Two organic salts mainly relying on hydrogen bonding: pyromellitic acid phenanthroline salts

Xiaoyong Tang[1,*], Guang Shi[2,b]

[1]School of Materials and Environment Zhuhai Campus of Beijing Institute of Technology Zhuhai 519088,P. R. China

[2]School of Chemistry South China Normal University Guangzhou 510006, P. R. China

*50240530@qq.com,bshiguang@scnu.edu.cn

Abstract. Two pure organic supramolecular complexes (Hphen)+[C6H2(COOH)3(COO)]- · H2O(1) and (Hphen)+ [C6H2(COOH)3(COO)]- (2) were synthesized by solution self-assembly method (natural volatilization method). The two organic salts were characterized by X-ray Single Crystal Diffraction, Elemental Analysis, Fourier Transform Infrared Spectrometer (FT-IR), Thermogravimetric Analysis (TG), Differential Scanning Calorimetry (DSC) and Fluorescence Spectroscopy (FL), etc. The results showed that two Organic complexes mainly rely on weak chemical effects such as hydrogen bonds to stably exist. Hydrogen bond is a bridge that connects molecules to form supramolecular compounds, it assembles ligand molecules (or ions) into new molecular aggregates with one-dimensional or multi-dimensional structure, and plays a huge role in the formation of the supramolecular structure of complexes. The complex (1) emits a strong characteristic spectrum of o-phenanthroline under 281 nm ultraviolet light.

Keywords: Pyromellitic acid；Phenanthroline；Crystal structure；Hydrogen bond; Self-assembly.

1. Introduction

In the structure construction of complexes, non-bonding interactions between molecules such as π-π stacking, hydrogen bonding, etc. have an important impact on the topological structure of the supramolecular complex formed[1]. Hydrogen bond is essentially electrostatic. As a long-range force with moderate strength and directionality, it has a clearer directionality than charge interaction and van der Waals force, and it plays a huge role in the formation of supramolecular structure. So it is often regarded as a bridge connecting molecules to form supramolecular compounds. Generally speaking, any oxygen or nitrogen atom with a free lone pair of electrons is defined as a hydrogen bond acceptor, and any hydrogen atom connected to oxygen or nitrogen is defined as a hydrogen bond donor. The hydrogen atom is compared with an electronegativity If the distance between large atoms is relatively short, hydrogen bonds may be formed. Among them, the C-H..O hydrogen bond, as a typical representative of weak hydrogen bonds, has important significance in crystal engineering [2,3].

It is an important research content in supramolecular chemistry, crystal engineering and other related fields that people use molecules (or ions) as templates to assemble molecules (or ions) into one-dimensional or multi-dimensional molecular aggregates through hydrogen bonds [4,5]. In this paper, two organic ligand complexes (Hphen)+[C6H2(COOH)3 (COO)]-·H2O (1) （CCDC No.682268）and (Hphen)+[C6H2 (COOH)3(COO)]- (2) （CCDC No.682393） were synthesized by self-assembly in solution. They are mainly connected by hydrogen bonding and exist stably.

2. Experimental

2.1 Experimental reagents and instruments

Phenanthroline (Abbreviated as phen) (AR), NaOH (AR), HNO3 (AR), Pyromellitic acid (Abbreviated as H4Btc) (AR), Ni(NO3)2·6H2O (AR). German Vario EL-III Elemental Analyzer; Perkin-Elmer 17300 FT-IR Infrared spectrometer, KBr tablet method, recording the infrared

spectrum data of the sample at 400~4000 cm-1; Thermogravimetric analysis (TG) in Germany Netzsch DSC1049-Under N2 atmosphere, the heating speed is 10°C/min; The fluorescence spectrum is recorded with the Hitachi F-2500 Fluorescence spectrophotometer; The single crystal X-ray diffraction: the single crystal is measured by Bruker SMART APEX II X-ray unit Crystal diffractometer measurement. The SHELXL-97 software package is analyzed by the direct method and refined by the least square method F2.

