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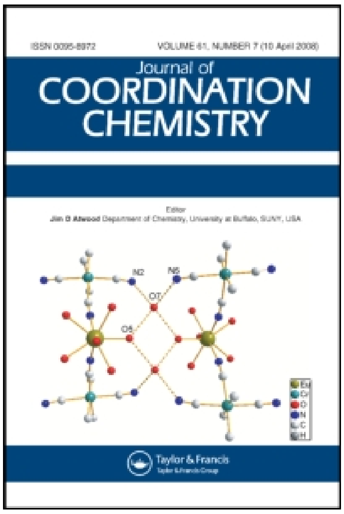

## Journal of Coordination Chemistry

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# Synthesis, crystal structure, and characterization of energetic complex $Pb(ATZ)(phen)_2 \cdot 3H_2O$

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A new energetic complex, $Pb(ATZ)(phen)_2 \cdot 3H_2O$ (**1**) (ATZ = 5,5′-azotetrazolate), was synthesized and characterized by single crystal X-ray diffraction. Crystal data: monoclinic, $P2(1)/n$ space group, $a = 8.4545(1)$ Å, $b = 25.846(2)$ Å, $c = 13.096(2)$ Å, and $\beta = 102.873(2)°$. In addition, elemental analysis, IR, and thermogravimetric analysis are presented. Furthermore, the complex was also explored as an additive to promote thermal decomposition of ammonium perchlorate.

*Keywords*: Energetic; Crystal structure; TG–DTG; Catalysis

## 1. Introduction

For synthesis of energetic materials, nitrogen-rich compounds have attracted attention [1–7]. These compounds rely on highly efficient gas production and high heat of formation for energy release, since elemental nitrogen is the major product of decomposition [8]. These compounds are prospective materials for generation of gases as blowing agents, solid propellants and other combustible and thermally unstable systems [9, 10].

5,5′-Azotetrazole dianion (abbreviate $ATZ^{2-}$) is an excellent energetic ligand with nitrogen content of 85.36%, higher than that of tetrazole and can display various coordination modes, and some complexes have been synthesized and characterized [11–16]. In this article, a novel energetic complex, $Pb(ATZ)(phen)_2 \cdot 3H_2O$ (**1**) (ATZ = 5, 5′-azotetrazole dianion, phen = 1,10-phenanthroline), has been synthesized and structurally characterized. In addition, the catalytic performance of **1** on ammonium perchlorate decomposition is presented, showing **1** can accelerate decomposition of ammonium perchlorate.

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## 2. Experimental

### 2.1. *Materials*

All reagents used for synthesis were purchased from commercial sources and used without purification. C, H, and N analyses were carried out using a Vario EL III instrument. IR spectra were recorded on a Bruker FTIR instrument with KBr pellets. TG–DTG experiments were performed on a NETZSCH STA 449C thermal analyzer from 25 to 800°C with heating rate of 10.0°C $\mathrm{min}^{-1}$ under static air. DSC experiment was performed on the Perkin–Elmer Pyris 6 DSC thermal analyzer (calibrated by standard pure indium and zinc) from 200 to 500°C. The sample was heated at a projected constant heat of 10.0°C $\mathrm{min}^{-1}$.

### 2.2. *Synthesis of the disodium 5,5′-azotetrazolate pentahydrate*

Disodium 5,5′-azotetrazolate pentahydrate was synthesized according to the reference [8], and characterized by IR and elemental analysis. Anal. Calcd for $C_2H_{10}Na_2N_{10}O_5$ (%): C, 8.00; H, 3.36; N, 46.67; Na, 15.31. Found: C, 8.42; H, 3.06; N, 46.16.

### 2.3. *Synthesis of 1*

About 15 mL $H_2O$ containing 2 mmol $Pb(NO_3)_2$ was added to 30 mL of water and ethanol (1 : 1) containing 2 mmol 1,10-phenanthroline (phen) and 2 mmol disodium 5,5′-azotetrazolate pentahydrate, forming precipitate. After filtering, single crystals were obtained from the solution which was allowed to evaporate at room temperature for two weeks. Complex **1** is insoluble in water, alcohol, acetone, and other organic solvents. Anal. Calcd for $C_{26}H_{22}PbN_{14}O_3$ (%): C, 39.74; H, 2.82; N, 24.96; Pb, 26.37. Found: C, 40.55; H, 2.15; N, 25.23; Pb, 26.60. IR ($\mathrm{cm}^{-1}$): 1620 s, 1585 m, 1510 m, 1425 s, 1400 s, 733 m.

