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# A Novel Nitrogen-Rich Cadmium Coordination Compound Based on 1,5-Diaminotetrazole: Synthesis, Structure Investigation, and Thermal Properties

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A new coordination compound $[Cd(DAT)_6](PA)_2 \cdot (H_2O)_4$ using 1,5-diaminotetrazole (DAT) as a ligand was synthesized and characterized by applying X-ray single crystal diffraction, elemental analysis, and Fourier transform infrared (FT-IR) spectroscopy. The central cadmium(II) cation is coordinated by six N atoms from six DAT molecules to form a six-coordinated and slightly distorted octahedral configuration. The coordination cation is situated between the two picrate (PA) anions whose benzene-ring planes are parallel to each other. All of the molecular units are linked together by intermolecular hydrogen bonds. The thermal decomposition mechanism of the title compound was investigated through differential scanning calorimetry (DSC), thermogravimetric/differential analysis (TG-DTG), and FT-IR analyses. The kinetic parameters of the first exothermic process of this complex were calculated by applying Kissinger's and Ozawa-Doyle's methods.

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## 1. Introduction

Energetic materials as controllable storage systems for relatively large amounts of chemical energy are widely applied in military and civil areas.[1,2] When undergoing decomposition, energetic materials produce energy by oxidation processes. Since energetic materials are sensitive to certain stimuli such as heat, impact, friction, and detonation, terrible accidents often occur in the processes of handling, transportation, and storage. Recently, a class of heterocyclic compounds with high nitrogen content has attracted considerable interest of chemists all over the world, due to their excellent stability, high heat of formation, and friendly environmental conditions.[3−8]

Energetic heterocyclic compounds with a high nitrogen content derive most of their energy from the transformation of the bonds between N-atoms. Such transformations are accompanied by an enormous energy release due to the wide difference in the average bond energies of N—N (160 kJ·mol$^{-1}$) and N═N (418 kJ·mol$^{-1}$), compared to that of N≡N (954 kJ·mol$^{-1}$).[9,10] Klapötke and his co-workers[5,11−14] and Shreeve's group[3,4,6,15,16] have done lots of studies of nitrogen-rich energetic compounds on the basis of triazole, tetrazole, tetrazine, and their derivatives. Talawar et al.[17] and Huynh et al.[7,18] investigated the coordination complexes of the 5-nitro-tetrazolate anion as potential primary explosives. 5-Substituted tetrazoles, such as 5-aminotetrazole (5-AT),[16,19−21] 5-nitriminotetrazole,[22−24] and 5-nitrotetrazole,[25−27] can form a series of metal salts or coordination compounds with transition metals and alkaline and alkaline earth metals due to its weak acidic properties. These tetrazole-based nitrogen-rich materials have extreme properties and potential application as solid propellants, explosives, and pyrotechnics.

Aminotetrazoles have the highest content of nitrogen among all organic substances, 82.3 % by weight for 5-AT and 84.0 % by weight for 1,5-diaminotetrazole. In spite of large positive enthalpies of formation, aminotetrazoles exhibit a surprisingly high thermal stability. The high nitrogen content and prominent thermal stability make them have a potential application as blowing agents, solid propellants, and other combustible and thermally decomposing systems. 5-AT is an especially valuable intermediate in the synthesis of tetrazole-based compounds because of its varied reaction and ease of preparation. 5-AT was synthesized by Kekue for the first time in 1892, by the reaction of nitrous acid with aminoguanidine. In the early 20th century, Hantzsch et al. obtained 5-AT with another scheme, by the reaction of hydrazoic acid with dicyandiamide. In 2007, Klapötke et al. reported the structures and physicochemical properties of the alkali salts of 5-aminotetrazole. All of the compounds were easily obtained with good thermal stability.[28] Except for lithium 5-aminotetrazolate, which shows a low impact sensitivity of more than 75 J, all compounds are insensitive toward friction and impact. Complexes with 5-AT as the ligand have been reported frequently, with the central metal cations including $Ca^{2+}$, $Mg^{2+}$, $Cu^{2+}$, $Ni^{2+}$, $Cd^{2+}$, $Zn^{2+}$, $Ag^{+}$, $Fe^{2+}$, $Fe^{3+}$, $Co^{2+}$, and $Co^{3+}$.[29−32] 1,5-Diaminotetrazole (DAT) as a simple tetrazole derivative is a ligand with six nitrogen atoms, five of them being potentially metal binding. Compared with 5-AT, DAT not only increases the nitrogen content and the heat of formation but also increases the possibility for hydrogen bonding, that improves the energetic properties and thermal stability greatly. DAT is considered as a promising material for different kinds of combustion and thermally decomposed systems. It is also a valuable intermediate