2.2 Synthesis of complexes (1) and (2)

(a) Synthesis of complex by self-assembly method in solution (1): Weigh pyromellitic acid (H4Btc) (0.5mmol), o-phenanthroline (phen) (0.5mmol) in a 100mL beaker, and add a volume ratio of 2:1 30 mL of ethanol-water mixed solution, adjusted to pH=6-7 with 40% KOH solution, placed in a magnetic stirrer controlled at 70-80°C under reflux and stirred for 6 hours, filtered while hot, the mother liquor evaporated naturally, and brown flake crystals were obtained after 2 days.

(b) Synthesis of complex by self-assembly method in solution (2): Weigh pyromellitic acid (H4Btc) (0.5mmol), phenanthroline (phen) (0.5mmol) in a 100mL beaker, and add a volume ratio of 1:1 30mL of ethanol-water mixed solution, adjust pH=7～8 with 40% KOH solution, put it under the control of a magnetic stirrer at 70～80°C, reflux and stir for 6h, filter while hot, the mother liquor will evaporate naturally, and a colorless stick-like crystal will be obtained after 4 days . Experimental results of elemental analysis of complex (2): C: 59.37; H: 3.19; N: 6.40; the theoretical value of complex C24H18Cl2N6O8(2): C: 60.78; H: 3.22; N: 6.45. FT/IR data (Blank is KBr tablet) (cm-1): 572(m), 719(s), 815(m), 844(m), 983(w), 1109(s), 1242(s), 1392(m), 1469(m), 1498(m), 1541(s), 1597(s), 1714(s), 2463(w), 2752(w), 3062(m), 3190(w).

2.3 X-ray crystallography experiments

A single crystal was glued on the top of glass fiber. Single crystal X-ray diffraction data collections of complex (1)-(2) were performed on a Bruker Apex II CCD diffractometer operating at 50 kV and 30 mA using Mo Ka radiation ($\lambda = 0.71073$ Å) at 293 K. Data collection and reduction were performed using the SMART and SAINT [6] software. A multi-scan absorption correction was applied using the SADABS program [7]. Two structures were solved by direct methods and refined by full-matrix least squares on F2 using the SHELXTL program package. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon were placed in geometrically idealized positions and refined using a riding model. Hydrogen atoms on water molecules or amino groups were located from difference Fourier maps and were refined using riding model. The final cycle of full-matrix least-squares refinement was based on 1160 (or 937) all reflections (I>2sigma(I)) and 92 (or 93) variable parameters and converged (the largest parameter shift was 0.00 times its esd.) with unweighted and weighted agreement factors of R=$\sum$｜C｜Fo｜－｜Fc｜｜/$\sum$｜Fo｜,Rw=[$\sum$w(｜Fo｜－｜Fc｜)2/$\sum$w｜Fo｜2]1/2 with w = 4｜Fo｜2 / σ2(｜Fo｜2)[7], respectively. CCDC numbers for the single crystals of complex (1) and (2) are 682268 and 682393. Crystal parameters and details of the data collection and refinement are given in Table 1.

3. Results and Discussion

3.1 Elemental analysis and IR spectra

Experimental results of elemental analysis of complex (1): C: 57.65; H: 3.28; N: 6.14; the theoretical value of complex C24H18Cl2N6O8(1): C: 58.36; H: 3.54; N: 6.19. FT/IR data (Blank is KBr tablet) (cm-1): 619(m), 719(m), 781(m), 815(s),844(s), 1109(s), 1242(s), 1392(m), 1469(s), 1541(s),1597(s),1714(s),2470(s),2620(s), 2879(w), 3076(w), 3522(m).

Experimental results of elemental analysis of complex (2): C: 59.37; H: 3.19; N: 6.40; the theoretical value of complex C24H18Cl2N6O8(2): C: 60.78; H: 3.22; N: 6.45. FT/IR data (Blank is

KBr tablet) (cm-1): 572(m),719(s), 815(m),844(m),983(w),1109(s),1242(s),1392(m),1469(m), 1498(m),1541(s),1597(s),1714(s),2463(w),2752(w),3062(m),3190(w).

The IR spectrum of complex (1) is shown in Figure 1a. Among them, the absorption peak at 3522 cm-1 is the stretching vibration of the O-H bond, and the absorption peak at 3076 cm-1 is the stretching vibration of the aromatic ring unsaturated C-H bond; there are aromatics at 1600~1580 cm-1 and 1500~1450 cm-1.

