O2W, O2WB and O3W) come from coordinated water molecules. The two carboxylate groups of the 5-OH–BDC ligands bond to Ba(II) ion in two modes: (i) unidentate coordination mode which means one oxygen atom (O4) connects one Ba(II) and the other oxygen atom (O3) does not connect Ba(II) ion, and the carboxylate group coordinates to one Ba(II) ion; (ii) $\mu3-\eta2$: $\eta1$ coordination mode which means one oxygen atom (O2) coordinates with two Ba(II) ions, the other (O1) coordinate with one Ba(II) ion, and the carboxylate group coordinates to two Ba(II) ions (Fig. 4), this coordination mode of the 5-OH–BDC ligand is not observed in previous work [5,6,13]. Water molecules also exhibit two coordination styles: one water molecule (O3W) serves as a terminal ligand, and the other water molecules (O1W, O1WA, O2W and O2WB) act as bridging ligands. The bond length of Ba–$O_{carboxylate}$ bonds range from 2.706(2) to 2.985(2) Å with the mean of 2.819(2) Å and Ba–O_W bonds from 2.794(3) to 3.146(3) Å with the mean of 2.922(3) Å, which compare well with the average values determined from the CSD [2.798(7) Å for Ba–$O_{carboxylate}$ bond and 2.847(7) Å for Ba–O_W bond].

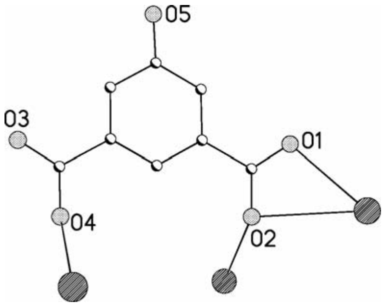

Fig. 4. Coordination modes of carboxylate groups of 5-OH–BDC in the title complex.

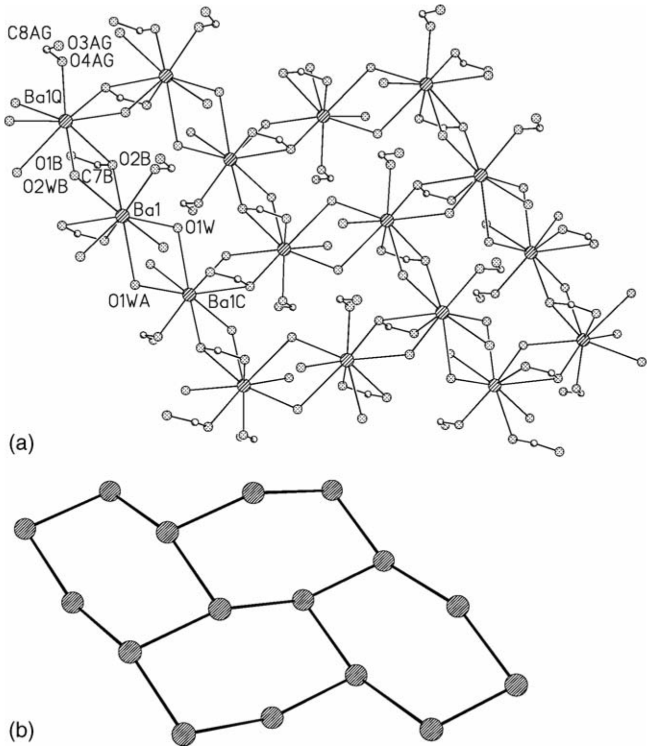

Fig. 5. (a) A fragment of the two-dimensional layer structure along *a* axis in the title complex. Benzene rings and hydrogen atoms are omitted for clarity. (b) View of two-dimensional (6, 3) layer in the title complex.

In the complex, every six Ba(II) ions form metal hexatomic rings which share common edges to construct a two-dimensional, infinite (6, 3) network observed in the *bc* plane (Fig. 5). Within the (6, 3) topology layer, the nodes are provided by Ba(II) ions while spacers are two oxygen atoms. There are two types of linking modes between two Ba(II) ions. On one hand, two Ba(II) ions (Ba1 and Ba1C) are connected by two oxygen atoms (O1W and O1WA) which belong to two bridging water molecules with the Ba···Ba distance of 5.138 Å; on the other hand, two Ba(II) ions (Ba1 and Ba1Q) are connected by two different oxygen atoms, one is oxygen atom (O2WB) of coordinated water molecule, the other one is oxygen atom (O2B) of carboxylate group, and the Ba···Ba distance is 4.818 Å. The two types of Ba···Ba distances are much more bigger compared with previous work [14,15].

