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Substituted group directed assembly of energetic lead(II) compounds based on structure-relevant ligands

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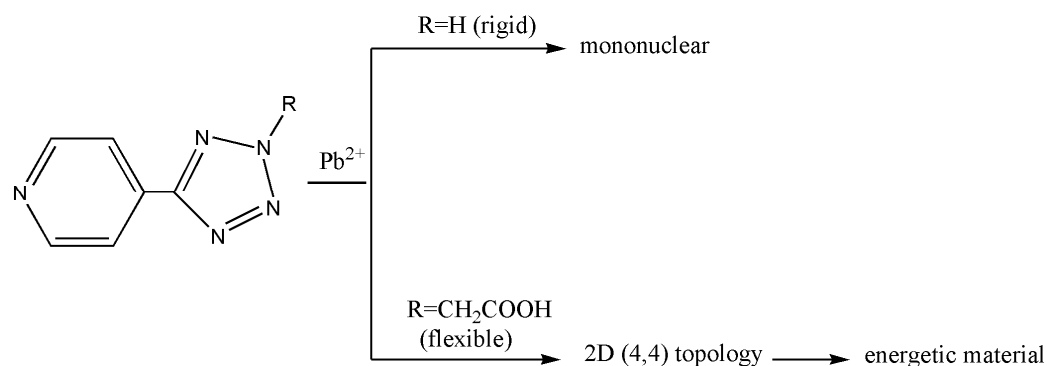
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5-(4-pyridyl)tetrazole (Hpytz) and 5-(4-pyridyl)tetrazole-2-acetic acid (Hpytza) and their Pb(II) compounds were prepared. The substituted group not only influences the crystal structures of these coordination compounds but also the thermal behavior. The luminescence properties were investigated. The DSC tests show compound **2** can be used as potential explosive materials. For compound **2**, the apparent activation energy E_a , pre-exponential constant A , critical temperature of thermal explosion T_b , thermodynamic parameters were calculated.



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Abstract: Reactions of two structure-relevant ligands, Hpytz [Hpytz=5-(4-pyridyl)tetrazole] and its 2*H*-tetrazole-carboxylate substituted derivative Hpytza [Hpytza=5-(4-pyridyl)tetrazole-2-acetic acid] with Pb(NO₃)₂ under the presence of potassium hydroxide, afforded a new mononuclear [Pb(pytz)₂(H₂O)₄]·3H₂O(**1**) and a two dimensional polymer [Pb(pytza)₂]_n (**2**) with (4,4) topology, respectively. The two compounds were characterized by elemental analysis, IR and single crystal X-ray diffraction. The luminescence properties of compounds **1** and **2** investigated at room temperature in the solid state show both intraligand emission and characteristic peak of Pb²⁺. Differential scanning calorimetry (DSC) and thermogravimetric-differential thermogravimetric (TG-DTG) analyses were applied to assess the thermal decomposition behavior of compounds **1** and **2**. The DSC test indicates that compound **2** can be taken advantaged of as a potentially explosive material.

Keywords: Hpytz/Hpytza; Pb(II); crystal structure; luminescence; energetic material

Introduction

The design and preparation of new energetic materials, such as lead salts[1], oxides[2], organic compounds [3] and coordination compounds[4] have attracted huge attention of scientists over the past decades. So far, it is universally acknowledged that tetrazole and its derivatives with high nitrogen percentage are potentially candidates as explosive materials[4]. For some time, we are dedicated to the design and synthesis of coordination compounds based on tetrazole derivatives, where we found that the different substituted group may not only have a great impact on the rigidity and flexibility of these ligands, thus leading to structure variation of such coordination compounds, but also influence their physical and chemical properties[5]. Owing to the excellent physical and chemical performance of lead(II) compounds, investigations on them are still of enormous significance, before other substitutes are developed, the application of which may lead to the toxic metal pollution, though. There is a need for exploiting the unique coordination chemistry of Pb(II) for the development of practical ligands as extractants, lead-poisoning treatment agents and sensors as well as energetic materials[6]. Therefore, such investigations are both theoretically and practically meaningful. For example, in 2011, *Zhang et.al* reported a three dimensional lead(II) compound $[Pb(tza)_2]$, where tza=tetrazole-1-acetato, with high energetic performance, which can be used as a potential energetic material[7]. And in 2012, *Fan et.al* reported two interesting lead(II) compounds with both intriguing topology with lifelong luminescence based on secondary building sites (SBU) $Pb(OH)_4^{4+}$ and 1,4-bis(tetrazol-5-yl)benzene[8]. However, investigations concerning such compounds both in structure and potential application are limited. Inspired by the observations, we have chosen a new rigid tetrazole derivative, namely, 5-(4-pyridyl)tetrazole (Hpytz) to be reacted with $Pb(NO_3)_2$ under the presence of potassium hydroxide, one new compound $[Pb(pytz)_2(H_2O)_4] \cdot 3H_2O$ (**1**) was obtained. When the hydrogen atom of the tetrazole ring was substituted by a carboxylate group,

Hpytz transfers from a rigid ligand to the flexible 5-(4-pyridyl)tetrazole-2-acetic acid (Hpytza) in which the $-\text{CH}_2-$ spacer between the tetrazolyl ring and the carboxylate group can offer flexible orientation of the carboxylate arm, allowing the formation of multiple structures[9]. Similar reactions of Hpytza with $\text{Pb}(\text{NO}_3)_2$ results in the formation of $[\text{Pb}(\text{pytza})_2]_n$ (**2**). In this paper, the luminescence properties of Hpytz, Hpytza, compounds **1** and **2** in the solid state were investigated at room temperature. Furthermore, differential scanning calorimetry (DSC) and thermogravimetric-differential thermogravimetric (TG-DTG) analyses of **1** and **2** show compound **2** is a good candidate for energetic material.