The strong absorption peak of the stretching vibration of the C=C double bond in the carbon skeleton of the ring indicates that the complex has an aryl group; at the same time, the stretching vibration of the ν(C=O) double bond in the carboxylic acid has a strong peak at 1714cm-1. There are strong peaks at 781cm-1 attributable to the three adjacent C-H bond surface bending vibration peaks on the phen pyridine ring. At the same time, the complex has a C-N bond stretching vibration peak at 1242 cm-1. These are consistent with the structure analysis results.

Table 1   Summarized crystal data and refinement parameters of (1) and (2)

Empirical formula	$C_{22}H_{16}N_2O_9$	$C_{22}H_{14}N_2O_8$
Formula weight	452.37	434.35
Crystal system	Triclinic	Monoclinic
space group	P -1	P2(1)/c
a(Å)	8.0221(2)	12.05860(1)
b(Å)	9.8342(2)	13.56240(1)
c(Å)	24.5485(6)	12.39570(1)
alpha(º)	94.897(2)	90
beta (º)	111.5600(10)	92.166(2)
gamma(º)	94.641(2)	90
Volume($Å^3$)	1921.31(8)	1885.40(3)
Z	4	4
Calculated density(g·cm⁻³)	1.564	1.530
Absorption coefficient(mm⁻¹)	0.124	0.119
F(000)	936.0	896.0
Crystal size(mm)	0.28 x 0.21 x 0.16	0.35 x 0.25 x 0.22
Theta range for data collection(º)	0.83 to 28.02	1.82 to 27.93
Reflections collected / unique	31301/9078[R(int)=0.0369]	23675/4519[R(int)=0.0308]
Completeness to theta = 28.02	97.7 %	99.6 %
Max. and min. transmission	0.9800 and 0.969	0.972 and 0.962
Data / restraints / parameters	9078 / 8 / 623	4502 / 0 / 299
Goodness-of-fit on F^2	1.009	1.044
Final R indices [I>2sigma(I)]	R1=0.0495,wR2=0.1307	R1=0.0414, wR2=0.1016
R indices (all data)	R1=0.1182, wR2= 0.1669	R1=0.0568, wR2=0.1107

$*R=\sum|C|Fo|-|Fc||/\sum|Fo|;wR=[\sum w(|Fo|-|Fc|)^2/\sum w|Fo|^2]^{1/2}$

The IR spectrum of complex (2) is shown in Figure 1b. The main peaks and their analysis are the same as those of the complex (1), except that there is no crystal water in the structure of the latter, and the O-H bond vibration peaks of water at 2470 cm-1 and 2620 cm-1 in the infrared spectrum have disappeared.
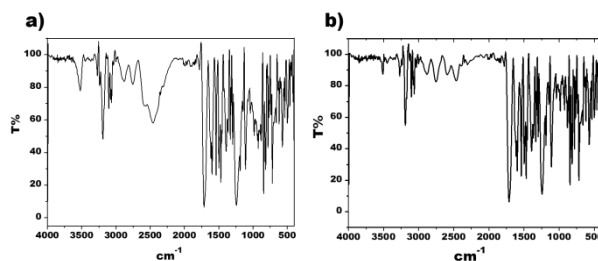

Figure 1. The IR spectrogram of complex (1)-a) and complex (2)-b).

3.2 Structure analysis

Single-crystal X-Ray diffraction analysis revealed the two compounds are new three-dimensional coordination polymers, (Hphen)+[C6H2(COOH)3(COO)]-·H2O(1)and (Hphen)+[C6H2(COOH)3(COO)]- (2). The asymmetric unit of complex (1) is shown in Figure 2. Its structural unit contains two [Hphen]+, two [H3btc]- （Pyromellitic acid trihydrogen ion）which shows -1 valence after one proton is removed, and two water molecules. These ions (or molecules) do not have the role of chemical bonds. The different colors in the figure more clearly indicate the

isolation between them. They are completely connected by hydrogen bonds, which makes the complexes extend into 2D or 3D network structures.
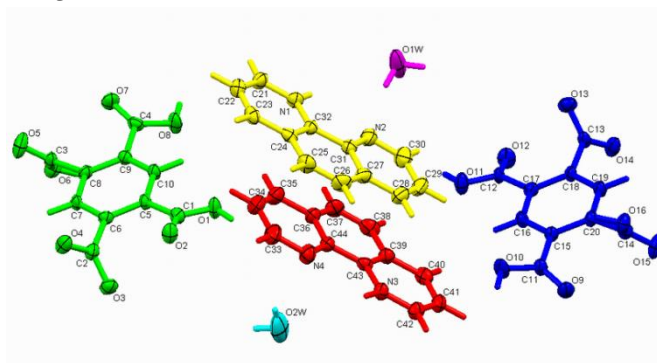

Figure 2. The asymmetric unit of complex (1).