### 2.4. *X-ray crystallography*

Single crystal X-ray experiments were performed on a Bruker Smart Apex CCD diffractometer equipped with graphite monochromated Mo-K$\alpha$ radiation ($\lambda = 0.71073$ Å) using $\omega$ and $\varphi$ scan mode. The single crystal structure was solved by direct methods and refined with full-matrix least-squares based on $F^2$ using SHELXS-97 and SHELXL-97 [17, 18]. All non-hydrogen atoms were located using subsequent Fourier-difference methods. In all cases, hydrogen atoms were placed in calculated positions and those of water were located from difference maps. Details of crystal data, data collection parameters, and refinement statistics are given in table 1. Selected bond distances and angles are given in table 2.

## 3. Results and discussion

### 3.1. *Structure description*

Single crystal X-ray analysis shows that **1** crystallizes in monoclinic space group $P2(1)/n$ and has a 3-D supramolecular structure featuring 2-D layers linked through hydrogen

Table 1. Crystal data and structure refinement parameters for **1**.

| | |
|---|---|
| Empirical formula | $C_{26}H_{22}PbN_{14}O_3$ |
| Formula weight | 785.78 |
| Crystal system | Monoclinic |
| Temperature (K) | 298(2) |
| Space group | $P2(1)/n$ |
| Unit cell dimensions (Å, °) | |
| $a$ | 8.4545(12) |
| $b$ | 25.846(2) |
| $c$ | 13.096(2) |
| $\alpha$ | 90.00 |
| $\beta$ | 102.873(2) |
| $\gamma$ | 90.00 |
| $Z$ | 4 |
| $D_{\text{Calcd}}$ ($\text{mg m}^{-3}$) | 1.871 |
| $F$ (000) | 1528 |
| Theta range for data collection (°) | 1.58–25.01 |
| Absorption coefficient ($\text{mm}^{-1}$) | 6.106 |
| Goodness-of-fit on $F^2$ | 1.007 |
| Reflections collected/unique | 13,122/4907 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.0285$, $wR_2 = 0.0482$ |
| $R$ indices (all data) | $R_1 = 0.0471$, $wR_2 = 0.0510$ |
| Largest difference peak and hole ($\text{eÅ}^{-3}$) | 1.248 and −0.679 |

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

| | | | |
|---|---|---|---|
| Pb(1)–N(14) | 2.484(3) | Pb(1)–N(1) | 2.723(5) |
| Pb(1)–N(12) | 2.500(4) | Pb(1)–N(11) | 2.546(4) |
| Pb(1)–N(13) | 2.599(4) | | |
| N(12)–Pb(1)–N(13) | 85.26(12) | N(14)–Pb(1)–N(13) | 64.88(12) |
| N(11)–Pb(1)–N(13) | 140.45(12) | N(14)–Pb(1)–N(1) | 76.69(13) |
| N(14)–Pb(1)–N(12) | 77.55(12) | N(12)–Pb(1)–N(1) | 145.42(13) |
| N(14)–Pb(1)–N(11) | 82.30(12) | N(11)–Pb(1)–N(1) | 88.18(15) |
| N(12)–Pb(1)–N(11) | 65.76(12) | N(13)–Pb(1)–N(1) | 104.02(15) |

bonding to give a 3-D network. As shown in figure 1, the molecule contains one ATZ dianion, two phen ligands, and three lattice water molecules. Each Pb(II) ion is coordinated by five nitrogens, one (N(1)) from $ATZ^{2-}$, and four (N(11), N(12), N(13) and N(14)) from two phen ligands, in a distorted square-pyramidal geometry. The basal plane is formed by N(1), N(11), N(12), and N(13), with Pb(1)–N(1) = 2.723(5) Å, Pb(1)–N(11) = 2.546(4) Å, Pb(1)–N(12) = 2.500(4) Å and Pb(1)–N(13) = 2.599(4) Å. The apical position is occupied by N(14) with Pb(1)–N(14) = 2.484(3) Å.