2. Experimental section

2.1 Materials and instruments

The ligands were prepared according to the literature methods[5,10]. Other chemicals were commercially available reagents of analytical grade used without further purification. The elemental analysis for C, H and N were obtained on a Perkin-Elmer 2400 microanalyzer. The IR spectra were recorded ($4000-400\text{ cm}^{-1}$) on a NICOLET 380 spectrometer with pressed KBr pellets. The photoluminescence spectra were recorded on a Hitachi F-4600 spectrofluorometer. Thermogravimetric analysis(TGA) and DSC experiments were carried out on a Perkin-Elmer TGA 7 thermogravimetric analyzer with the heating rate of $10^\circ\text{C}/\text{min}^{-1}$ from 30 to 600°C under nitrogen atmosphere.

2.2 Synthesis of $[\text{Pb}(\text{pytz})_2(\text{H}_2\text{O})_4] \cdot 3\text{H}_2\text{O}$ (**1**)

Hpytz (0.0147g, 0.1mmol) was dissolved in distilled water (3mL), and the pH value was adjusted to 6 with KOH solution (0.2M). Then $\text{Pb}(\text{NO}_3)_2$ (0.0662g, 0.2mmol) was added, the mixture was heated at 80°C for 1 h and then cooled to room temperature, slow evaporation give colorless prismatic crystals of **1**. For **1**, yield: 45% based on Pb^{2+} . Anal. Calcd. for $\text{C}_{12}\text{H}_{22}\text{N}_{10}\text{O}_7\text{Pb}$: C, 23.04; H, 3.54; N, 22.39%. Found: C, 23.23; H, 3.50; N, 22.56%. IR (KBr, cm^{-1}): 3381(s), 1528(s), 1437(m), 1384(s), 1099(w),

1045(w), 1015(w), 846(m), 755(w), 713(w).

2.3 Synthesis of $[Pb(py\text{tza})_2]_n$ (**2**)

A similar procedure to compound **1** was adopted to prepare compound **2** except that Hpytz was replaced by Hpytza (0.0205g, 0.1mmol). Light orange block crystals of **2** were obtained. For **1**, yield: 47% based on Pb^{2+} . Anal. Calcd. for $C_{16}H_{12}N_{10}O_4Pb$: C, 31.22; H, 1.97; N, 22.76%. Found: C, 31.23; H, 2.02; N, 22.66%. IR (KBr, cm^{-1}): 1668(m), 1624(s), 1590(m), 1565(w), 1455(w), 1425(w), 1385(s), 1265(w), 1050(w), 727(m), 683(m).

2.4 X-Ray crystallography

Single crystal X-ray crystal data were collected on a Rigaku SCX mini CCD diffractometer equipped with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). The intensity data were collected by the ω scan technique and were reduced using the Crystal-Clear program[11], and an absorption correction (multi-scan) was applied. The reflection data were also corrected for Lorentz and polarization effects. The structures were solved by direct methods and refined on F^2 by full matrix least squares using SHELXTL[12]. All the non-hydrogen atoms were located from the Fourier maps and were refined anisotropically. All H atoms were refined isotropically, with the isotropic vibration parameters related to the non-H atom to which they were bonded. Crystallographic data are summarized in Table 1. Selected bond lengths and angles are listed in Table 2. Compounds **1-2** are deposited with CCDC number 1413198-1413199.

Table 1-2 here

3. Results and discussions

3.1 Synthesis consideration and general characterization of compounds **1** and **2**

In this paper, two structure-relevant ligands, 5-(4-pyridyl)tetrazole and 5-(4-pyridyl)tetrazole-2-acetic acid with different flexibility were selected to be

reacted with $\text{Pb}(\text{NO}_3)_2$. Compounds **1** and **2** can also be obtained when the reaction system was sealed in a 25 mL teflon-lined stainless steel container and heated at 120°C for 24h or $\text{Pb}(\text{NO}_3)_2$ was replaced by $\text{Pb}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$, $\text{Pb}(\text{OAc})_2 \cdot 3\text{H}_2\text{O}$, showing the temperature and anion have little influence on the formation of the two compounds. The elemental analyses were consistent with their chemical formula. In the IR spectra of **1**, strong absorption at 3381 cm^{-1} is ascribed to the O-H vibration of both coordinated and uncoordinated water molecules. Compound **2**, however, does not show a similar peak in that it contains neither coordinated nor uncoordinated waters. Compound **2** show an asymmetric -COO vibration peak at 1617 cm^{-1} while **1** does not. For compound **2**, the symmetric vibration of the carboxylate may be overlapped by the typical peaks ($1568\text{-}1384\text{ cm}^{-1}$) of the tetrazole and pyridine rings. The identities of **1-2** were finally confirmed by X-ray crystallography. It is worthwhile to point out that compounds **1** and **2** can be hardly dissolved in water and some common organic solvents, such as DMF, DMSO, this makes it easy to be separated from the system. Also, compounds **1** and **2** are stable towards acid or base.