In the complexes, there are intramolecular hydrogen bonds between the ortho carboxyl oxygen and hydrogen of the same [H3btc]-：between the carboxyl oxygen and the C-H on the aromatic ring （(O..O) spacing 2.956 Å and O..C spacing 2.943 Å）. There are intermolecular hydrogen bonds between [H3btc]- and free water, between free water and [Hphen]+, [Hphen]+ and [H3btc]-, forming a ring, as shown in Figure 3a, Figure 4.. The hydrogen bond H...A bond length of the complex varies from 1.51 Å to 2.57 Å, the distance between D..A varies from 2.4337 Å to 3.3613 Å, and the bond angle of D-H..A ranges from 100° to 175° (Where D represents C, N, O atoms that donate electrons, and A represents O or N atoms that accept electrons). The hydrogen bonds of (1) are listed in Table 2.

The asymmetric structural unit of complex (2) is shown in Figure 3. In this basic structural unit, there is a protonated phenanthroline，represented as [Hphen]+, and two pyromellitic acid trihydrogen radicals that are coupled to remove one proton，written as [H3Btc]-, which makes the entire molecule appear electrically neutral. Compared with the complex (1), the complex (2) has no crystal water, and the space group is P2(1)/c, which belongs to the monoclinic crystal system. In the complex, two adjacent [H3Btc]- are connected by H bridges and intermolecular hydrogen bonds, while [H3Bta]- and [Hphen]+ are connected by intermolecular hydrogen bonds to form a one-dimensional chain structure, as shown in Figure 4b. In complex (2)，the bond length of H..A varies from 1.30 Å to 2.58 Å, the distance between D..A varies from 2.4541 Å to 3.4656 Å, and the bond angle of D-H...A ranges from 101° to 167°. The hydrogen bonds of complex (2) is shown in Table 3.

In these two compounds, the bridging effect is all hydrogen bonds, and there is no obvious π-π stacking effect in the two complexes. The hydrogen bond is essentially electrostatic.

Table 2   Hydrogen-bond geometry (Å , °) of complex (1)

D－H....A	D - H	H...A	D...A	D - H...A
O(1)－H(1)..O(1W)[1]	0.82	1.75	2.5634	175
N(1)－H(1B)..O(2)[3]	0.90	2.04	2.7346	134
N(1)－H(1B)..N(2)[3]	0.90	2.41	2.7625	103'
O(1W)－H(1W)..O(15)[3]	0.84	1.96	2.7330	152
O(1W)－H(2W)..N(2)[3]	0.84	2.20	3.0175	163
N(3)－H(3B)..N(4)[3]	0.90	2.36	2.7626	107
N(3)－H(3B)..O(12)[4]	0.90	2.07	2.7382	130
O(2W)－H(3W)..O(5)[2]	0.85	1.89	2.7392	171
O(6)－H(6A)..O(3)[2]	0.92	1.51	2.4337	175
O(8)－H(8)..O(4)[3]	0.82	1.85	2.6656	171
O(10)－H(10A)..O(14)[3]	0.82	1.86	2.6642	169
O(11)－H(11)..O(2W)[4]	0.82	1.76	2.5717	169
O(16)－H(16A) ..O(13)[4]	0.91	1.55	2.4346	163
C(10)－H(10)..O(1)[4]	0.93	2.41	2.7332	100
C(16)－H(16)..O(11)[4]	0.93	2.42	2.7372	100
C(21)－H(21)..O(2)[3]	0.93	2.53	2.9694	109
C(21)－H(21) ..O(7)[5]	0.93	2.43	3.0970	129
C(22)－H(22)..O(4)[6]	0.93	2.39	3.2714	159
C(23)－H(23)..O(5)[6]	0.93	2.33	3.2523	174
C(26)－H(26)..O(16)[6]	0.93	2.52	3.3320	146
C(30)－H(30)..O(11)[7]	0.93	2.57	3.3613	143
C(33)－H(33)..O(1)[7]	0.93	2.57	3.3542	142
C(37)－H(37)..O(6)[8]	0.93	2.49	3.3150	148
C(40)－H(40)..O(15)[9]	0.93	2.33	3.2555	173
C(41)－H(41)..O(14)[9]	0.93	2.38	3.2641	158
C(42)－H(42)..O(9)[9]	0.93	2.43	3.0966	128
C(42)－H(42)..O(12)[4]	0.93	2.53	2.9682	110