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**Table 1. Crystallographic Data and Structure Determination Details for $[Cd(DAT)_6](PA)_2 \cdot (H_2O)_4$**

| | |
|---|---|
| empirical formula | $C_{18}H_{36}CdN_{42}O_{18}$ |
| formula mass/g·mol$^{-1}$ | 1241.29 |
| temperature/K | 293(2) |
| crystal dimension/mm | 0.26 × 0.22 × 0.18 |
| crystal system | triclinic |
| space group | $P\bar{1}$ |
| $a$/Å | 10.3425(13) |
| $b$/Å | 10.3727(13) |
| $c$/Å | 11.9922(15) |
| $\alpha$/deg | 110.546(2) |
| $\beta$/deg | 104.412(2) |
| $\gamma$/deg | 97.464(2) |
| $V$/Å$^3$ | 1132.8(2) |
| $Z$ | 1 |
| $\rho$/g·cm$^{-3}$ | 1.820 |
| $\mu$/mm$^{-1}$ | 0.618 |
| $F$(000) | 630 |
| $\theta$ ranges/deg | 1.93 to 25.02 |
| limiting indices | $-12 \le h \le 12$, $-12 \le k \le 9$, $-14 \le l \le 13$ |
| reflections collected | 5549 |
| independent reflections ($R_{int}$) | 3847(0.0172) |
| data/restraints/parameters | 3847/3/366 |
| goodness-of-fit on $F^2$ | 1.079 |
| final $R_1$, $wR_2$ $[I > 2\sigma(I)]^a$ | 0.0291, 0.0705 |
| $R_1$, $wR_2$ indices (all data)$^a$ | 0.0334, 0.0732 |
| largest difference peak and hole (e·Å$^{-3}$) | 0.499 and −0.702 |

[a] $w = 1/[\sigma^2(F_0^2) + (0.0360P)^2 + 0.6410p]$, where $P = (F_0^2 + 2F_c^2)/3$.

in the synthesis of various useful tetrazole-containing compounds. Lyakhov et al. investigated the structure of DAT in 2000, and the tetrazole ring is planar to within 0.001 (1) Å. The 5-amino group is conjugated with the $\pi$-system of the tetrazole ring.[33] Shreeve and his co-workers synthesized a series of DAT derivatives; all of these compounds have high nitrogen content and excellent energetic properties.[6] Huynh has done a lot of work on complexes with DAT as a ligand, especially the copper and iron coordination compounds which use the perchlorate anion as an outer coordination shell ion, which exhibits prominent properties as a green primary explosive to be a prospective replacement for service lead azide in explosive initiators.[34] Reedijk et al. synthesized a new 2-dimensional coordination polymer $Cu(DAT)_2Cl_2$. This structure makes impossible any type of strong magnetic interactions, but a weak antiferromagnetic interaction can occur.[35]

In recent years, Cui et al. synthesized a series of coordination compounds using DAT as the ligand, transition metal ions (such as cobalt(III), cadmium(II), manganese(II), and zinc) as the central metal cation, and perchlorate, picrate, styphnate, nitrate, and chloride as the outer ion.[36−39] In most of the complex molecular units, six 4-site N atoms from six DAT molecules coordinate with central ions and formed a six-coordinated complex cation. Compared with other anion ligands, the coordination of neutral diaminotetrazole with metal ions should increase the content of the outer-sphere ions, which will affect the properties of the complex. The picrate can improve the sensitivity of the complex, and it is more sensitive to the stimulation of flame.

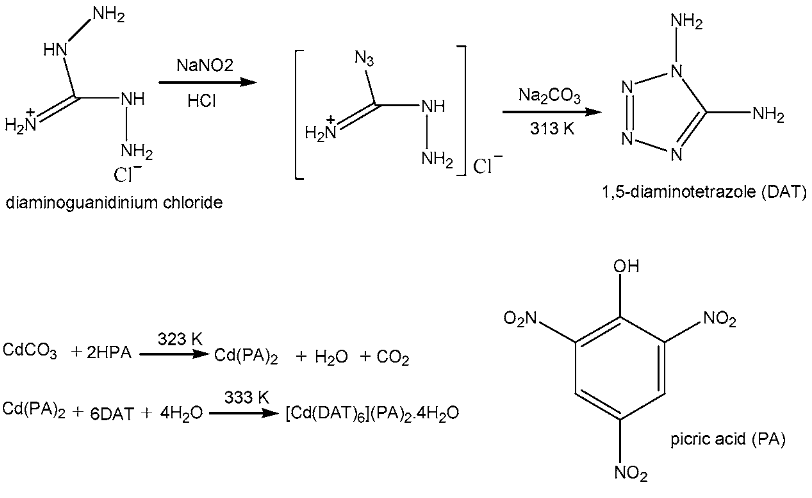
To explore new coordination compounds using DAT as a ligand, we investigated the preparation, crystal structure, thermal decomposition mechanism, and nonisothermal kinetics of $[Cd(DAT)_6](PA)_2 \cdot (H_2O)_4$ which uses DAT as the ligand and picrate as the outer anions.

## 2. Experimental Section

***Caution.*** Although none of the compounds described herein have exploded or detonated in the course of this research, these materials should be handled with extreme caution using the best safety practices because DAT and the title compound are high-nitrogen materials and may be sensitive toward certain stimuli in their surroundings such as heat, flame, friction, and impact.

***2.1. General Method.*** All chemical reagents and solvents of analytical grade were obtained from commercial sources and used without further purification unless stated otherwise. The Flash EA 1112 fully automatic trace element analyzer was used to analyze the content of each element of the title compound. The Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Equinox 55 infrared spectrometer [KBr pellets, (4000 to 400) cm$^{-1}$ with the resolution of 4 cm$^{-1}$]. Thermal properties were studied by using a Perkin-Elmer Pyris-1 differential scanning calorimeter and thermogravimetric analyzer for differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), respectively. A sample (about 0.5 mg) was sealed in aluminum pans for DSC with various heating rates [(2, 5, 10, 15, and 20) K·min$^{-1}$] from (293 to 873) K. TGA was calculated under the same conditions. The nonisothermal kinetic parameters were computed by using the Non-Isothermal Kinetics Computation of Energetic Materials software, which was developed by our group. The calculated method is on the basis of the Kissinger and Ozawa-Doyle equations, using the different peak temperatures obtained in the thermal decomposition process with various heating rates.