3.2 Crystal structure of $[\text{Pb}(\text{pytz})_2(\text{H}_2\text{O})_4] \cdot 3\text{H}_2\text{O}$ (**1**)

The X-ray diffraction reveals that compound **1** crystallizes in the triclinic lattice space group $P\bar{1}$. As shown in Fig1, each Pb(II) center is hexacoordinated by two nitrogen atoms from two pyridyl rings of two pytz ligands and four oxygen atoms from four water molecules, forming a severely distorted octahedral coordination arrangement. The Pb-O bond lengths ranging from 2.370 to 2.698 \AA are in good agreement with those of $[\text{Pb}(\text{pztza})_2] \cdot \text{H}_2\text{O}$ [13] (pztza=5-(2-pyrazinyl)tetrazole-2-acetato) and a little longer than those of $[\text{Pb}(\text{atza})_2\text{Cl}]$ or $[\text{Pb}(\text{a4-ptz})_2\text{Cl}]$ (atza=5-aminotetrazole-1-acetato, a4-ptz=5-[N-acetato(4-pyridyl)tetrazole])[14]. So are the Pb-N bond lengths. Compared with $[\text{Pb}_4(\text{OH})_4(\text{BDT})_2] \cdot 2\text{H}_2\text{O}$ (BDT=1,4-benzeneditetrazol-5-ylanion) which consists of a cubic $\text{Pb}(\text{OH})_4^{4+}$ and two BDT^{2-} anion[8], pytz only acts as a monodentate ligand to coordinate to one Pb(II) center via the nitrogen atom of the pyridyl ring, thereby forming a mononuclear structure, which is analogous to that of $[\text{Cd}(\text{pytz})_2(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}$ [10]. The dihedral angles between the tetrazole and pyridine

rings are 1.670 and 8.025°, respectively. Adjacent mononuclear units are held together, forming a 3D supramolecular network (FigS1, TableS), as result of eight hydrogen bonds between the coordinated water and the nitrogen atom of the tetrazolyl ring [O(1)—H(1B)⋯N(7), O(4)—H(4C)⋯N(8)], between the coordinated water and the oxygen atom of the guest water [O(1)—H(1C)⋯O(5), O(2)—H(2C)⋯O(7), O(4)—H(4B)⋯O(5)], between the guest water and the nitrogen atom of the tetrazolyl ring [O(5)—H(5B)⋯N(9)], between the guest water and the oxygen atom of the coordinated water [O(5)—H(5C)⋯O(4)] and between the C-H group of the pyridyl ring and the oxygen atom of the coordinated water [C(4)—H(4A)⋯O(4)].

Fig 1 here

3.3 Crystal structure of [Pb(pytza)₂]_n (2)

The X-ray diffraction analysis reveals that compound **2** consists of one Pb²⁺ and two pytza ligands with monoclinic space group *P2₁/n*. As shown in Fig2, each Pb(II) center is in a slightly distorted octahedral coordination arrangement surrounded by two nitrogen atoms from two pyridyl rings of two pytza ligands and four oxygen atoms from four carboxylate groups. The Pb-O (Pb-N) bond lengths from 2.530 to 2.558Å (2.666Å) fall in the range of those of [Pb(tza)₂][7] or [Pb₃(pypza)₃Cl₄][15] where tza=tetrazole-1-acetato and pypza=3-(2-pyridyl)-1-pyrazolyl acetato. Compared with [Pb(a4-ptz)₂Cl][14] or [Pb(3-pytza)₂][16] which derive from 5-(3-pyridyl)tetrazole-2-acetic acid or 5-[N-acetato(4-pyridyl)]tetrazole, two isomers of 5-(4-pyridyl)tetrazole-2-acetic acid, each pytza in compound **2** acts as a tridentate ligand to bridge three Pb(II) centers via the nitrogen atom of the pyridyl ring and two carboxylate atoms in a μ_{1,3}-COO *syn-anti* mode, thereby forming a two dimensional layer structure(Fig3(a)). The structure can be simplified as a (4,4) rhomboidal grid topology with diagonal lengths of 11.814 and 13.789Å(Fig3(b)). All the dihedral angles between the tetrazole and pyridine rings are 2.900°. When the hydrogen atom of the tetrazole ring is substituted by a carboxylate group, the structure of compound **2** is substantially distinct since the coordination of the carboxylate group not only

increases the dimension of the structure, but also prevents the coordination of the water molecule. There are no classic hydrogen bonds in compound **2**. Non-classic hydrogen bonds, however, exist between the C-H group of the carboxylate group and the oxygen atom of the carboxylate group [C(2)—H(2A)···O(2)], the C-H group of the tetrazolyl ring and the oxygen atom of the carboxylate group [C(3)—H(6)···O(2)], the C-H group of the pyridyl ring and the oxygen atom of the carboxylate group [C(7)—H(7)···O(1)] and the C-H group of the pyridyl ring and the nitrogen atom of the tetrazolyl ring [C(8)—H(8)···N(4)], by which adjacent layers are held together to generate a three dimensional supramolecular network(FigS2, TableS).