Symmetry code: 1)x,-1+y,z; 2)1-x,-y,-z; 3)x,1+y,z; 4)1-x,-y,1-z; 5)-x,1-y,-z; 6)-x,-y,-z; 7)1-x,1-y,1-z; 8)1-x,1-y,-z; 9)1+x,1+y,z.

Table 3   Hydrogen-bond geometry (Å , °) of complex (2)

D－H....A	D－H	H...A	D...A	D－H...A
N(1)－H(1A)..O(7)[1]	0.91	2.17	2.9162	138
N(1)－H(1A)..N(2)[1]	0.91	2.32	2.7191	106
O(2)－H(2A)..O(6)[1]	1.16	1.30	2.4541	174
O(4)－H(4A)..O(5)[2]	0.82	1.83	2.6213	163
O(8)－H(8A)..O(1)[3]	0.82	1.74	2.5388	166
C(2)－H(2)..O(3)[4]	0.93	2.53	3.1992	129
C(5)－H(5)..O(4)[5]	0.93	2.58	3.3884	145
C(6)－H(6)..O(1)[6]	0.93	2.54	3.4528	167
C(8)－H(8)..O(8)[7]	0.93	2.57	3.4656	163
C(9)－H(9)..O(5)[8]	0.93	2.55	3.4057	153
C(22)－H(22)..O(8)[1]	0.93	2.37	2.7102	101

Symmetry code: 1) 1-x,1-y,1-z;   2) 1-x,1/2+y,1/2-z;   3) x,1/2-y,1/2+z;
4) 1-x,-1/2+y,1/2-z;   5) x,-1+y,z;   6) 1+x,1/2-y,1/2+z;   7) 2-x,-y,1-z;
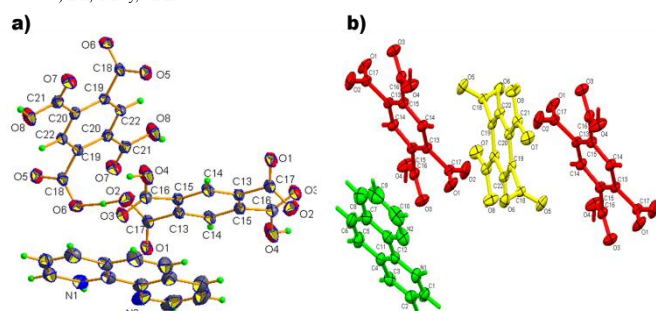8) 2-x,-1/2+y,3/2-z.

Figure 3. a) The asymmetric unit of complex (2); b) The molecule structure of complex (2).

As a long-range force with moderate strength and directionality, it plays a huge role in the formation of supramolecular structure. Therefore, it is often regarded as a bridge connecting molecules to form supramolecular compounds. In comlplex (2), the coupling of two pyromellitic acids through H atoms is actually a hydrogen bond [8]. The intermolecular or intramolecular hydrogen bonds in the basic structural units of complex (1) and (2) are shown in Figure 4.
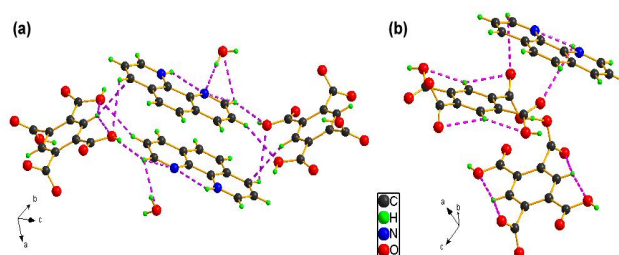
Figure 4. The intermolecular or intramolecular hydrogen bonds in basic unit of complex (1)-(a) and complex (2)-(b).

