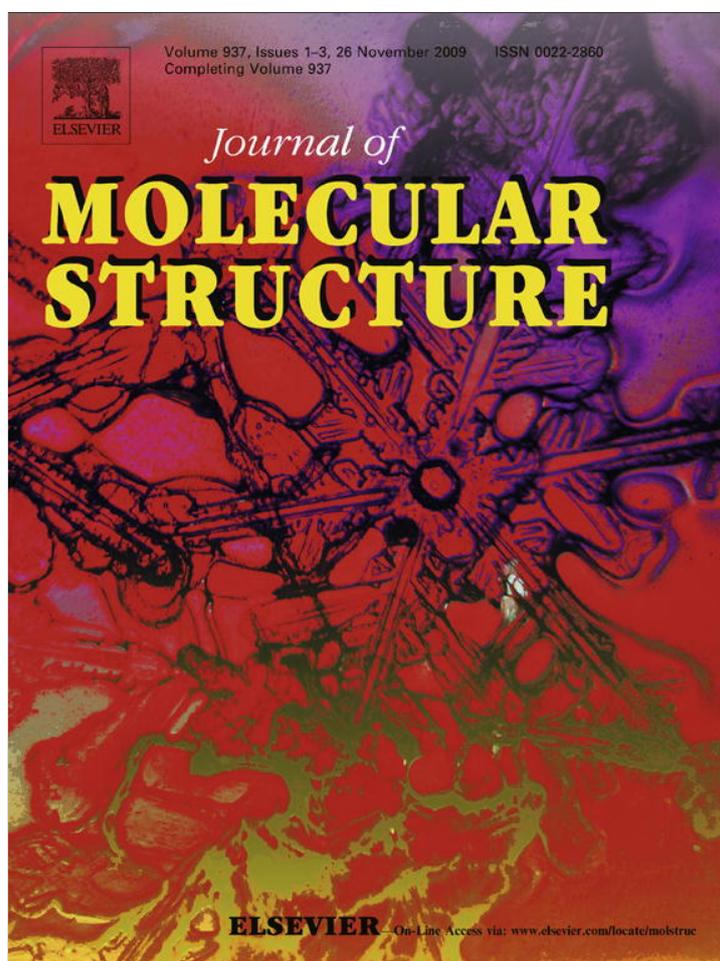


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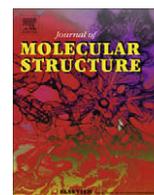
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Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstrucA ternary supramolecular compound of *p*-sulfonatocalix[8]arene with 1D channelsWenwei He^{a,b}, Yanfeng Bi^{a,b}, Wuping Liao^{a,*}, Deqian Li^a^a State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, PR China^b Graduate University of Chinese Academy of Sciences, Beijing 100049, PR China

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ABSTRACT

A ternary supramolecular complex of $[\text{Ni}(\text{bipy})_2(\text{H}_2\text{O})_4](\text{C8AS}) \cdot 17.6(\text{H}_2\text{O})$ (bipy = 4,4'-dimethyl-2,2'-bipyridine and C8AS = *p*-sulfonatocalix[8]arene) has been synthesized by a hydrothermal method and characterized by FT-IR spectroscopy, TG-DTA analysis and single crystal X-ray diffraction. In the structure, the water-soluble *p*-sulfonatocalix[8]arene molecule adopts a double partial cone conformation and is coordinated by four nickel atoms each of which is bonded by two 4,4'-dimethyl-2,2'-bipyridine molecules and one water molecule at the same time. The tetranuclear subunits are stacked into an extended 3D structure with 1D water-filled channels via hydrogen bonds and C–H... π interactions.