Fig 2-3 here

3.4 Luminescence properties

In view of the potential application of lead(II) compounds in photochemistry, we are dedicated to investigating the luminescence properties of Hpytz, Hpytza, compounds **1** and **2** at room temperature in the solid state. As shown in Fig4, Hpytz and Hpytza exhibits emission with maximum intensity at 465 and 393nm upon excitation at 383 and 327nm, respectively. In contrast to Hpytz, a blue shift of 72nm was observed for Hpytza, which may be probably caused by the carboxylate group. Compounds **1** and **2** show maximum emission peaks at 410, 516 nm and 435, 538 nm upon excitation at 327 and 394 nm, respectively. The peaks at 410 and 435 nm are ascribed to the ligand centered emission since similar emission peaks were observed for the free ligands, respectively. Compared with Hpytz and Hpytza, a blue shift of 55nm of compound **1** and a red shift of 42 nm of compound **2** was observed. Generally, the intraligand fluorescence emission wavelength is related to the extent of π conjugation and determined by the energy gap between the π and π^* molecular orbitals of the free ligands[13-16]. Peaks at 516 and 538 nm are tentatively attributed to the metal-centered transition of Pb^{2+} , involving the s and p metal orbit as proposed by Vogler [13]. Compared with Hpytz, compound **1** exhibits weaker emission, this can be explained by the fact that compound **1** contains either coordinated or uncoordinated

water molecule, whose O-H oscillator quenches luminescence. To the opposite, however, compound **2** contains neither coordinated nor guest water molecules, whose emission intensity is stronger than Hpytza.

Fig4 here

3.5 TG , DTG and DSC of compounds **1** and **2**

To characterize the thermal stabilities of compounds **1** and **2**. The thermogravimetric analysis of compounds **1** and **2** were investigated from 30 to 600 °C under nitrogen atmosphere. From the TG and DTG curve, compound **1** show initial weight loss of 20.65% from 71 to 208°C, which may be ascribed to the removal of both coordinated and uncoordinated water molecules (calculated 20.16%), further weight loss starting at 298°C are attributed to the collapse of the framework(Fig5(a)). Compound **2** begins to decompose at 277°C of pytza ligands(Fig6(a)), leading to the collapse of the coordination polymer. From the DSC curve(Fig5(b),Fig6(b)), two endothermic peaks at 86.6, 196.6°C and an exothermic one at 327.2°C were found, respectively, while an exothermic one of compound **2** at 290.2°C was also observed. The exothermic enthalpy of compounds **1** and **2** are calculated as $189.6\text{J}\cdot\text{g}^{-1}$ and $-456.1\text{J}\cdot\text{g}^{-1}$, respectively, indicating the decomposition of compound **1** is an endothermic process while that of compound **2** is an exothermic one. Therefore, it is apparent that the substituted group make a great difference on the thermal behavior of these compounds.

Fig5-6 here

3.6 Non-isothermal kinetics of compound **2**

Since the decomposition of compound **1** is an endothermic process while that of compound **2** is an exothermic one. For exploring potential energetic materials, theoretical calculation was applied to estimate the energy of compound **2**. Kissinger's method [17](equation1) and Ozawa's method [18,19] (equation2) were applied to understand the decomposition mechanism and calculate the apparent activation energy ($E_a/\text{kJ}\cdot\text{mol}^{-1}$) and pre-exponential constant (A/s^{-1}).

$$\ln(\beta/T_p^2) = \ln(RA/E_a) - E_a/(RT_p) \quad (1)$$

$$\lg\beta + 0.4567E_a/(RT_p) = C \quad (2)$$

Where T_p stands for the peak temperature (K); R represents the gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$); β is the linear heating rate ($\text{K}\cdot\text{min}^{-1}$); C is a constant. The peak temperature in the non-isothermal DSC curves are correspondent to the same conversion degrees at various heating rate.

The peak temperatures of the first exothermic process at different heating rates (5, 10, $20 \text{ K}\cdot\text{min}^{-1}$) of $[\text{Pb}(\text{pytza})_2]_n$ are 535, 550 and 563K. The apparent activation energy calculated by Ozawa's method is $E_o = 118.6 \text{ kJ}\cdot\text{mol}^{-1}$, which is approximately in agreement with that of the Kissinger method $E_k = 115.6 \text{ kJ}\cdot\text{mol}^{-1}$. The pre-exponential constant $\ln A_k$ was calculated as 24.5. And the Arrhenius equations can be expressed as follows: $\ln k = 24.5 - 117.1 \times 10^3/RT$, where E stands for the average value of E_k and E_o .

3.7. Critical temperature of thermal explosion of compound 2

T_b , the critical temperature of thermal explosion, is an important parameter for energetic materials in terms of thermal safety, referring to the lowest temperature to which a specific charge might be heated without undergoing thermal runaway. In order to obtain the critical temperature of thermal explosion of $[\text{Pb}(\text{pytza})_2]_n$, the following equations were used [20].

$$T_{pi} = T_{p0} + b\beta_i + c\beta_i^2 \quad (3)$$

$$T_{bp} = \{E_o - [E_o^2 - (4E_oRT_{p0})]^{1/2}\} / 2R \quad (4)$$

The value of the peak temperature is 550 K of the first exothermic step of $[\text{Pb}(\text{pytza})_2]_n$ when $\beta \rightarrow 0$, where b and c are coefficients. The corresponding critical temperature of thermal explosion (T_{bp}) obtained from the above equation is 573 K, where R stands for the gas constant, E_o represents the apparent activation energy calculated by Ozawa's method.

3.8 Thermodynamic parameters of compound 2

The thermodynamic parameters of the decomposition of compound 2 were calculated based on E_a and A . The entropy of activation (ΔS), enthalpy of activation (ΔH), and

free energy of activation (ΔG) of the first exothermic decomposition reaction of $[\text{Pb}(\text{pytza})_2]_n$ corresponding to $T = T_{p0}$, $E_a = E_K$, and $A = A_K$ obtained by the following equations[21-24] are $\Delta S = -46.31 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, $\Delta H = 111.03 \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta G = 136.50 \text{ kJ} \cdot \text{mol}^{-1}$.

$$A = (k_B T e^{\Delta S/R}) / h$$

$$\Delta H = E_a - RT$$

$$\Delta G = \Delta H - T \Delta S$$

Where k_B is the Boltzmann constant ($1.3807 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$), and h is the Plank constant ($6.626 \times 10^{-34} \text{ J} \cdot \text{s}^{-1}$).