For the crystal structure of the complex (1) observed along the a-axis, the pyromellitic acid radicals are connected to form a one-dimensional chain in the transverse direction through adjacent intermolecular hydrogen bonds O-H..O. In the longitudinal direction, pyromellitic acid and water molecules form a hydrogen bond OH..O is connected to form a one-dimensional chain structure, where hydrogen bonds such as H(3W)..O(5) The bond length is 1.89 Å and H(11)..O(2W) bond length is 1.76 Å, (as shown in Figure 5a). The vertical and horizontal one-dimensional chains are staggered to form a pore structure，the pore size is 11.919 Å in length and 9.077 Å in width, and the effective pore area reaches 50 Å2 or more (7.039×7.634 Å2)), as shown in Figure 5b, [Hphen]+ is filled in these cavities. In the b-axis direction, [H3btc]- and [Hphen]+ are arranged longitudinally spaced by hydrogen bonds to form the ABAB two-dimensional planar structure shown in Figure 5c.
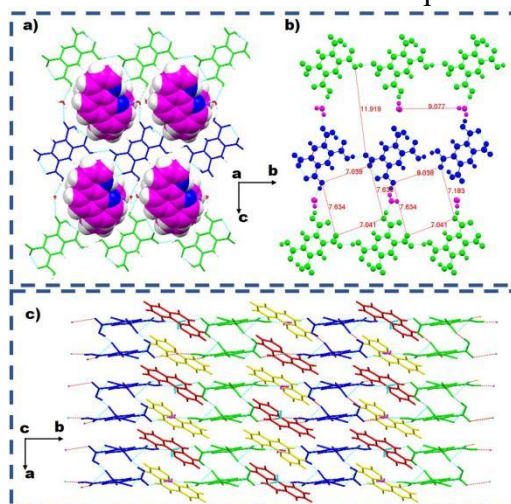

Figure 5. a) Views of 2-D network linked by H-bonds and the molecular arrangement along a-axis with the ligands monomer in different colour of complex (1)；b) View of the structure linked by H-bonds and showing the hole of complex (1) when omited [Hphen]+；c) The molecular arrangement view along b-axis with the ligands monomer in different colour of complex (1).(The blue dashed lines were showing intermolecular or intramolecular hydrogen bonds，The red dashed line and the red number indicate the distance between two atoms to show the size of the hole.)

In complex (2), [H3Btc]- and [Hphen]+ are evenly spaced in the a-axis direction. On the one hand, the aromatic rings of the two pyromellitic acid radicals ([H3Btc]-) overlap each other. Each [Hphen]+ is connected to two [H3Btc]- through hydrogen bonds and distributed in the cavity surrounded by four [H3Btc]- to form a 2D network structure (as shown in Figure 6a). In the b-axis direction, the complex (2) is connected into an inclined linear structure through the hydrogen bond between adjacent [H3btc]- ions, as shown in Figure 6b, while [Hphen]+ is filled between the inclined lines connected by [H3btc]- through the hydrogen bond, so that the complex forms a stable two-dimensional network structure.

The complex (2) is arranged into an interesting ABAB shaped spacer chain structure in two vertical and horizontal mutually perpendicular ways in the c direction, as shown in Figure 6c. In the figure, the two mutually perpendicular trihydrogen ions of benzoic acid are distinguished by red and yellow colors.
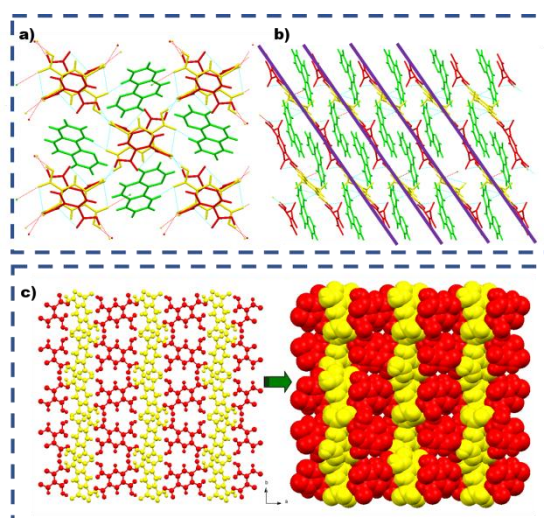
Figure 6. a) The crystal structure of complex (2) with a view along a axis； b) View of the 2-D network which was formed by alternation tactic btc and phen along b axis of complex (2)；c) View of the ABAB packing structure along c-axis of complex (2), and the ABAB structure was constructed by btc only, Omited phen for clarity，the right for spacefill mode. (In Figure a and b,the blue dashed lines were showing the intermolecular or intramolecular hydrogen bonds.)