**Scheme 1. Synthesis of DAT and the Title Compound**



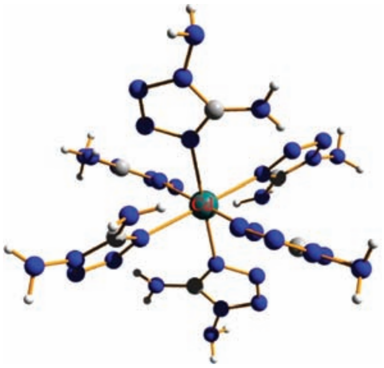


**Figure 1.** Coordination environment of the cadmium(II) center in $[Cd(DAT)_6](PA)_2 \cdot (H_2O)_4$.

***2.2. X-ray Single-Crystal Determination.*** A white $[Cd(DAT)_6](PA)_2 \cdot (H_2O)_4$ crystal of 0.26 × 0.22 × 0.18 $mm^3$ size was obtained as described below and used in the X-ray diffraction study. Data were collected on a Rigaku diffractometer equipped with a Saturn 70 CCD using graphite monochromatic Mo Kα radiation ($\lambda = 0.071073$ nm) at 293(2) K in the $\omega$ scans mode. Unit-cell parameters were obtained by least-squares in the range of $1.93° \leq \theta \leq 25.02°$. The structure was solved by direct methods using SHELXS-97[40] and refined by means of full-matrix least-squares procedures on $F^2$ with the SHELXL-97[41] program. All non-hydrogen atoms were obtained from the difference Fourier map and refined anisotropically. All hydrogen atoms were located from difference Fourier electron-density maps and refined isotropically. Detailed information concerning crystallographic data collection and structure refinement is summarized in Table 1. Further information concerning the crystal-structure determinations in CIF format is available in the Supporting Information.

***2.3. Synthesis of DAT as a Ligand.*** A portion of 12.55 g (0.1 mol) of diaminoguanidinium chloride, which was purchased commercially and recrystallized twice with distilled water, was dissolved in 50 mL water, and 4.2 mL of concentrated hydrochloric acid (37 %) was added to the solution and cooled to 273 K. With the temperature kept at (273 to 275) K, a solution of sodium nitrite (6.9 g, 0.2 mol) in 15 mL of water was added slowly via a dropping funnel under stirring. Then, the solution obtained was kept in an ice-bath for half an hour. Sodium carbonate was used to keep the pH of the solution to 8 and stirred for 20 min at 313 K. Part of the water in the solution was evaporated by a rotary evaporator and cooled, and DAT was precipitated and recrystallized with water. Yield 62 %. Anal. Calcd (%) for $CH_4N_6$: C, 12.00; H, 4.03; N, 83.97. Found (%): C, 12.12; H, 4.13; N, 83.65. IR (KBr pellent, $\nu$ $cm^{-1}$): 3322, 3235, 3158, 1653, 1579, 1328, 1310, 1132, 1115, 1073, 1006, 934, 793, 741, 704, 683, 636, 614, 487.

***2.4. Synthesis of $[Cd(DAT)_6](PA)_2 \cdot (H_2O)_4$.*** Cadmium carbonate ($CdCO_3$) (3.79 g, 0.022 mol) was added slowly to a solution of picric acid (PA) (9.17 g, 0.04 mol) in 20 mL of distilled water at 323 K. The mixture was stirred at the same temperature until there was no gas release and then cooled to room temperature. The cadmium picrate ($Cd(PA)_2$) solution was obtained after filtration. DAT (12.00 g, 0.12 mol) was dissolved in 40 mL of deionized water and heated to 333 K. The cadmium picrate solution obtained above was added gradually dropwise under stirring. The solution obtained was stirred at 333 K for 30 min, then naturally cooled to room temperature, and allowed to stand 1 h until a yellow precipitate formed. The precipitate was collected by filtration, washed with deionized water (5 mL), and dried in a vacuum drier. The title compound $[Cd(DAT)_6](PA)_2 \cdot (H_2O)_4$ was obtained with a yield of 91 % (based on DAT). White hexagon block single crystals of the title compound suitable for X-ray analyses were obtained by slow crystallization from the filtrate for 25 days. Anal. Calcd (%) for $[Cd(DAT)_6](PA)_2 \cdot (H_2O)_4$: C, 17.40; H, 2.90; N, 47.37. Found (%): C, 17.49; H, 2.92; N, 47.71. IR data (KBr pellent, $\nu$ $cm^{-1}$): 3340, 3315, 3233, 1666, 1648, 1583, 1560, 1559, 1331, 1152, 1121, 1086, 997, 928, 910, 783, 725, 706, 521.

**Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[Cd(DAT)_6](PA)_2 \cdot (H_2O)_4$[a]**

| | | | | | |
|---|---|---|---|---|---|
| Bond Lengths | | | | | |
| Cd(1)−N(1) | 2.321(2) | N(3)−N(4) | 1.347(3) | N(10)−N(11) | 1.377(3) |
| Cd(1)−N(1)#1 | 2.321(2) | N(4)−C(1) | 1.329(3) | N(12)−C(2) | 1.314(3) |
| Cd(1)−N(7)#1 | 2.331(2) | N(4)−N(5) | 1.375(3) | N(13)−C(3) | 1.322(3) |
| Cd(1)−N(7) | 2.331(2) | N(6)−C(1) | 1.307(3) | N(13)−N(14) | 1.359(3) |
| Cd(1)−N(13) | 2.351(2) | N(7)−C(2) | 1.317(3) | N(14)−N(15) | 1.268(3) |
| Cd(1)−N(13)#1 | 2.351(2) | N(7)−N(8) | 1.358(3) | N(15)−N(16) | 1.350(3) |
| N(1)−C(1) | 1.325(3) | N(8)−N(9) | 1.267(3) | N(16)−C(3) | 1.325(3) |
| N(1)−N(2) | 1.362(3) | N(9)−N(10) | 1.342(3) | N(16)−N(17) | 1.382(3) |
| N(2)−N(3) | 1.269(3) | N(10)−C(2) | 1.328(3) | N(18)−C(3) | 1.326(3) |
| Bond Angles | | | | | |
| N(1)−Cd(1)−N(1)#1 | 179.999(1) | C(1)−N(1)−Cd(1) | 137.22(17) | C(3)−N(13)−Cd(1) | 137.27(16) |
| N(1)−Cd(1)−N(7)#1 | 91.42(7) | N(2)−N(1)−Cd(1) | 116.13(15) | N(14)−N(13)−Cd(1) | 116.04(15) |
| N(1)#1−Cd(1)−N(7)#1 | 88.58(7) | N(3)−N(2)−N(1) | 111.2(2) | N(15)−N(14)−N(13) | 111.3(2) |
| N(1)−Cd(1)−N(7) | 88.58(7) | N(2)−N(3)−N(4) | 106.1(2) | N(14)−N(15)−N(16) | 105.9(2) |
| N(1)#1−Cd(1)−N(7) | 91.42(7) | C(1)−N(4)−N(3) | 109.6(2) | C(3)−N(16)−N(15) | 109.6(2) |
| N(7)#1−Cd(1)−N(7) | 179.999(1) | C(1)−N(4)−N(5) | 125.1(2) | C(3)−N(16)−N(17) | 125.5(2) |
| N(1)−Cd(1)−N(13) | 87.06(7) | N(3)−N(4)−N(5) | 125.3(2) | N(15)−N(16)−N(17) | 124.8(2) |
| N(1)#1−Cd(1)−N(13) | 92.94(7) | C(2)−N(7)−N(8) | 106.05(19) | N(6)−C(1)−N(1) | 128.5(2) |
| N(7)#1−Cd(1)−N(13) | 88.79(7) | C(2)−N(7)−Cd(1) | 139.12(16) | N(6)−C(1)−N(4) | 124.3(2) |
| N(7)−Cd(1)−N(13) | 91.21(7) | N(8)−N(7)−Cd(1) | 114.27(14) | N(1)−C(1)−N(4) | 107.2(2) |
| N(1)−Cd(1)−N(13)#1 | 92.94(7) | N(9)−N(8)−N(7) | 111.1(2) | N(12)−C(2)−N(7) | 128.5(2) |
| N(1)#1−Cd(1)−N(13)#1 | 87.06(7) | N(8)−N(9)−N(10) | 106.1(2) | N(12)−C(2)−N(10) | 124.2(2) |
| N(7)#1−Cd(1)−N(13)#1 | 91.21(7) | C(2)−N(10)−N(9) | 109.4(2) | N(7)−C(2)−N(10) | 107.3(2) |
| N(7)−Cd(1)−N(13)#1 | 88.79(7) | C(2)−N(10)−N(11) | 125.1(2) | N(13)−C(3)−N(16) | 107.2(2) |
| N(13)−Cd(1)−N(13)#1 | 179.999(1) | N(9)−N(10)−N(11) | 125.4(2) | N(13)−C(3)−N(18) | 128.0(2) |
| C(1)−N(1)−N(2) | 105.90(19) | C(3)−N(13)−N(14) | 106.05(19) | N(16)−C(3)−N(18) | 124.8(2) |

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x, -y + 2, -z + 2$.