4. Conclusions

In summary, we have reported two Pb(II) compounds derived from two structure-relevant ligands, Hpytz and Hpytza. The two compounds display mononuclear or two dimensional structure with (4,4) topology, respectively. The luminescence properties show both ligand centered emission and characteristic peaks of Pb^{2+} . The DSC tests indicates compound **2** are potential candidate for explosive material. Our research results show that the substituted group has a great impact on either the crystal structures of the coordination compounds or the energetic performance of such compounds. Compound **2** can be used as eco-friendly replacements of lead primary explosive in initiators. We are currently devoted to investigating other compounds based on tetrazole derivatives.

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Caption list

Fig1. The coordination environment of Pb(II) in compound **1**, showing the mononuclear structure.

Fig2. The coordination environment of Pb(II) in compound **2**. Hydrogen atoms are omitted for clarity.

Fig3. (a) The 2D layer structure of compound **2**. Hydrogen atoms are omitted for clarity; (b) The (4,4) topology of compound **2**.

Fig4. The emission spectra of Hpytz, Hpytza, compounds **1** and **2** at room temperature in the solid state.

Fig5. (a) TG-DTG curve of compound **1** from 30 to 600°C with the heating rate of 10°C/min; (b) DSC curve of compound **1** from 30 to 600°C with the heating rate of 10°C/min.

Fig6. (a) TG-DTG curve of compound **2** from 30 to 600°C with the heating rate of 10°C/min; (b) DSC curve of compound **2** from 30 to 600°C with the heating rate of 10°C/min.

Table **1** Selected crystallographic data for compounds **1-3**

Table **2** Selected bond distances (Å) and angles (°) for compounds **1-3**

Table **S** Hydrogen bond parameter for compounds **1-3** (Å/°)

FigS1. The 3D supramolecular network structure of compound **1** formed by hydrogen bonds.

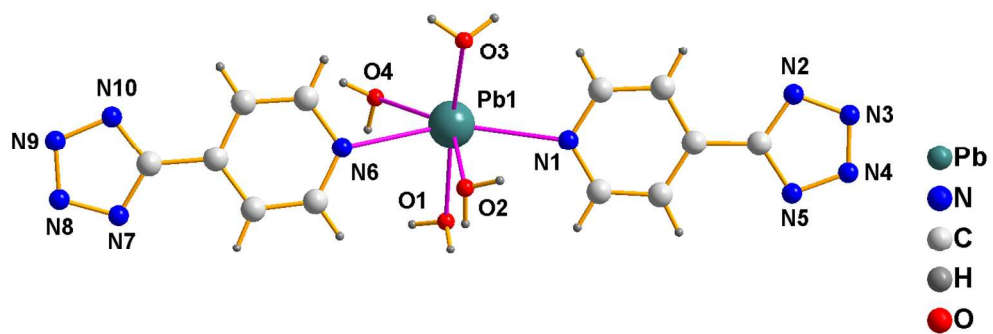
FigS2. The 3D supramolecular network structure of compound **2** formed by hydrogen bonds.

