



Synthesis, structural investigation, thermal decomposition mechanism and sensitivity properties of an energetic compound $[\text{Cd}(\text{DAT})_6](\text{ClO}_4)_2$ (DAT = 1,5-diaminotetrazole)

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ABSTRACT

An energetic coordination compound $[\text{Cd}(\text{DAT})_6](\text{ClO}_4)_2$ has been synthesized by using 1,5-diaminotetrazole (DAT) as ligand and its structure has been characterized by applying X-ray single crystal diffraction, elemental analysis and FT-IR spectroscopy. The central cadmium(II) cation is coordinated by six N atoms from six DAT molecules to form a six-coordinated and distorted octahedral structure. Di-dimension layer structure was formed and the layers were linked together by the extensive intermolecular hydrogen bonds between DAT ligands and ClO_4^- anions. Thermal decomposition mechanism of the title compound was predicted based on DSC, TG-DTG and FT-IR analyses results. The kinetic parameters of the first exothermic process of the title compound were studied by applying the Kissinger's and Ozawa–Doyle's methods. Sensitivity tests reveal that the title compound has sensitive nature.

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1. Introduction

Tetrazole derivatives have gained more and more attention as ligands to transition metals [1–15]. The high positive enthalpies of formation and high nitrogen content of tetrazoles have made their complexes interesting for energetic materials. The energetic complexes which use 5-cyano-tetrazolate [16,17], 5-nitro-tetrazolate [18–23] and 5,5-azotetrazolate [24] anions or 5-aminotetrazole [25–27], 1-methyl-5-amino-tetrazole [28,29] and 1,5-diaminotetrazole (DAT) [29,30] neutral molecules as ligands have been studied.

Aminotetrazoles have the highest content of nitrogen among the organic compounds, 82.3% for 5-amino-1H-tetrazole (AT) and 84.0% for DAT. They are heterocyclic compounds rich in electron pairs, and can coordinate with transition-metal ions. Compared with anion ligands, the coordination of neutral aminotetrazoles with metal ions should increase the content of the outer-sphere ions, which will affect the properties of the complex. DAT-based energetic salts have become hot issues in recent years [31–34], but only little work has been done on complexes with DAT as ligands

[29,35]. The energetic coordination compound (DAT) pentammine cobalt(III) perchlorate, which uses DAT and NH_3 as mixed ligands, possesses high-energy-capacity and is a promising primary explosive for safe priming charges [29].

In order to explore new energetic coordination compounds, we investigate the preparation, crystal structure, thermal decomposition mechanism and sensitivity properties of $[\text{Cd}(\text{DAT})_6](\text{ClO}_4)_2$ which uses DAT as ligand and ClO_4^- as outer anions.

2. Experimental

General caution: DAT and the title compound are energetic materials and tend to explode under certain conditions. Appropriate safety precautions (safety glasses, face shields, leather coat and ear plugs) should be taken, especially when these compounds are prepared on a large scale.

2.1. Materials and instruments

All chemical reagents and solvents of analytical grade were bought from the reagents company and used as supplied. Diaminoguanidinium chloride was purchased commercially and recrystallized twice with distilled water before use. DAT was prepared according to the literature method [29].

Elemental analyses were performed on a Flash EA 1112 full-automatic trace element analyzer. The FT-IR spectra were recorded

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Table 1
Crystal data and structure refinement for $[\text{Cd}(\text{DAT})_6](\text{ClO}_4)_2$

Empirical formula	$\text{C}_6\text{H}_{24}\text{CdCl}_2\text{N}_{36}\text{O}_8$
Formula mass	911.91
Temperature (K)	293(2)
Crystal dimension (mm)	$0.28 \times 0.20 \times 0.14$
Crystal system	Trigonal
Space group	$P\bar{3}c1$
Z	2
a (Å)	11.9445(7)
b (Å)	11.9445(7)
c (Å)	13.2162(14)
γ (°)	120
Cell volume (Å ³)	1633.0(2)
Density, calculated (g cm ⁻³)	1.855
Absorption coefficient (mm ⁻¹)	0.929
F(0 0 0) (Å)	916
θ range for data collection (°)	1.97 to 26.37
h, k, and l range	–10 to 14, –14 to 14, –16 to 16
Reflection measured	8699
Independent reflection (R_{int})	1124 (0.0290)
Goodness-of-fit on F^2	0.951
Final R_1 and wR_2 [$I > 2\sigma(I)$] ^a	$R_1 = 0.0228$, $wR_2 = 0.0682$
R_1 and wR_2 indices (all data) ^a	$R_1 = 0.0294$, $wR_2 = 0.0756$
Largest differential peak and hole (e Å ⁻³)	0.426 and –0.373

$$^a w = 1/[\sigma^2(F_o^2) + (0.0534p)^2 + 0.9373p], \text{ where } p = (F_o^2 + 2Fc^2)/3.$$

on a Bruker Equinox 55 infrared spectrometer (KBr wafers) in the range of 4000–400 cm⁻¹ with the resolution of 4 cm⁻¹. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were carried out on a model Pyris-1 differential scanning calorimeter and a model Pyris-1 thermogravimeter analyser, respectively, using dry oxygen-free nitrogen as atmosphere with the flowing rate of 20 mL/min. The sample of about 0.5 mg was sealed in aluminum pans for DSC and held in platinum pans for TG.