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1. Introduction

Water-soluble *p*-sulfonatocalix[*n*]arenes ($n = 4, 5, 6, 8, \text{CnAS}$), possessing strongly hydrophilic upper and lower rims and hydrophobic cone-like cavities, have attracted considerable attention in the field of supramolecular chemistry and crystal engineering [1]. Commonly they were used for the construction of various supramolecular aggregations with 'molecular capsules', hydrogen-bonded polymers, 1D or 2D coordination polymers, water-filled channels, nanometer scale spheres or tubules [2]. While C4AS has been widely studied, the bigger ones (CnAS, $n = 5, 6$ or 8) have been studied less due to their higher charges, more flexible frameworks and bigger cavities. Especially for C8AS, as we know, there are only four publications on its solid-state coordination/supramolecular structures [3–6]. For instance, Raston and co-workers reported a complex 3D "wavy brick wall" coordination polymer of C8AS with the first reported "pleated loop" conformation [3]. Later they reported another extended structure with 2D porosity of C8AS in the same conformation [4]. They also found a way to form a chalice-like cavity using C8AS [5]. In this structure, large diameter, negatively charged channels propagate through the material in three dimensions. Coleman and co-workers presented two examples of C8AS with two different conformations, one being the "pleated loop" and the other being inverted double partial cone, and found that the differences in the molecular conformations lead to highly different packing arrangements in the structures [6]. Re-

cently, we observed another new conformation of C8AS, the 1,2,3,4-alternate double cone conformation, in the solid state for the first time [7]. Here we will present another example of C8AS with the inverted double partial cone conformation, $[\text{Ni}(\text{bipy})_2(\text{H}_2\text{O})_4](\text{C8AS}) \cdot 17.6(\text{H}_2\text{O})$ (**1**) (bipy = 4,4'-dimethyl-2,2'-bipyridine and C8AS = *p*-sulfonatocalix[8]arene), which are synthesized by a hydrothermal method.

2. Experimental

2.1. Preparation of **1**

An aqueous solution (7 ml, pH 2.78) of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.12 mmol), C8AS (0.04 mmol) [8] and bipy (4,4'-dimethyl-2,2'-bipyridine) (0.32 mmol) was transferred into a Teflon-lined stainless-steel autoclave (10 ml) and heated to 130 °C within 90 min. The autoclave was kept at 130 °C for 3 days, and then cooled gradually to room temperature at 5 °C/h. The final aqueous solution pH is about 2.45 and the brown block single crystals of **1** were obtained in 50% yield based on C8AS and isolated for X-ray diffraction determination and other measurements. TG/DTA measurement was performed in the flow of air using a SDT 2960 simultaneous DSC-TGA instrument (TA instruments).

2.2. X-ray crystallography

A single crystal of compound **1** with dimensions of $0.28 \times 0.20 \times 0.14 \text{ mm}^3$ was selected for X-ray diffraction data collecting on a Bruker SMART APEX CCD diffractometer with

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graphite-monochromatized Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The crystal structure was solved by means of Direct Methods and refined employing full-matrix least squares on F^2 (SHELXTL) [9]. Crystal data for **1**: C₁₅₂H_{171.16}N₁₆Ni₄O_{49.58}S₈, $M = 3506.81 \text{ g/mol}$, monoclinic, $P2_1/c$ (14), $a = 19.6490(10) \text{ \AA}$, $b = 17.0803(9) \text{ \AA}$, $c = 29.7359(12) \text{ \AA}$, $\beta = 123.480(2)^\circ$, $V = 8323.8(7) \text{ \AA}^3$, $Z = 2$, $D_{\text{calcd}} = 1.399 \text{ g cm}^{-3}$, $\mu = 0.632 \text{ mm}^{-1}$, $T = 184(2) \text{ K}$, $\theta_{\text{max}} = 25.00^\circ$, $F(000) = 3664$, reflections collected/unique, 43,496/14,636 ($R_{\text{int}} = 0.0261$), final $R_1 = 0.1035$,

$wR_2 = 0.3480$ [$I > 2\sigma(I)$], GOF = 1.012. After the contribution from the disordered solvent molecules were subtracted by the SQUEEZE command [10] in PLATON, $R_1 = 0.0693$, $wR_2 = 0.2051$ [$I > 2\sigma(I)$], GOF = 1.107. All the non-hydrogen atoms were refined anisotropically, and hydrogen atoms of the ligands were placed at calculated idealized positions attached to their parent atoms and refined isotropically as riding atoms with fixed thermal factors related to those of the parent atoms using SHELXTL default values. The hydrogen