As shown as in Fig. 6(a), all of the coordinated water molecules and four oxygen atoms (O1, O3, O4 and O5) of 5-OH–BDC form O–H···O hydrogen bonds. There are three types of O–H···O hydrogen bonds in the title complex: (i) the coordinated water molecules form O–H···O hydrogen bonds to the carboxylate oxygen of 5-OH–BDC on a neighboring strand such as O1W–H1WA···O4A, O2W–H2WB···O4B, O3W–H3WA···O1D, O1W–H1WB···O1D and O3W–H3WB···O3F with the O···O distance ranges from 2.797(4) Å to 3.108(4) Å and O–H···O angle ranges from 109(7)° to 173(5)°; (ii) the coordinated water molecules form O–H···O hydrogen bonds to the hydroxyl oxygen such as O2W–H2WA···O5F with the O···O distance of 2.692(4) Å and O–H···O angle of 169(4)°; (iii) the carboxylate group can offer an oxygen atom forming an O–H···O hydrogen bond [O···O, 2.582(3) Å; O–H···O, 172(9)°] with hydroxy group (O5–H5A···O3C). Among all the O–H···O hydrogen bonds in the complex (Table 3), O1W–H1WA···O4, O2W–H2WB···O4, O3W–H3WA···O1 and O1W–H1WB···O1 exist in the interior of each two-dimensional polymeric layer, and the adjacent two-dimensional polymeric layers can be assembled into a three-dimensional framework (Fig. 6(c)) via O–H···O hydrogen bonds of O2W–H2WA···O5, O3W–H3WB···O3 and O5–H5A···O3. The hydrogen bonds among the two-dimensional layers could be clearly seen in Fig. 6(b).

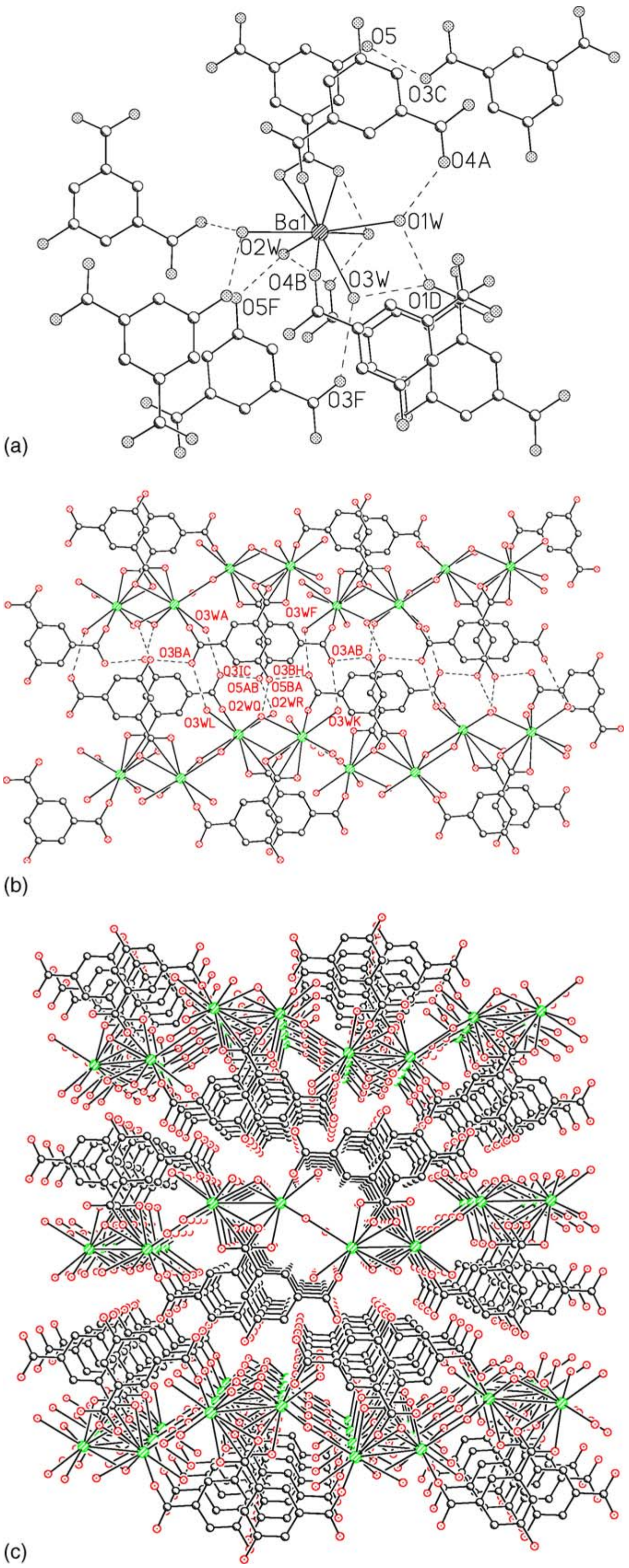

Fig. 6. (a) View of hydrogen bonds around Ba(II) ion in the title complex. Hydrogen bond are shown as dashed lines. (b) View of hydrogen bonds among the two-dimensional layers along *c* axis. Some redundant atoms are omitted for clarity. Hydrogen bonds are shown as dashed lines. (c) View of three-dimensional layer structure along *c* axis in the title complex.