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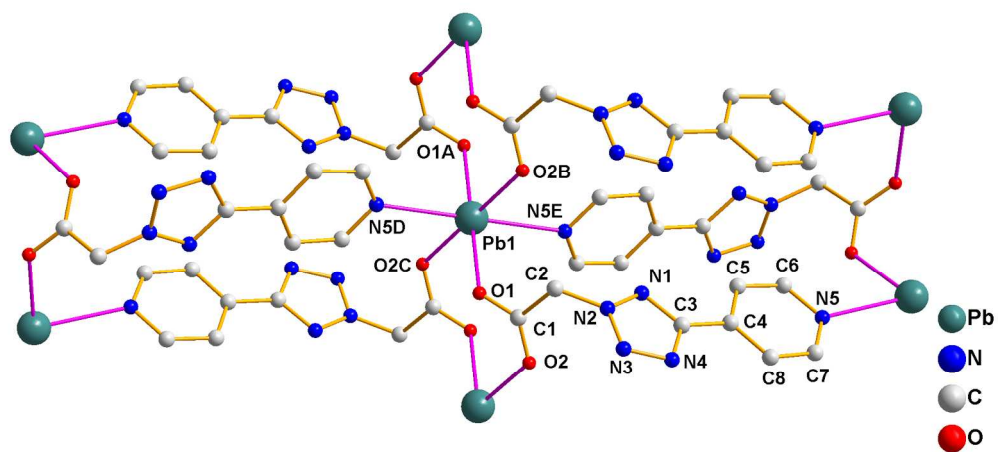
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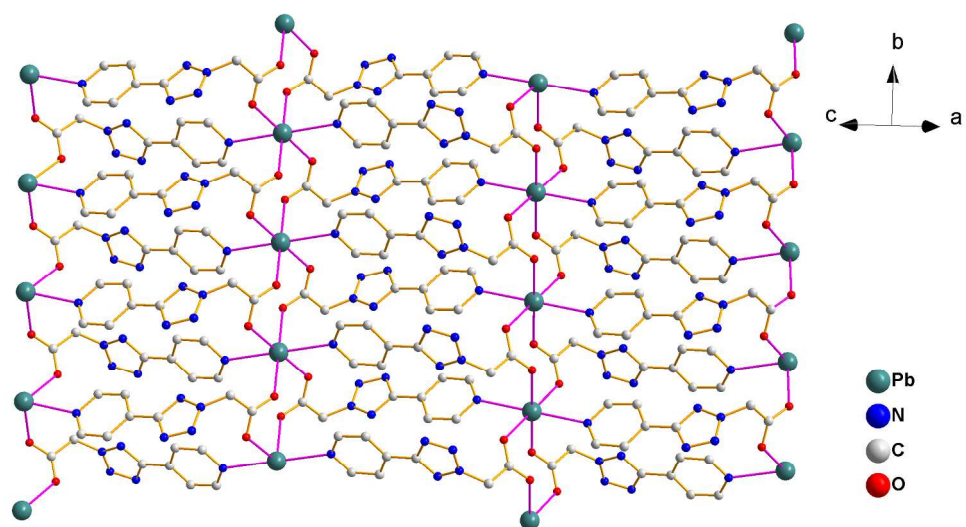
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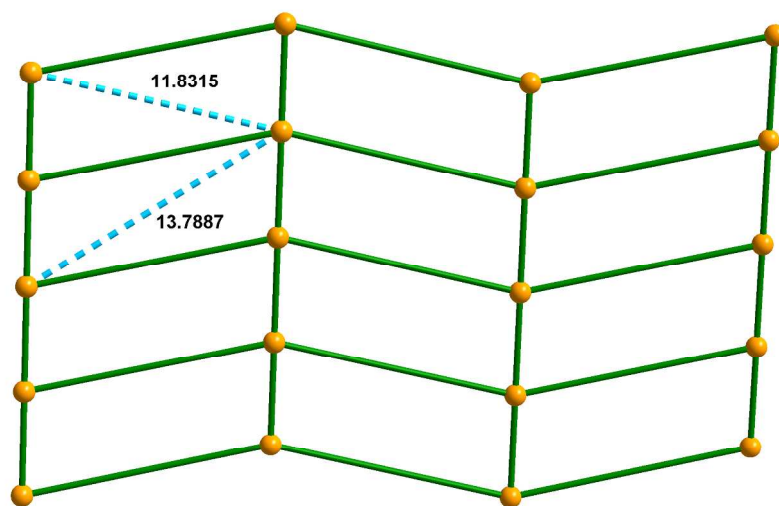
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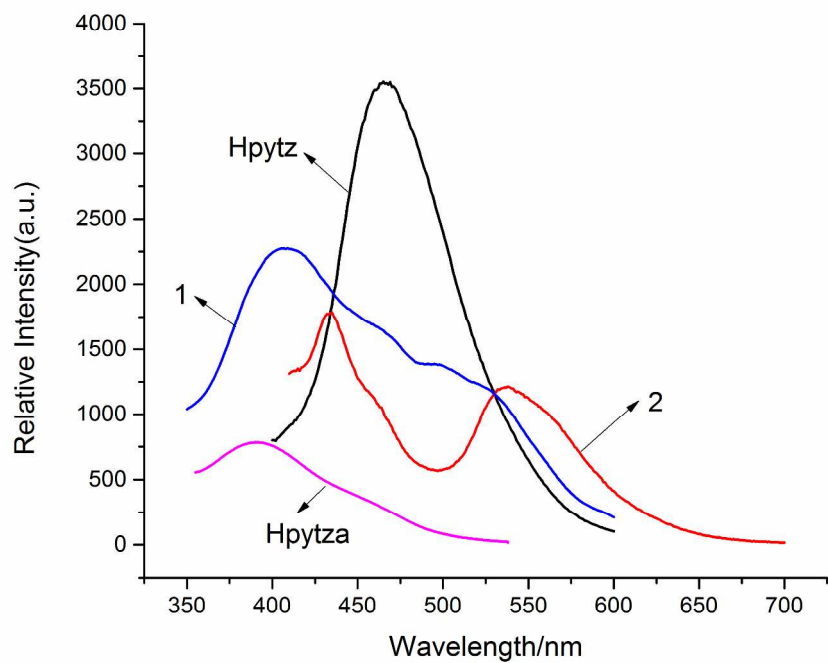