Within the crystal structure, tetrazole and phen from adjacent units are involved in intermolecular offset face to face $\pi$–$\pi$ stacking interactions generating 1-D chains (figure 2) with distances of 3.693 Å between the tetrazole and phen. Meanwhile, each pair of neighboring 1-D chains are further extended to a 2-D supramolecular layer, shown in figure 3, by the offset face to face $\pi$–$\pi$ stacking interactions between tetrazole and phen at 3.624 Å. In addition, three uncoordinated waters, O(1), O(2), and O(3), are linked through hydrogen bonding interactions to form a V-shape water cluster; every two contiguous supramolecular layers are interconnected through hydrogen bonds between nitrogens from tetrazole and water clusters to afford a 3-D supramolecular

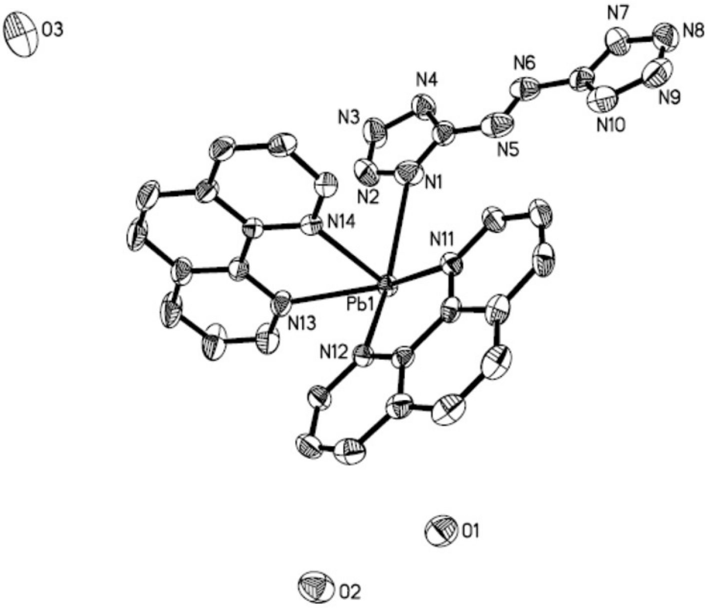

Figure 1. Molecular structure for **1**. H atoms are omitted for clarity.

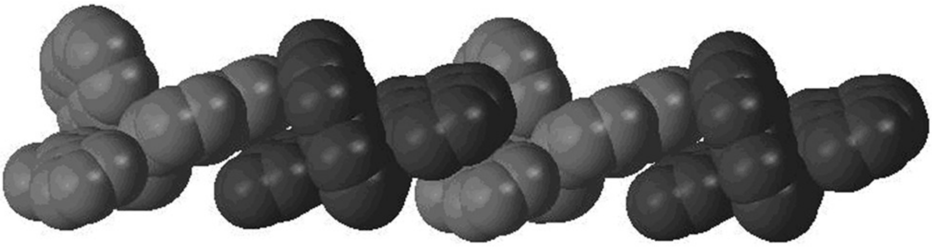

Figure 2. 1-D chain structure of **1**.

network, shown in figure 4. The details of hydrogen bonding interactions are listed in table 3.

### 3.2. *Thermal analysis*

The TG–DTG curves of **1** were performed on a NETZSCH STA 449C thermogravimetric instrument from 25 to 800°C with heating rate of 10°C $\text{min}^{-1}$ under static air. The thermal decomposition processes TG–DTG results is shown in figure 5.

The overall decomposition process can be divided into two stages. In the range 65–131°C, removal of three lattice water molecules and the formation of $Pb(ATZ)(phen)_2$, accompany a loss of 6.4% (calculated value: 6.9%). In the broad second stage from 161 to 561°C, $Pb(ATZ)(phen)_2$ is transformed to PbO with a residue of 28.3% (calculated value 28.4%).