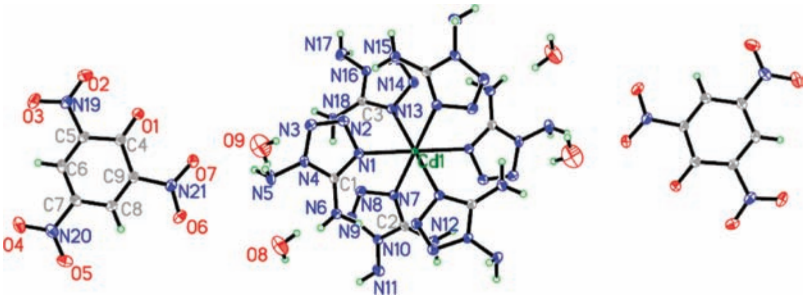


**Figure 2.** Molecular unit and labeling scheme for $[Cd(DAT)_6](PA)_2 \cdot (H_2O)_4$.

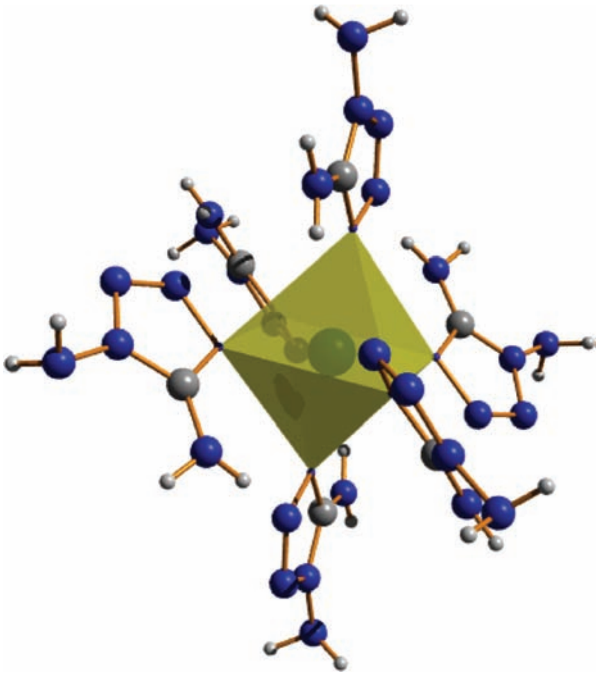


**Figure 3.** Slightly distorted octahedron of cadmium center coordinated by six N-atoms from the six DAT molecules.

**Table 3. Hydrogen Bond Lengths (Å) and Angles (deg) for $[Cd(DAT)_6](PA)_2 \cdot (H_2O)_4$[a]**

| D−H···A | d(D−H) | d(H···A) | d(D···A) | angle (DHA) |
|---|---|---|---|---|
| N(5)−H(5A)···O(1) | 0.9 | 2.11 | 2.959(3) | 158 |
| N(5)−H(5A)···O(2) | 0.9 | 2.33 | 2.836(4) | 115 |
| N(5)−H(5B)···O(7)#2 | 0.9 | 2.52 | 3.050(4) | 118 |
| N(6)−H(6A)···N(15)#3 | 0.89 | 2.33 | 3.163(3) | 156 |
| N(6)−H(6B)···O(6)#4 | 0.89 | 2.42 | 2.958(3) | 119 |
| N(6)−H(6B)···N(14)#1 | 0.89 | 2.28 | 3.044(4) | 145 |
| O(8)−H(8B)···O(1) | 0.95(6) | 2.11(6) | 3.027(5) | 163(5) |
| O(8)−H(8B)···O(7) | 0.95(6) | 2.38(5) | 3.004(4) | 123(5) |
| O(9)−H(9B)···O(2)#5 | 0.86 | 2.35 | 3.158(5) | 157 |
| O(9)−H(9B)···N(17)#6 | 0.86 | 2.6 | 3.105(5) | 119 |
| N(11)−H(11A)···O(3)#7 | 0.89 | 2.47 | 2.905(4) | 110 |
| N(11)−H(11B)···O(8)#8 | 0.9 | 2.17 | 3.036(4) | 163 |
| N(12)−H(12A)···O(8)#4 | 0.88 | 2.53 | 3.390(5) | 165 |
| N(12)−H(12B)···N(2)#1 | 0.88 | 2.26 | 3.019(4) | 144 |
| N(17)−H(17A)···O(2)#9 | 0.89 | 2.33 | 3.061(5) | 139 |
| N(17)−H(17A)···O(9)#6 | 0.89 | 2.39 | 3.105(5) | 137 |
| N(17)−H(17B)···O(5)#6 | 0.9 | 2.4 | 3.276(5) | 165 |
| N(18)−H(18A)···N(8) | 0.89 | 2.18 | 2.990(3) | 151 |
| N(18)−H(18A)···O(4)#5 | 0.89 | 2.6 | 3.104(4) | 117 |
| N(18)−H(18B)···N(9)#10 | 0.89 | 2.19 | 3.028(3) | 157 |

[a] Symmetry transformations used to generate equivalent atoms #1: $-x, -y + 2, -z + 2$; #2: $-x, 1 - y, 1 - z$; #3: $x, -1 + y, z$; #4: $x, y, 1 + z$; #5: $1 - x, 1 - y, 1 - z$; #6: $1 - x, 2 - y, 1 - z$; #7: $1 - x, 1 - y, 2 - z$; #8: $1 - x, 2 - y, 2 - z$; #9: $x, 1 + y, z$; #10: $1 - x, 2 - y, 2 - z$.

## 3. Results and Discussion

***3.1. Synthesis.*** The method of preparing DAT was optimized on the basis of the literature,[42] and the yield was improved. The reaction of preparing DAT was done through two steps as shown in Scheme 1. After study, we found that four main factors have an effect on the yield of DAT: the ratio of the amount of diaminoguanidinium chloride and concentrated hydrochloric acid, the temperature of the second step, the time of the first step, and the time of the second step. To make the production more pure and safer, we used deionized water for crystallization instead of ethanol.

The scheme for preparing $[Cd(DAT)_6](PA)_2 \cdot (H_2O)_4$ is shown in Scheme 1. When preparing the $Cd(PA)_2$, the amount of water has an effect on the concentration of solution of $Cd(PA)_2$ directly and then the efficiency of the reaction. Each of the factors of the amount of water, temperature, and time all played an important role in the reaction of the preparation of $[Cd(DAT)_6](PA)_2 \cdot (H_2O)_4$.

***3.2. Structural Description of $[Cd(DAT)_6](PA)_2 \cdot (H_2O)_4$.*** The coordination environment of the cadmium cation and the molecular unit of the title complex with atom labeling are shown in Figures 1 and 2. Selected bond lengths and bond angles are listed in Table 2, and the hydrogen bond lengths and angles are listed in Table 3.