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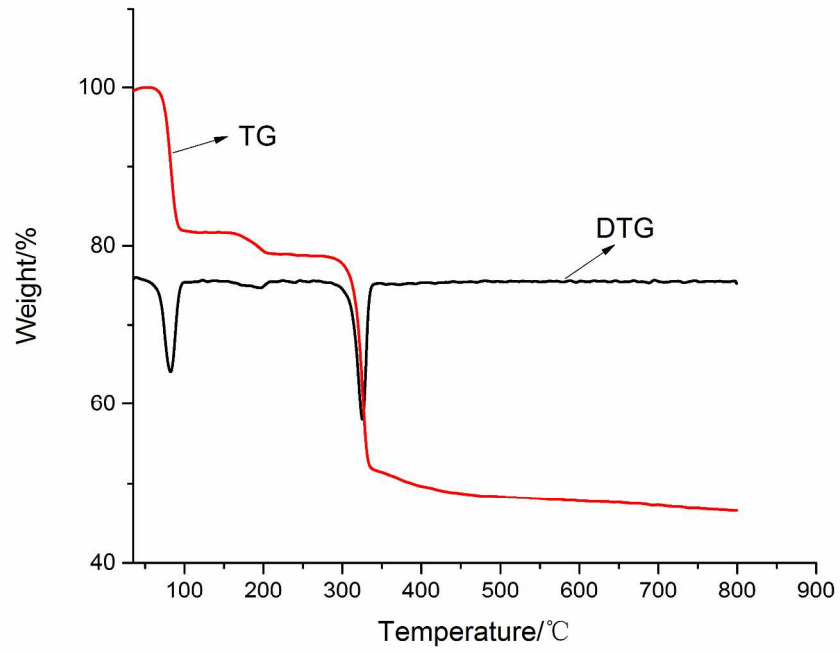
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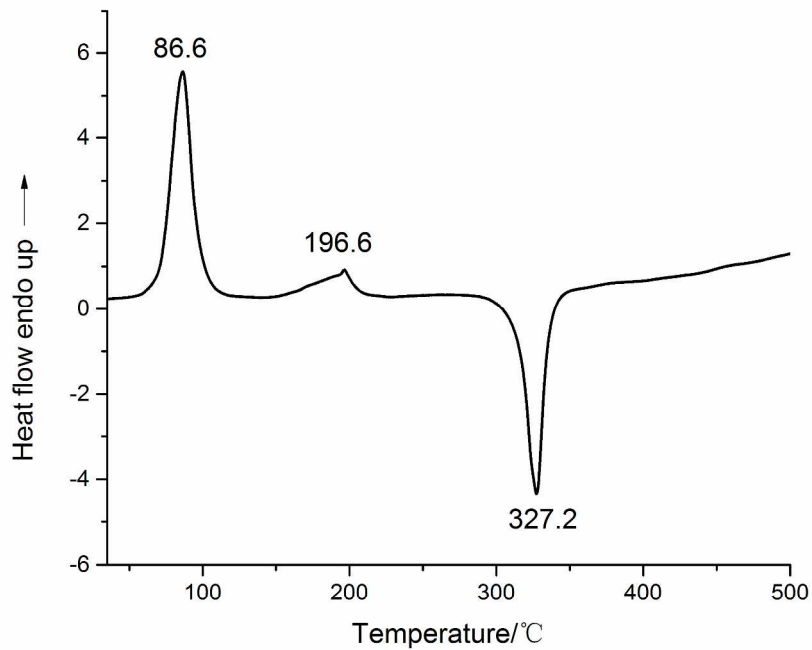
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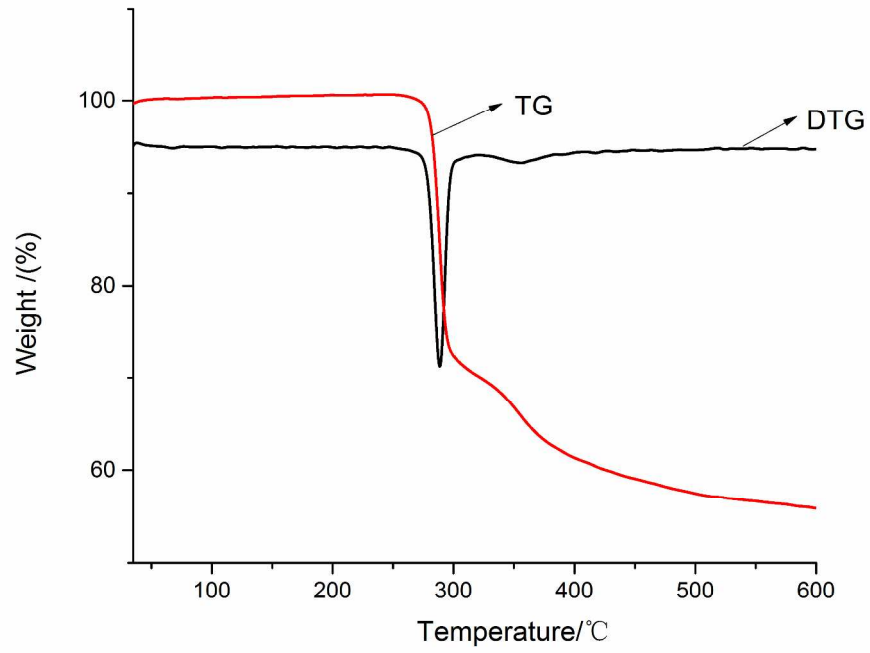
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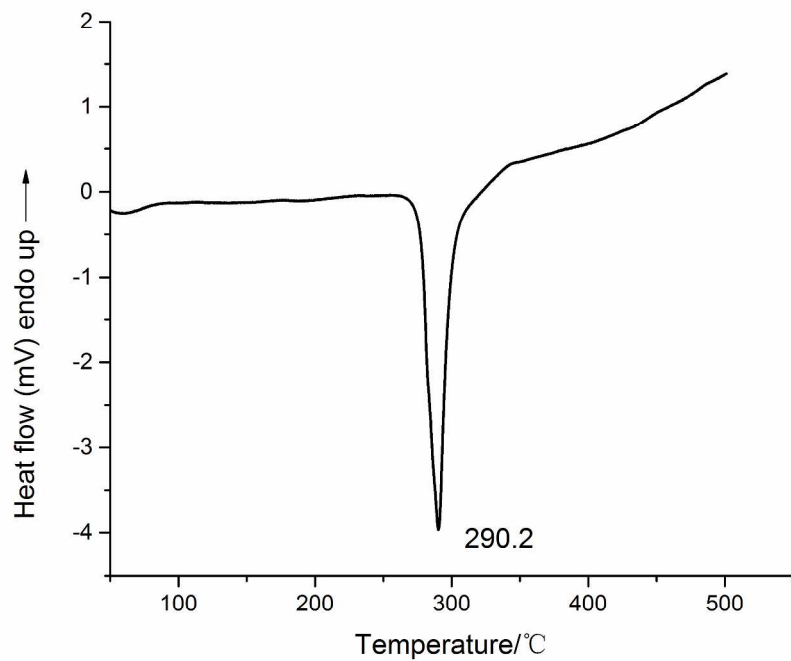
279x215mm (300 x 300 DPI)