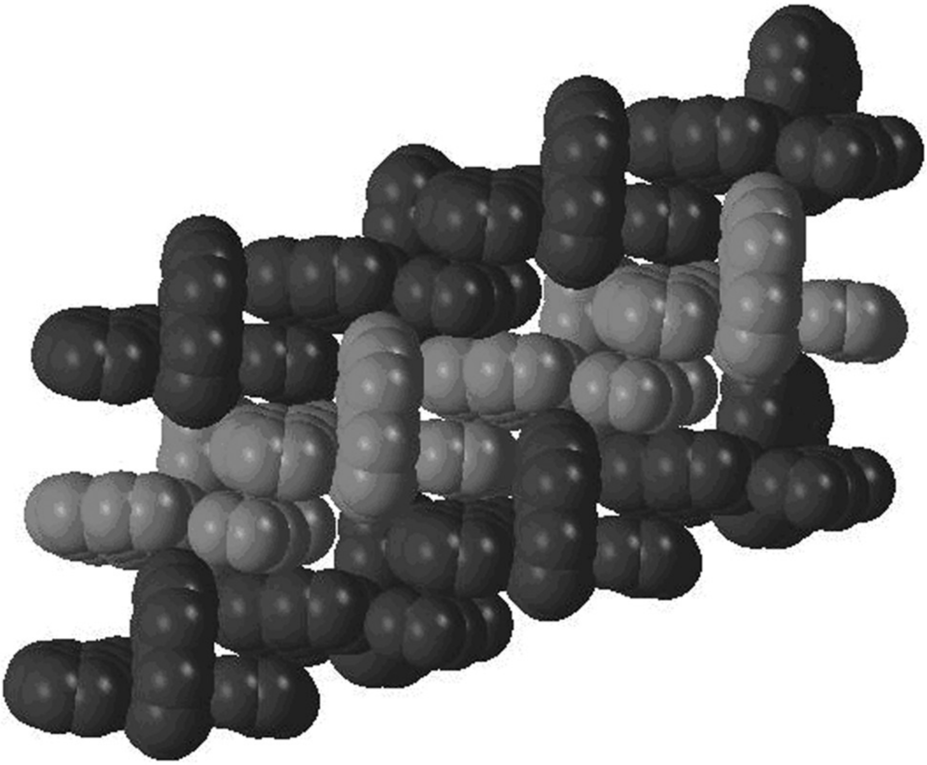

Figure 3. 2-D supramolecular layers of **1**.

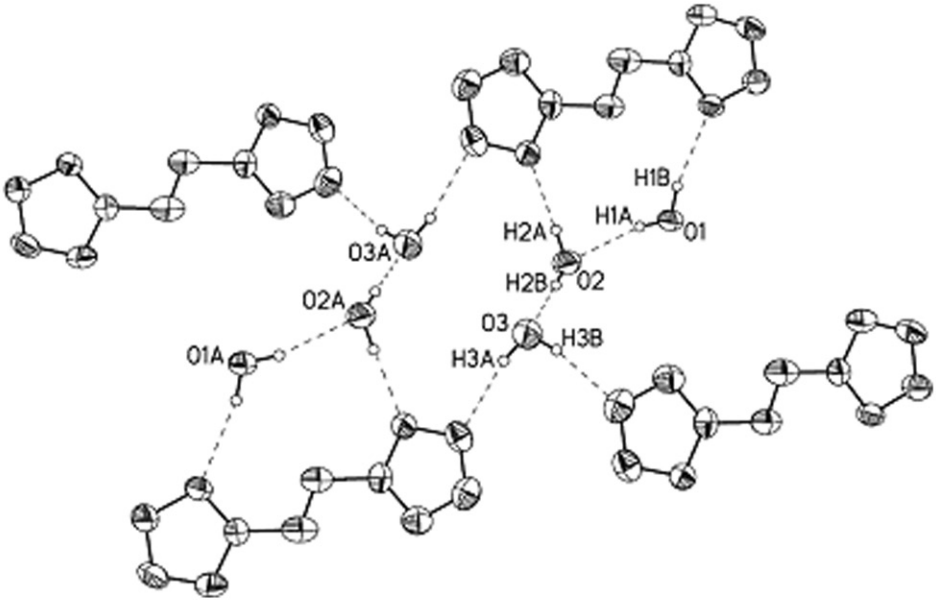

Figure 4. Trimer water cluster of **1**.