Structure analysis shows that the symmetric unit of the title complex is comprised of one central cadmium cation, six DAT neutral molecules, two PA anions, and four lattice $H_2O$ molecules. Six N-atoms from the six DAT molecules coordinated with the central cadmium ion to form a six-coordinated centrosymmetric coordination cation, which was situated between two PA anions whose benzene-ring planes are parallel to each other. The coordination geometry around the cadmium ion can be described as a slightly distorted octahedral configuration (Figure 3). The bond lengths between the central cadmium ion and the N-coordination atoms are approximately the same and can be observed to be 2.321(2) Å for Cd(1)−N(1) and Cd(1)−N(1)#1, 2.331(2) Å for Cd(1)−N(7) and Cd(1)−N(7)#1, and 2.351(2) Å for Cd(1)−N(13) and Cd(1)−N(13)#1. As shown in Figure 4, any two pairs of centrosymmetric N-coordination atoms and the central Cd cation in the coordination compound can form planes: N(1)−N(7)−Cd(1)−N(1)#1−N(7)#1 (plane **A**), N(1)−N(13)−Cd(1)−N(1)#1−N(13)#1 (plane **B**), and N(7)−N(13)−Cd(1)−N(7)#1−N(13)#1 (plane **C**). All of the atoms are in the corresponding planes without any deviations. The angles between planes **A** and **B**, **A** and **C**, and **B** and **C** are 91.3°, 93.0°, and 88.5°, respectively, slightly deviate from 90°.

The triangle composed of the three coordination atoms N1, N7, and N13 is approximately equilateral, and the three corresponding DAT ligands are located on vertexes of the triangle. The angles between each tetrazole-ring plane of the

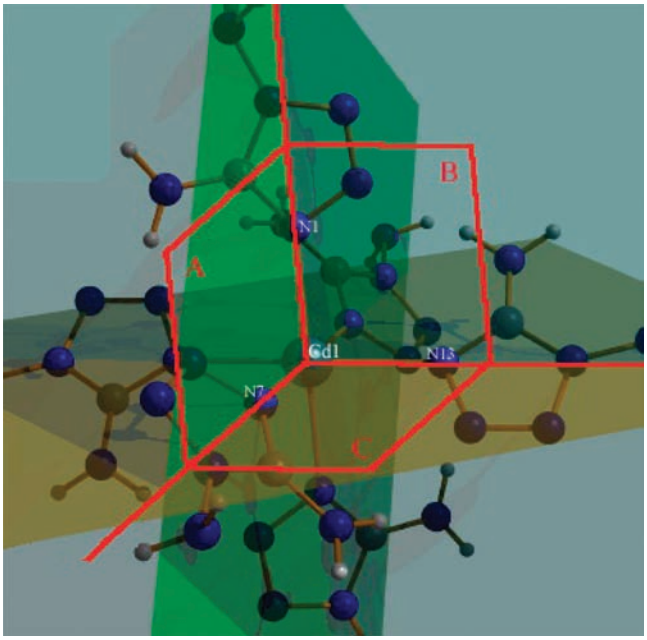


**Figure 4.** Planes formed by the centrosymmetric N-coordination atoms and the central cadmium ion.

above three DAT ligands and the triangle plane are 28°, 27.1°, and 27.3°, respectively. The angles between each two tetrazole-ring planes of the above three DAT molecules are 48.8°, 45°, and 47.4°. The other three coordination N-atoms as well as the three DAT ligands is the same as they are centrosymmetric distributed through the central cadmium ion. This kind of arrangement facilitates the H-bond interactions between the DAT ligands as well as between DAT ligands and the outer PA anions. It can also ease the steric hindrance caused by the six big-sized DAT ligands in the title coordination compound.

In $[Cd(DAT)_6](PA)_2 \cdot (H_2O)_4$ most of the bond angles and lengths for the DAT ligands are similar with the corresponding ones in the molecular crystal of DAT, and only the amino-groups differ slightly from the ones in the DAT molecules.[37] It may be caused by the hydrogen-bond interaction in the crystal structure of the title complex, which can be seen from the packing diagram (Figure 5).

As there are so many $NH_2$ groups, N-atoms in the tetrazole ring, $NO_2$ group, and O-atoms, a lot of intermolecular and intramolecular hydrogen bonds are formed (Figure 6). A circular outline was formed as a result of the intramolecular H-bond between the $NH_2(C)$-group of DAT and the adjacent tetrazole-ring N-atom of another DAT molecule in the same molecular unit. The O-atom in the PA anion can form an intramolecular hydrogen bond with the O-atom of $NO_2$ in an outer PA anion. Except for the two types of intramolecular hydrogen bonds, many intermolecular hydrogen bonds were formed between the molecules. The amino-groups of DAT molecules can form intermolecular H-bonds with O-atoms of lattice water molecules, nitro-groups and the deprotonated hydroxyl-group of PA, as well as the tetrazole-ring N-atoms of DAT in different molecular units. At the same time, the O−H of the lattice water molecules can form intermolecular H-bonds with O-atoms of the deprotonated hydroxyl group of PA. It can be seen from the packing diagram that all of the molecular units are linked together into the crystal structure by the extensive intermolecular hydrogen bonds, of which the DAT ligand plays an important role.

***3.3. Thermal Decomposition.*** To assess the thermal properties of $[Cd(DAT)_6](PA)_2 \cdot (H_2O)_4$, DSC and TG experiments were carried out. The DSC curve of the title complex is shown in Figure 7, with a heating rate of $\beta = 10\ K \cdot min^{-1}$, and TG-DTG curves at the heating rate of $10\ K \cdot min^{-1}$ in a nitrogen atmosphere flowing at the rate of $20\ mL \cdot min^{-1}$ are illustrated in Figure 8.