3.2. IR spectroscopy

The IR spectrum of the complex shows the presence of the characteristic bands of carboxylate unit at 1666 cm^{-1} for asymmetric stretching and 1420 cm^{-1} for symmetric stretching. The broad bands at 3239–3411 cm^{-1} are attributed to the vibrations of the water ligand. No absorption of any protonated 5-OH–$\mathrm{H_2}$BDC (1715–1680 cm^{-1}) confirms that 5-OH–$\mathrm{H_2}$BDC is completely deprotonated by NaOH. This agrees with the measurement result for crystal structure.

3.3. Thermogravimetric analysis

The typical TG–DTG and DSC curves for the thermal decomposition of the title complex were depicted in Fig. 7. The TG curve consists of four-stage mass loss processes, which could be described that the complex was thermally decomposed into anhydrous Ba(5-OH–BDC) firstly and further transformed to $\mathrm{BaCO_3}$ finally. The final product $\mathrm{BaCO_3}$ is confirmed by XRD. The dehydration enthalpy is 319.9 J g^{-1}.

3.4. Combustion energy, standard enthalpy of combustion and standard enthalpy of formation

3.4.1. Combustion energy

The methods of determination and calculation of the constant-volume combustion energy for the complex is the same as for the calibration of the calorimeter with benzoic acid. The

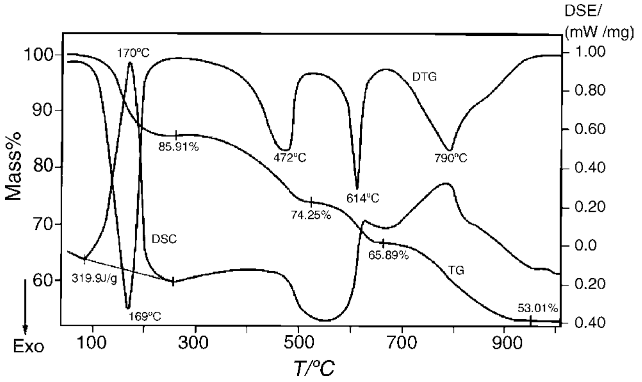

Fig. 7. TG–DTG and DSC curves of the title complex.

Table 4
The experimental result of constant-volume combustion energy for the title complex

Sample	No. of experiments	Mass of complexes m/g	Calibrated heat of compound wire Q_c/J	Calibrated heat of acid Q_N/J	Calibrated ΔT/K	Combustion energy of complex $-\Delta_c U/(\mathrm{J\,g^{-1}})$
Complex	1	1.23501	12.60	14.67	0.6018	8639.43
	2	1.21469	12.60	14.80	0.5913	8630.19
	3	1.20897	12.60	14.76	0.5897	8647.54
	4	1.25430	12.70	14.58	0.6114	8643.39
	5	1.23565	12.60	14.68	0.6033	8656.52
	6	1.24587	12.60	14.66	0.6068	8635.46
Mean ± S.D.						8642.09 ± 3.80

values are calculated by means of Eq. (6):

$$\Delta_c U(\text{complex, s}) = \frac{W\Delta T - bG - Q_N}{m} \tag{6}$$

where $\Delta_c U$ (complex, s) denotes the constant-volume combustion energy of the complex, W the energy equivalent of the rotating-bomb calorimeter (in $\mathrm{J\,K^{-1}}$), ΔT the correct value of the temperature rise, b the length of the actual Ni–Cr wire consumed (in cm), G the combustion enthalpy of Ni–Cr wire consumed (in cm), Q_N the calibrated heat of acid and m is the mass in g of the complex. The results are given in Table 4.