Table 3. Hydrogen bonding interactions in **1**.

| D–H···A | D···A (Å) | H···A (Å) | D–H···A (°) |
|---|---|---|---|
| O1–H1A···O2 | 2.924 | 2.092 | 165.94 |
| O2–H2B···O3#2 | 2.763 | 1.914 | 176.62 |
| O1–H1B···N4#1 | 2.969 | 2.136 | 166.40 |
| O1–H1B···N6#1 | 3.263 | 2.687 | 126.39 |
| O2–H2A···N7#1 | 2.827 | 1.978 | 177.23 |
| O3–H3A···N8#3 | 2.939 | 2.102 | 168.30 |
| O3–H3B···N9#4 | 2.879 | 2.042 | 168.10 |
| O3–H3B···N10#4 | 3.427 | 2.622 | 158.51 |

Note: Symmetry transformations: #1 $x+1/2, -y+1/2, z-1/2$; #2 $x-1, y, z-1$; #3 $-x+1/2, y-1/2, -z+3/2$; #4 $x+1/2, -y+1/2, z+1/2$.

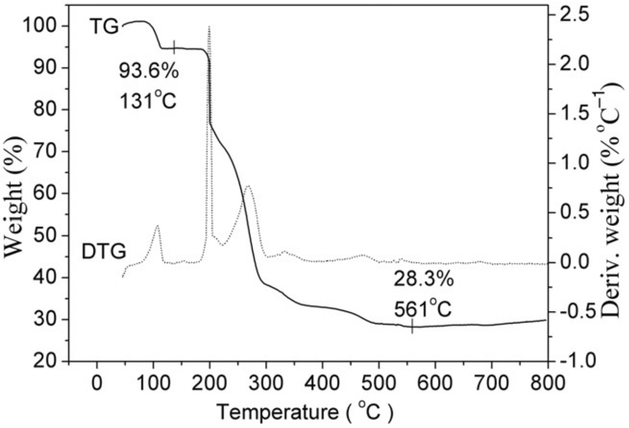

Figure 5. TG–DTG curves of **1** at 10°C min$^{-1}$.

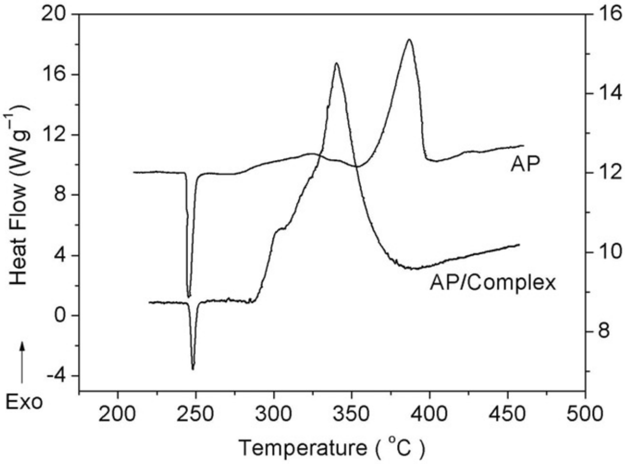

Figure 6. DSC curves of pure AP and the mixture of AP with **1**.

### 3.3. *Catalytic decomposition of ammonium perchlorate*

Complex **1** was explored as an additive to the thermal decomposition of ammonium perchlorate (abbreviate AP), the key component of composite solid propellants. The performance of **1** in thermal decomposition of AP with mass ratio 1 : 3 was investigated by DSC measurements from 200 to 500°C.

Addition of **1** dramatically decreased the AP decomposition temperature, consistent with our DSC measurements. Figure 6 shows the DSC curves of both pure AP and the mixture of AP with **1**. The first endothermic peak of pure AP at about 250°C is due to the crystal transformation from orthorhombic to cubic phase, while exothermic peaks at temperatures above 300°C are attributed to AP decomposition. The thermal decomposition of pure AP usually undergoes two or more steps. From figure 6, it is seen that for pure AP there are two obvious exothermic peaks centered at about 320 and 442°C, corresponding to the low-temperature decomposition and high-temperature decomposition, respectively. In the presence of **1**, low-temperature decomposition is at about 302°C while high-temperature decomposition is 330°C; AP decomposition was accelerated by **1**.

## Supplementary material

CCDC No. 650736 contains the supplementary crystallographic data for this article. These data can be obtained free of charge at http://www.ccdc.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Center (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; Email: deposit@ccdc.cam.ac.uk).

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