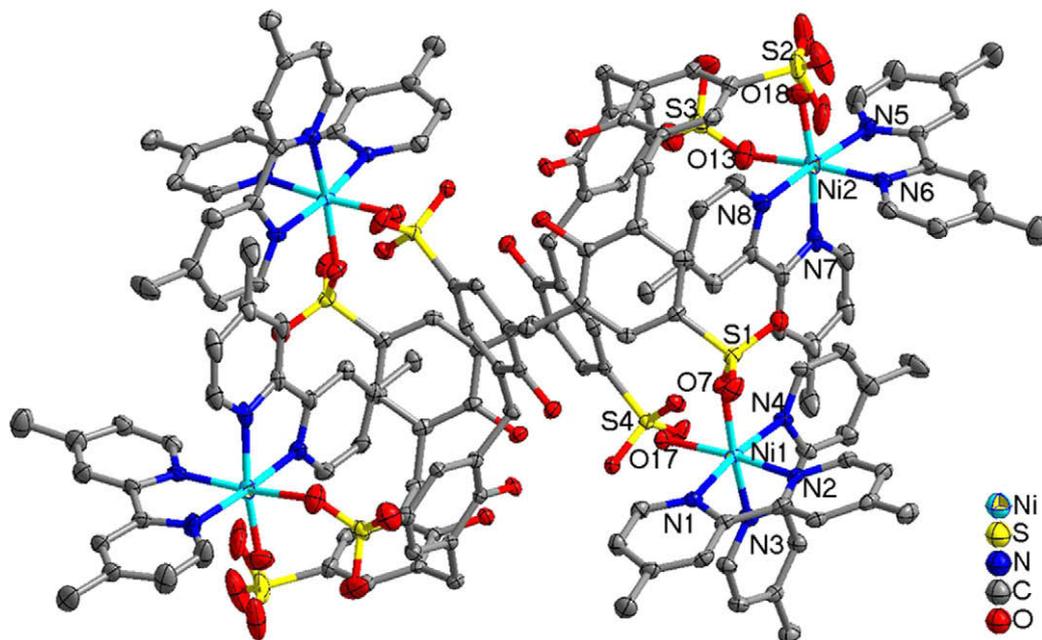


Fig. 1. Molecular structure of complex **1**.

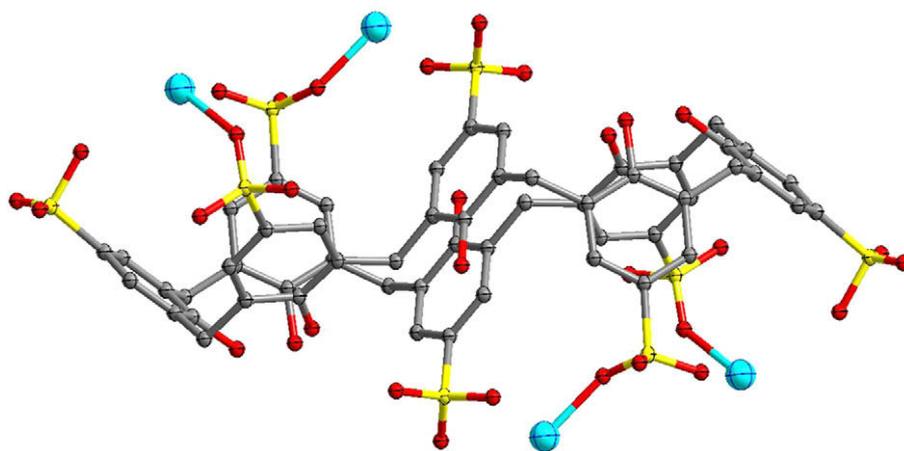


Fig. 2. Double partial cone conformation of *p*-sulfonatocalix[8]arene with four Ni ions.

Table 1
Hydrogen-bonding geometry (\AA , $^\circ$) for complex **1**.