3.3 TG and DSC analysis of complexes (1) and (2)

The TG and DSC curves of complex (1) are shown in Figure 7a. It can be seen from the figure that the weight loss of the complex can be regarded as two stages. There is a small step in the short temperature range of 203.27 ℃~ 256.78 ℃, corresponding to the loss of crystal water, the weight loss is 11.23% (theoretical value is 8.96%), and then the complex decreases sharply with the increase of temperature from 256.78 ℃ to about 401.67 ℃, and the complex is basically completely decomposed.The TG and DSC curves of complex (2) are shown in Figure 7b. Relative to complex (1), there is no loss of crystal water.
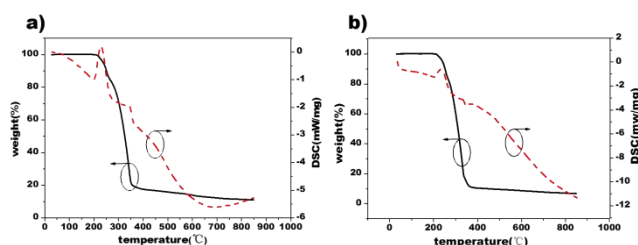
Figure 7. TG and DSC curves of complex (1)-a) and complex (2)-b).

The complex begins to decompose obviously at about 223.69 ℃ and completely decomposes at about 398.35 ℃, basically without residue. The decomposition temperature and complete decomposition temperature are slightly lower than that of complex (1).

3.4 Fluorescence spectrum analysis of complex (1)

The solid-state fluorescence spectrum of complex (1) is shown in Figure 14. It can be seen from the figure that under the excitation of 281nm excitation light, complex (1) has relatively strong emission at 393nm and 416nm, which can be attributed to the characteristic excitation spectrum of phen ligand[9], while the fluorescence of complex (2) is much weaker than that of complex (1), which can not be shown in the figure, but the fluorescence wavelength is roughly the same.
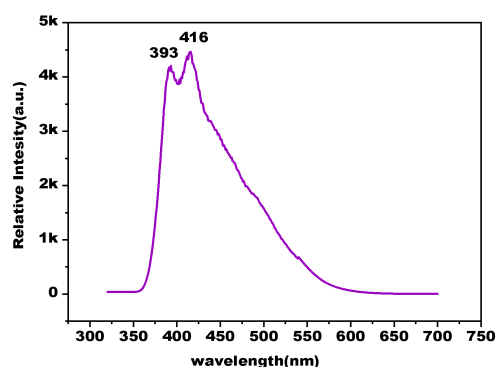
Figure 8. Solid fluorescence spectrogram of complex (1)(λ_{ex}= 281nm).

4. Conclusion

Complexes (1) and (2) are stable supramolecular structures constructed by hydrogen bonding with trimethyl benzoate ion（[C6H2(COOH)3(COO)]-）and protonated o-phenanthroline [(Hphen)+]. Among them, each crystal cell of complex (1) also brings in a molecule of water, which makes the hydrogen bond formed more abundant. TG and DSC show that its stability is also slightly higher than that of complex (2). Complex (1) has strong o-phenanthroline characteristic fluore- scence under the excitation of 281nm ultraviolet light. This also fully shows that in the structure of complexes, non-bonding interactions between molecules, such as hydrogen bonding, π-π stacking, etc., can have an important impact on the topological structure of the supramolecular complexes formed. As a long-range force with moderate strength and directivity, weak chemical interaction hydrogen bond has a clearer directivity than charge interaction and van der Waals force, and plays a great role in the formation of supramolecular structure, Assembling molecules (or ions) into molecular aggregates with one-dimensional or multi-dimensional structure through hydrogen bonding is an important direction in supramolecular chemistry, crystal engineering and other related fields.

Acknowledgment

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