3.4.2. Standard enthalpy of combustion

The standard enthalpy of combustion of the complex, $\Delta_c H_m^\theta$ (complex, s, 298.15 K), refers to the combustion enthalpy changes of the following ideal combustion reaction at 298.15 K and 100 kPa.

$$\mathrm{Ba(5\text{-}OH\text{–}BDC)\cdot 3H_2O(s)} + 7\mathrm{O_2(g)} \rightarrow \mathrm{BaO(s)} + 8\mathrm{CO_2(g)} + 5\mathrm{H_2O(l)} \tag{7}$$

The standand enthalpy of combustion of the complex is calculated by Eq. (8):

$$\Delta_c H_m^\theta (\text{complex, s, 298.15 K}) = \Delta_c U (\text{the complex, s, 298.15 K}) + \Delta n RT \tag{8}$$

$$\Delta n = n_g(\text{products}) - n_g(\text{reactants}) \tag{9}$$

Where n_g is the total amount in mole of gases present as products or as reactants, $R = 8.314\ \mathrm{J\,K^{-1}\,mol^{-1}}$, $T = 298.15$ K.

The result of the calculation about $\Delta_c H_m^\theta$ is $(-3207.97 \pm 1.41)\ \mathrm{kJ\,mol^{-1}}$.

3.4.3. Standard enthalpy of formation

The standard enthalpy of formation of the complex, $\Delta_f H_m^\theta$ (complex, s, 298.15 K), is calculated by Hess's law according to the above thermochemical Eq. (7):

$$\begin{aligned}
&\Delta_f H_m^\theta\,[\mathrm{Ba(5\text{-}OHBDC)\cdot 3H_2O, s}]\\
&= \Delta_f H_m^\theta(\mathrm{BaO, s}) + 8\Delta_f H_m^\theta(\mathrm{CO_2, g})\\
&\quad + 5\Delta_f H_m^\theta(\mathrm{H_2O, l}) - \Delta_c H_m^\theta\\
&= [(-553.543 \pm 0) + 8(-393.51 \pm 0.13)\\
&\quad + 5(-285.83 \pm 0.042)]\ \mathrm{kJ\,mol^{-1}}\\
&\quad - (-3207.97 \pm 1.41)\ \mathrm{kJ\,mol^{-1}}\\
&= (-1922.80 \pm 1.76)\ \mathrm{kJ\,mol^{-1}}
\end{aligned}$$

3.5. Specific heat capacity

3.5.1. Specific heat capacities of the empty cell and the standard substances

The specific heat capacities of the empty cell and the standard substances were determined according to the above method and listed in Table 5. The measurement precisions are in the range of $(1\text{–}3) \times 10^{-4}$. All the measurement accuracies of the two standard samples are 2×10^{-4}.

The mean of the heat of disequilibrium for the complex ($m = 3.02632$ g) was (7684.799 ± 1.024) mJ, which was measured by the above method (measuring 6 times for each sample),

Table 5
Data of the heat and heat capacities of the empty cell and the standard substances (298.15 K)

Heats of disequilibrium and specific heat capacity	The empty cell	Standard α-$\mathrm{Al_2O_3}$	Sublimed benzoic acid
$q(1)$ (mJ)	1695.476	1764.116	1905.010
$q(2)$ (mJ)	1697.610	1763.883	1906.384
$q(3)$ (mJ)	1696.718	1763.066	1905.886
$q(4)$ (mJ)	1694.408	1765.069	1907.533
$q(5)$ (mJ)	1696.220	1763.756	1908.145
$q(6)$ (mJ)	1695.372	1764.878	1907.946
q(Mean ± S.D.) (mJ)	1695.967 ± 0.460	1764.128 ± 0.304	1906.817 ± 0.512
The relative standard deviation	2.713×10^{-4}	1.723×10^{-4}	2.686×10^{-4}
Specific heat capacity, c ($\mathrm{J\,mol^{-1}\,K^{-1}}$)		79.020 ± 2.133 (79.03 [16])	145.345 ± 0.410 (145.327 [17])

and its specific heat capacity which was calculated from the data in Table 5 by Eq. (5) was (6158.387 ± 0.187) J mol^{-1} K^{-1}.

4. Conclusions

In summary, this study provides an example of an alkaline earth metal Ba(II) coordination polymer constructed from the flexible ligand 5-OH–H_2BDC. In this case, the carboxylate groups of the 5-OH–BDC bonding to Ba(II) ion adopt a novel mode which has not been reported in the previous work. The most striking structural feature of the complex is that an ordered two-dimensional polymeric layer with a (6, 3) topology is observed in the *bc* plane. Moreover, the two-dimensional layers extend into a three-dimensional supramolecular architecture via intermolecular hydrogen bonds (O–H···O). Based on calorimetry, the standard enthalpy of formation and the specific heat capacity of the compound at 298.15 K were determined as being (−1922.80 ± 1.76) kJ mol^{-1} and (6158.387 ± 0.187) J mol^{-1} K^{-1}, respectively.

Supplemental material

Supplementary data are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk) on request, quoting the Deposit No. 294887.

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