D–H...A	D–H	H...A	D...A	$\angle\text{D–H...A}$	Symmetry code
C(16)–H(16A)...O(15)	0.95	2.59	3.328(10)	134	$-x, 1/2 + y, 3/2 - z$
C(51)–H(51A)...O(6)	0.98	2.59	3.478(11)	150	$-x, -1/2 + y, 3/2 - z$
C(52)–H(52A)...O(6)	0.95	2.38	3.242(9)	151	$-x, -1/2 + y, 3/2 - z$
C(53)–H(53A)...O(9)	0.95	2.43	3.294(13)	152	$1 - x, -1/2 + y, 3/2 - z$
C(68)–H(68A)...O(14)	0.98	2.45	3.339(9)	151	$-x, 1/2 + y, 3/2 - z$
C(72)–H(72A)...O(9)	0.98	2.52	3.438(16)	155	$1 - x, -1/2 + y, 3/2 - z$

Table 2
C–H... π geometry (Å, °) for complex 1.^a

	H...Cg	\angle X–H...Cg	X...Cg
C(5)–H(5B)···Cg(1)	2.94	113	3.441(5)
C(18)–H(18B)···Cg(2)	2.71	140	3.525(6)
C(51)–H(51B)···Cg(3)	2.99	126	3.655(8)
C(51)–H(51C)···Cg(4)	2.97	128	3.654(7)
C(58)–H(58C)···Cg(5)	2.69	143	3.521(8)

^a Cg(1): N(2), C(26), C(47), C(43), C(16), C(32); Cg(2): C(10), C(12), C(13), C(34), C(17), C(44); Cg(3): C(3), C(15), C(40), C(41), C(36), C(23); Cg(4): N(1), C(14), C(38), C(61), C(49), C(46); Cg(5): C(1), C(8), C(19), C(31), C(24), C(25).

atoms of the water molecules could not be located and were included in the molecular formula directly.

3. Results and discussion

3.1. Synthesis

The successful isolation of compound **1** depends on the exploitation of hydrothermal techniques. No target crystals were obtained from the same feeds at room temperature.

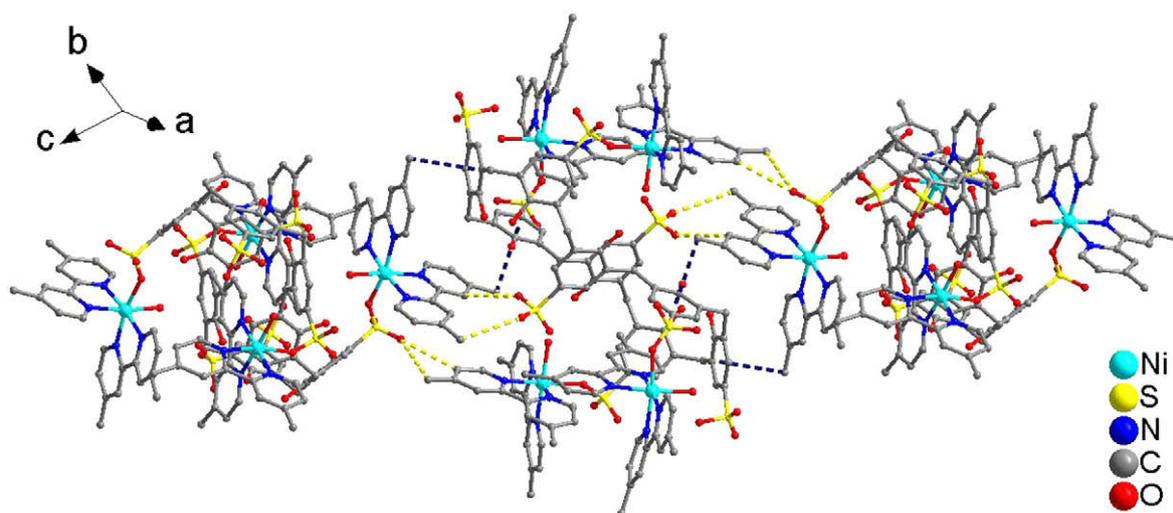


Fig. 3. Supramolecular interactions among the tetranuclear subunits.