279x215mm (300 x 300 DPI)



279x215mm (300 x 300 DPI)



279x215mm (300 x 300 DPI)

Table 1. Crystallographic data for 1- 2

| Compound | 1 | 7 |
|---|--|--|
| Empirical formula | C ₁₂ H ₂₂ PbN ₁₀ O ₇ | C ₁₆ H ₁₂ PbN ₁₀ O ₄ |
| Formula mass | 625.59 | 615.55 |
| Crystal system | Triclinic | monoclinic |
| Space group | <i>P</i> $\bar{1}$ | <i>P</i> 2 ₁ / <i>n</i> |
| <i>a</i> (Å) | 8.1250(16) | 12.9920(15) |
| <i>b</i> (Å) | 10.772(2) | 4.9834(6) |
| <i>c</i> (Å) | 12.866(3) | 15.3611(18) |
| α (°) | 70.45(3) | 90.00 |
| β (°) | 76.89(3) | 109.3490(17) |
| γ (°) | 89.02(3) | 90.00 |
| <i>V</i> (Å ³) | 1031.4(4) | 938.37(19) |
| <i>Z</i> | 2 | 2 |
| <i>T</i> /K | 291(2) | 296(2) |
| <i>D</i> _{calcd} (g·cm ⁻³) | 2.014 | 2.179 |
| μ (mm ⁻¹) | 8.237 | 9.041 |
| Reflections collected | 10658 | 6275 |
| Unique Reflections(<i>R</i> _{int}) | 4695(0.0449) | 1908 (0.0354) |
| No. Observations (<i>I</i> > 2.00 σ (<i>I</i>)) | 4170 | 1698 |
| No. Variables | 271 | 142 |
| <i>R</i> ^[a] , <i>wR</i> ^[b] | 0.0366, 0.1013 | 0.0715, 0.1827 |
| GOF ^c | 0.786 | 1.208 |
| Δ/ρ_{\max} (e/Å ³) | 0.819 | 2.001 |

| | | |
|--|--------|--------|
| $\Delta/\rho_{\min} (\text{e}/\text{\AA}^3)$ | -1.338 | -2.138 |
|--|--------|--------|

^[a] $R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$ ^[b] $R_w = \left\{ \frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right\}^{1/2}$ ^[c] $\text{GOF} = \left\{ \frac{\sum w(F_o^2 - F_c^2)^2}{(n-p)} \right\}^{1/2}$, where n = number of reflections and p = total numbers of parameters refined.

Table 2 Selected bond distances and angles for compounds **1** and **2** (Å/°)

| | | | |
|--|-----------|-------------------|------------|
| [Pb(pytz) ₂ (H ₂ O) ₄]·3H ₂ O(1) | | | |
| Pb(1)–O(2) | 2.370(5) | Pb(1)–O(1) | 2.490(5) |
| Pb(1)–N(6) | 2.614(5) | Pb(1)–N(1) | 2.631(5) |
| Pb(1)–O(3) | 2.698(5) | | |
| O(2)–Pb(1)–O(1) | 82.13(18) | O(2)–Pb(1)–N(6) | 75.45(17) |
| O(1)–Pb(1)–N(6) | 85.82(17) | O(2)–Pb(1)–N(1) | 75.04(16) |
| O(1)–Pb(1)–N(1) | 87.92(16) | N(6)–Pb(1)–N(1) | 150.40(17) |
| O(2)–Pb(1)–O(3) | 78.71(19) | O(1)–Pb(1)–O(3) | 160.84(17) |
| N(6)–Pb(1)–O(3) | 89.79(17) | N(1)–Pb(1)–O(3) | 86.73(17) |
| [Pb(pytza) ₂](2) | | | |
| Pb(1)–O(1) | 2.530(8) | Pb(1)–O(2) | 2.558(8) |
| Pb(1)–N(5D) | 2.666(8) | | |
| O(1A)–Pb(1)–O(1) | 180.0(5) | O(1A)–Pb(1)–O(2B) | 83.4(3) |
| O(1)–Pb(1)–O(2B) | 96.6(3) | O(2B)–Pb(1)–O(2C) | 180.0(3) |
| O(1A)–Pb(1)–N(5E) | 92.1(3) | O(1)–Pb(1)–N(5E) | 87.9(3) |
| O(2B)–Pb(1)–N(5E) | 79.8(3) | O(2C)–Pb(1)–N(5E) | 100.2(3) |
| O(1A)–Pb(1)–N(5D) | 87.9(3) | O(1)–Pb(1)–N(5D) | 92.1(3) |
| O(2B)–Pb(1)–N(5D) | 79.8(3) | N(5D)–Pb(1)–N(5E) | 180.0(5) |

Symmetry code

For **2**: A: 2-x, 1-y, -z; B: x, -1+y, z; C: 2-x, 2-y, -z; D: 0.5+x, 1.5-y, -0.5+z; E: 1.5-x, -0.5+y, 0.5-z;