As seen in the DSC curve shown, there are three endothermic processes in the range of (381.3 to 468.9) K. The third endothermic peak is very sharp with a peak temperature of 450.9 K; in contrast, the first two endothermic peaks are flat. That is because the first two endothermic peaks were caused by the loss of the lattice water molecules from the title complex, and the sharp peak shows the melting process of the complex, which can be confirmed from the TG-DTG curves with the mass loss of 8.7 % of the initial mass in corresponding temperature range and the disappearance of the absorption band at $3436\ cm^{-1}$ in the FT-IR spectra of the residue at 453 K.

The melted title complex is very unstable and decomposes immediately. From the DSC curve, we found that the decomposition of the title compound occurs over the temperature range of (468.9 to 873) K with three exothermic stages. The first exothermic stage occurs in the range (468.9 to 544.4) K with the peak temperature at 498.8 K, and there is a mass loss of 45.3 % of the initial mass corresponding to this process in the TG-DTG curves. The cleavage of the nitro-group and amino-group, and the breaking of benzene and tetrazole rings can be confirmed by the disappearance of the characteristic absorption bands of $\nu_{as}$ ($NO_2$) and $\nu_s$ ($NO_2$) at (1559 and 1332) $cm^{-1}$, the vibrations at (3325 and 3240) $cm^{-1}$ for amino groups, and the