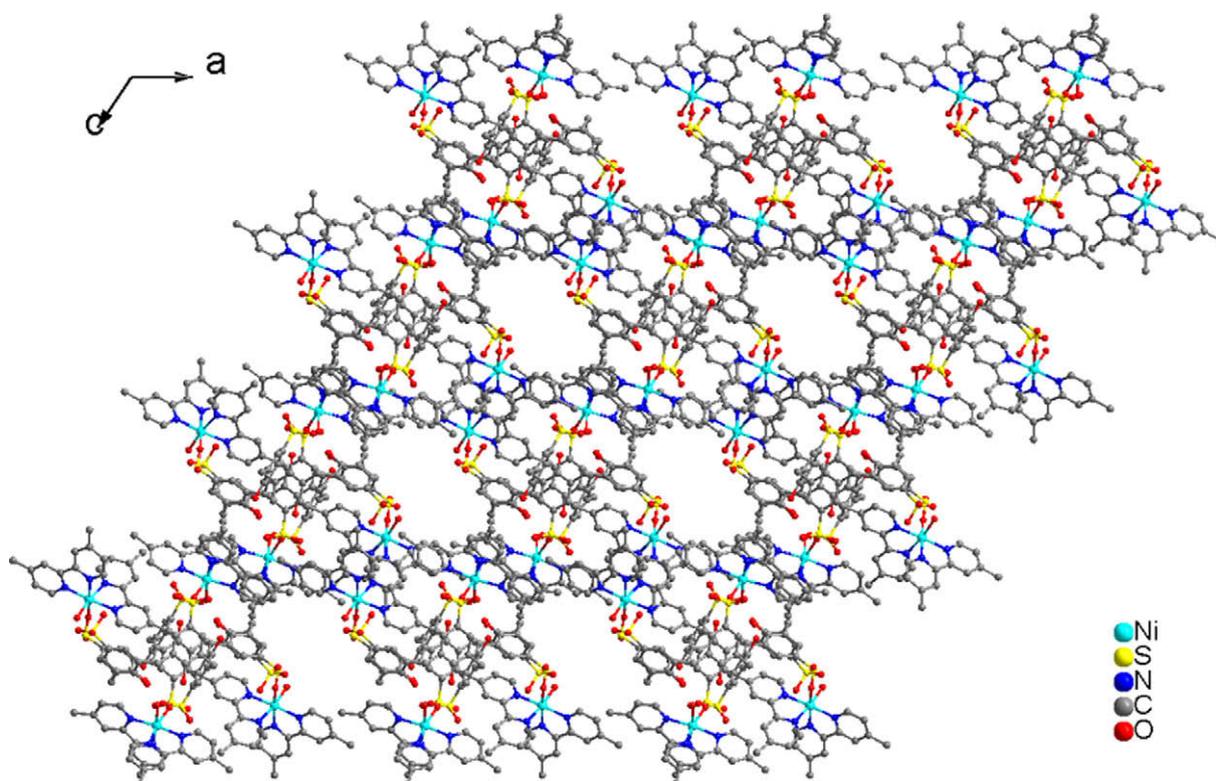


Fig. 4. View of the 3D supramolecular structure of complex 1.

3.2. Crystal structure of **1**

Compound **1** crystallizes in a monoclinic system in the space group $P2_1/c$. There are two independent nickel atoms and a half of C8AS molecule in an asymmetric unit. Both the nickel sites are six-coordinated by one water molecule, two chelating bipy molecules and one oxygen atom of sulfonate group. The distances of Ni–N bonds are located in the range of 2.04–2.08 Å and the Ni–O bonds being of 2.07–2.21 Å. A tetranuclear subunit with a whole C8AS molecule and four metals was generated by an inversion operation (Fig. 1). It is obvious that the C8AS molecule adopts a double partial cone conformation coordinated by four nickel ions (Fig. 2). According to the Uguzzoli–Andreotti convention [11], the actual φ and χ torsion angles values, which define the solid-state conformation of C8AS, are +79.7, –102.3; +82.9, –89.8; +12.5, +91.8; +93.3, +95.2; –79.7, +102.3; –82.9, +89.8; –12.5, –91.8; –93.3, –95.2. On close examination of the structure, one can find that the bipy molecule with N(7) and N(8) penetrates into the cavity of the partial cone of C8AS. The penetration depth [12] reaches 4.02 Å and the heterocyclic ring with N(8) of bipy molecule forms a $\pi\cdots\pi$ stacking interaction (face to face ca. 3.67 Å) with the calixarene aromatic ring. Otherwise all the other bipy molecules are located outside the calixarene cavity.

The intermolecular hydrogen bonds and C–H $\cdots\pi$ interactions (Tables 1 and 2, Fig 3) connected the tetranuclear Ni clusters into a 3D supramolecular structure. As shown in Fig. 4, the extended supramolecular structure has 1D channels occupied by the solvent water molecules.

3.3. TG–DTA and FT-IR analysis of complex **1**

As shown in Fig. 5, thermal gravimetric (TG) curve exhibits an obvious weight loss in the range of 30–365 °C, corresponding to the release of all the isolated water and coordinated water molecules. The whole weight loss (8.98%) agrees with the calculated value of 9.03%. The compound begins to decompose at 365 °C with a strong exothermic peak at 495 °C in the DTA curve. During the range of 365–520 °C, the TG curve shows a two-step weight loss corresponding to the combustion of the organic components. Later, the weight increases a little with the increasing temperature after 560 °C, which might be caused by the oxidation of the reductive intermediate product.

The features in the FT-IR spectra of compound **1** (Fig. 6) at 1618–555 cm^{-1} can be attributed to the C8AS and bipy molecules. Peaks at about 1040, 1167 cm^{-1} can be assigned to the vibration of $-\text{SO}_3$ group while the strong and broad peak at about 3427 cm^{-1}

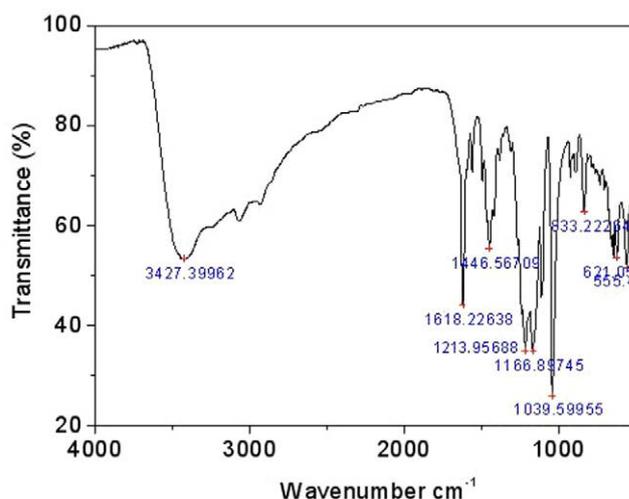


Fig. 6. FT-IR spectrum of compound **1**.

can be assigned to the contributions of $-\text{OH}$ group from both C8AS and the water molecules.

4. Conclusion

A ternary supramolecular complex of $[\text{Ni}(\text{bipy})_2(\text{H}_2\text{O})_4](\text{C8AS}) \cdot 17.6(\text{H}_2\text{O})$ has been synthesized by hydrothermal method. The X-ray diffraction determination reveals a 3D extended structure with 1D water-filled channels, in which the tetranuclear subunits of $[\text{Ni}(\text{bipy})_2(\text{H}_2\text{O})_4](\text{C8AS})$ are linked by hydrogen bonds and C–H $\cdots\pi$ interactions. *p*-Sulfonatocalix[8]arene molecule adopts here a double partial cone conformation.

Acknowledgements

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Appendix A. Supplementary data

CCDC 672264 contains the supplementary crystallographic data for this paper. These data 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 336033). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2009.08.023.

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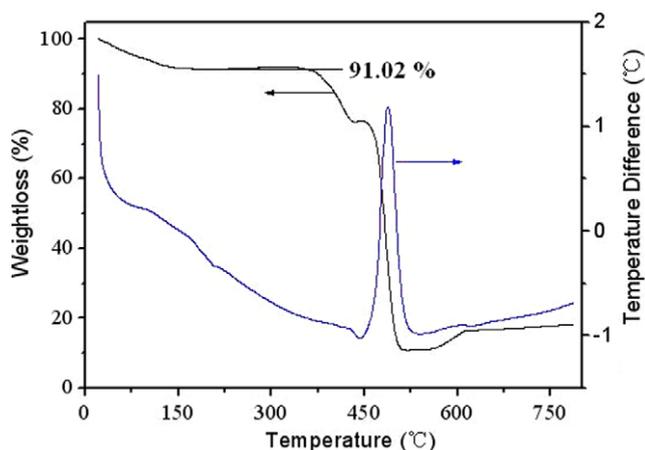


Fig. 5. TG–DTA curve of compound **1**.

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