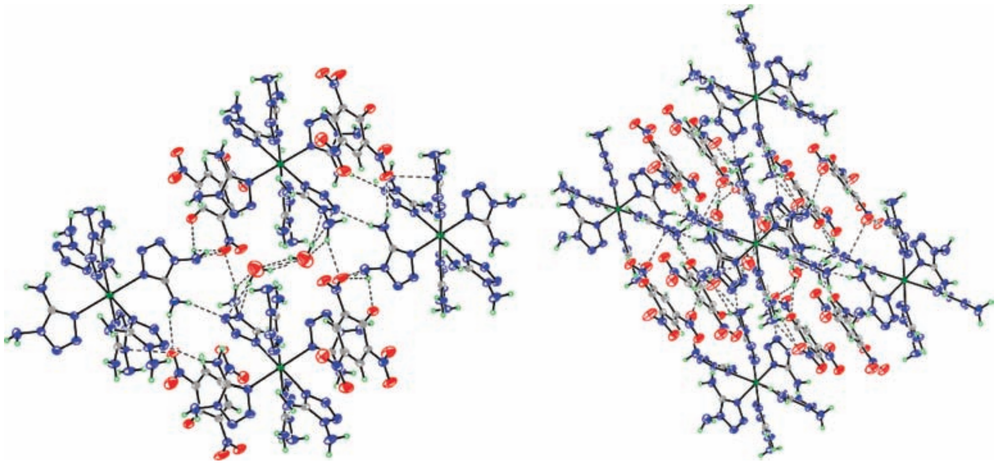


**Figure 5.** Packing diagram of $[Cd(DAT)_6](PA)_2 \cdot (H_2O)_4$ in crystal viewed along the *a* axis and *c* axis.

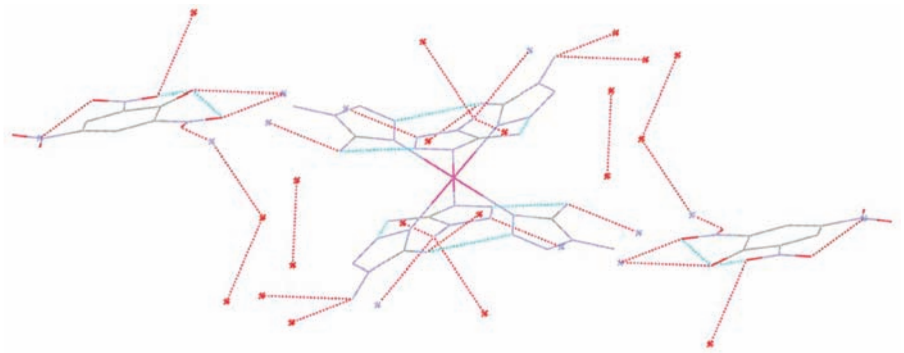


**Figure 6.** H-bonds of intermolecular and intramolecular.

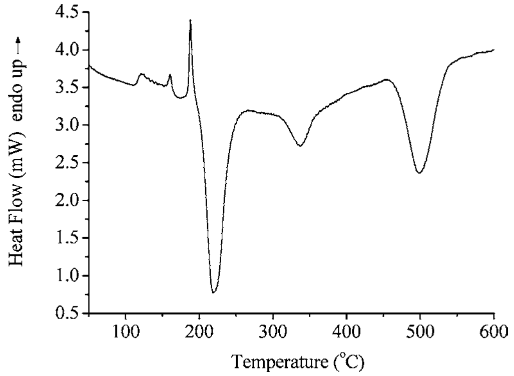


**Figure 7.** DSC curve of the title complex with the heating rate of 10 $K \cdot min^{-1}$.

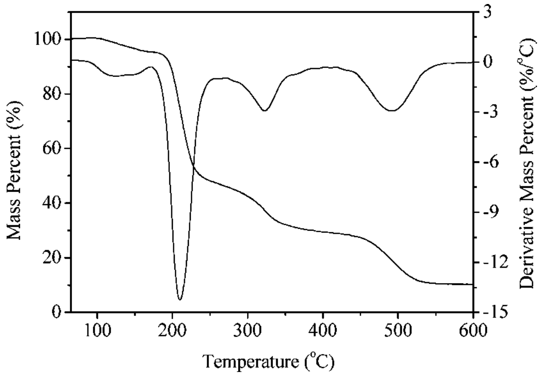


**Figure 8.** TG-DTG curve of the title complex with the heating rate of 10 $K \cdot min^{-1}$.

characteristic absorption bands in (1649 to 1440) $cm^{-1}$ for benzene and tetrazole ring skeleton in the FT-IR spectra of the residue at 536 K. New bonds at (3419, 1625, 1538, and 1385) $cm^{-1}$ prove the existence of −CO−NH− polymer and $Cd(RCOO)_2$ in the solid residue at 536 K.

Further decomposition of the title coordination compound occurs in the range of (544.4 to 727.2) K with the peak temperature of 611.6 K shown in the DSC curve, and corresponding to this temperature range a mass loss shown in the TG-DTG curves is 19.0 %. During this process, $Cd(RCOO)_2$ decomposed to $Cd(NCO)_2$ with the characteristic bands at 2163 $cm^{-1}$ in the FT-IR spectra of the residue at 673 K. The −CO−NH− polymer was missing, and some thermostable products formed in this process, which may act as a source of heat at a higher temperature.

The last exothermic process occurs in the range of (727.2 to 873) K, and the peak temperature is 774.3 K. There is a mass loss of 16.7 % in the TG-DTG curves corresponding to this temperature range. The mass of the final residue is 10.3 % of the initial mass, coincident with the calculating value of CdO, 10.3 %. The band at 721 $cm^{-1}$ in the FT-IR spectrum of the residue at 873 K proves that the final residue is CdO.

The decomposition pathway of the title compound can be described as follows:

$$[Cd(DAT)_6](PA)_2 \cdot (H_2O)_4 \rightarrow [Cd(DAT)_6](PA)_2$$
$$\rightarrow Cd(RCOO)_2 + -CO-NH- \text{ polymer} + \text{gas products}$$
$$\rightarrow Cd(NCO_2) + \text{gas products}$$
$$\rightarrow CdO + \text{gas products}$$

***3.4. Nonisothermal Kinetic Analysis.*** From the multiple nonisothermal DSC curves obtained under the condition of flowing oxygen-free nitrogen gas with heating rates of (2, 5, 10, 15, and 20) $K \cdot min^{-1}$, we can infer that the first exothermic process makes a dominant effect on the decomposition of the title compound. The values of the apparent activation energy $E_a$ and the pre-exponential factor $A$ of this exothermic decomposition process were calculated using Kissinger's method and Ozawa-Doyle's method. The two equations can be described as follows:

$$\frac{d \ln(\beta/T_p^{\,2})}{d(1/T_p)} = -\frac{E_a}{R}$$

$$\log \beta + \frac{0.4567 E_a}{R T_p} = C$$

where $T_p$ is the peak temperature, K; $R$ is the gas constant, 8.314 $J \cdot mol^{-1} \cdot K^{-1}$; $\beta$ is the linear heating rate, $K \cdot min^{-1}$; $C$ is a constant.

**Table 4. Peak Temperatures of the First Exothermic Stage at Different Heating Rates and the Kinetic Parameters**[a]

| heating rates ($K \cdot mol^{-1}$) | 2 | 5 | 10 | 15 | 20 |
|---|---|---|---|---|---|
| peak temperatures (K) | 467.8 | 481.3 | 492.0 | 499.6 | 500.9 |
| Kissinger's method: $E_k(kJ \cdot mol^{-1})/\ln(A_k/s^{-1})/R_k$ | 121.8/10.94 /−0.9964 | | | | |
| Ozawa-Doyle's method: $E_o(kJ \cdot mol^{-1})/R_o$ | 123.5/0.9968 | | | | |

[a] Subscript k: Kissinger's method; o: Ozawa-Doyle's method.

The peaking temperatures of the first exothermic process at different heating rates, the apparent activation energy, and the pre-exponential factor and linear correlation coefficient were determined and are listed in Table 4. The calculated results using both methods were similar, and they were all in the normal range of kinetic parameters for the thermal decomposition reaction of solid materials.[43]

The Arrhenius equation can be expressed by using the calculators $E_a$ (the average of $E_k$ and $E_o$) and ln $A_k$ as follows: $\ln k = 10.94 - 121.8 \cdot 10^3/RT$ for the first exothermic process. This equation can be used to estimate the rate constants of the initial thermal decomposition process of $[Cd(DAT)_6](PA)_2 \cdot (H_2O)_4$.

## 4. Conclusion

We have successfully synthesized and characterized a novel coordination compound $[Cd(DAT)_6](PA)_2 \cdot (H_2O)_4$, which used DAT as a ligand. The results show that the central cadmium cation is coordinated with six N atoms of six bulky DAT molecules forming a slightly distorted octahedral structure. The coordination site is the N(4) atom of the DAT molecule. The molecular units of the title complex were linked together, forming a three-dimensional network through extensive intermolecular hydrogen bonds. The high enthalpy of formation and high nitrogen content of the ligand indicated a high energy output of the title complex, which could be a kind of potential energetic material.

### Supporting Information Available:

Supplementary crystallographic data for this paper. These data can also be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk). This material is available free of charge via the Internet at http://pubs.acs.org.

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