2.2. Synthesis

CdCO_3 (5 mmol) was added to 1 mol/l HClO_4 solution (10 ml) at 50 °C. The mixture was stirred at the same temperature for 15 min and then cooled to room temperature. After filtration, the solution of $\text{Cd}(\text{ClO}_4)_2$ was obtained. DAT (30 mmol) was dissolved in 20 ml distilled water and heated. When the temperature of the DAT solution reached 80 °C, $\text{Cd}(\text{ClO}_4)_2$ solution was added dropwise under stirring. The solution obtained was allowed to stir at 80 °C for 30 min. Then it was naturally cooled to room temperature and allowed to stand for 1 h until white precipitate was formed.

Table 2
Selected bond lengths (Å) and bond angles (°) for $[\text{Cd}(\text{DAT})_6](\text{ClO}_4)_2$ ^a

Bond lengths					
Cd(1)–N(1)#1	2.371(1)	N(1)–C(1)	1.326(2)	N(5)–H(5A)	0.8957
Cd(1)–N(1)#2	2.371(1)	N(1)–N(2)	1.373(2)	N(5)–H(5B)	0.8920
Cd(1)–N(1)#3	2.371(1)	N(2)–N(3)	1.280(2)	N(6)–C(1)	1.333(2)
Cd(1)–N(1)	2.371(1)	N(3)–N(4)	1.361(2)	N(6)–H(6A)	0.8785
Cd(1)–N(1)#4	2.371(1)	N(4)–C(1)	1.334(2)	N(6)–H(6B)	0.8830
Cd(1)–N(1)#5	2.371(1)	N(4)–N(5)	1.390(2)		
Bond angles					
N(1)#1–Cd(1)–N(1)#2	82.58(6)	N(1)#2–Cd(1)–N(1)#5	91.02(4)	N(3)–N(4)–N(5)	126.50(1)
N(1)#1–Cd(1)–N(1)#3	91.02(4)	N(1)#3–Cd(1)–N(1)#5	170.43(6)	N(4)–N(5)–H(5A)	105.60
N(1)#2–Cd(1)–N(1)#3	96.17(7)	N(1)–Cd(1)–N(1)#5	91.02(4)	N(4)–N(5)–H(5B)	107.20
N(1)#1–Cd(1)–N(1)	170.44(6)	N(1)#4–Cd(1)–N(1)#5	82.58(6)	H(5A)–N(5)–H(5B)	114.00
N(1)#2–Cd(1)–N(1)	91.02(4)	C(1)–N(1)–N(2)	105.65(1)	C(1)–N(6)–H(6A)	118.50
N(1)#3–Cd(1)–N(1)	82.58(6)	C(1)–N(1)–Cd(1)	129.15(1)	C(1)–N(6)–H(6B)	120.10
N(1)#1–Cd(1)–N(1)#4	91.02(4)	N(2)–N(1)–Cd(1)	121.11(9)	H(6A)–N(6)–H(6B)	117.90
N(1)#2–Cd(1)–N(1)#4	170.44(6)	N(3)–N(2)–N(1)	111.41(1)	N(1)–C(1)–N(6)	128.60(1)
N(1)#3–Cd(1)–N(1)#4	91.02(4)	N(2)–N(3)–N(4)	105.74(1)	N(1)–C(1)–N(4)	107.82(1)
N(1)–Cd(1)–N(1)#4	96.17(7)	C(1)–N(4)–N(3)	109.38(1)	N(6)–C(1)–N(4)	123.51(1)
N(1)#1–Cd(1)–N(1)#5	96.17(7)	C(1)–N(4)–N(5)	124.07(1)		

^a Symmetry transformations used to generate equivalent atoms: #1: $-x+2, -x+y+1, -z+3/2$; #2: $-y+2, x-y+1, z$; #3: $y, x, -z+3/2$; #4: $x-y+1, -y+2, -z+3/2$; #5: $-x+y+1, -x+2, z$.

The precipitate was collected by filtration, washed with distilled water (5 ml) and dried in a vacuum drier. The title compound $[\text{Cd}(\text{DAT})_6](\text{ClO}_4)_2$ was obtained with the yield of 72.1% (based on DAT). Single crystals of the title compound suitable for X-ray analyses were obtained by slow crystallization from the filtrate. Anal. Calcd. (%) for $[\text{Cd}(\text{DAT})_6](\text{ClO}_4)_2$: C, 7.90; H, 2.63; N, 55.27. Found (%): C, 7.93; H, 2.64; N, 55.47. IR data (KBr pellet, ν cm⁻¹): 3406s, 3381s, 3320s, 3261s, 3181m, 1677s, 1626s, 1561w, 1503w, 1358w, 1337m, 1316w, 1095s, 992m, 859m, 696m, 627s, 594w, 512m.

2.3. X-ray crystallography

A Bruker Smart 1000 CCD diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) was applied for structure analyses of $[\text{Cd}(\text{DAT})_6](\text{ClO}_4)_2$. The data were collected at 293(2) K using φ and ω scan modes. The programs SHELXS-97 [36] and SHELXL-97 [37] were used for structure determination and refinement. The structures were solved by direct methods, and all non-hydrogen atoms were obtained from the difference Fourier map and subjected to anisotropic refinement by full-matrix least squares on F^2 . All hydrogen atoms of $[\text{Cd}(\text{DAT})_6](\text{ClO}_4)_2$ were generated geometrically and treated by a constrained refinement. Detailed information concerning crystallographic data collection and structure refinement is summarized in Table 1.

3. Results and discussion

3.1. Structure description

Fig. 1 shows the molecular unit of $[\text{Cd}(\text{DAT})_6](\text{ClO}_4)_2$ with the atom labeling scheme. Selected bond lengths and bond angles of the title compound are listed in Table 2. The hydrogen bond lengths and bond angles are listed in Table 3.

There are one cadmium(II) cation, six DAT neutral molecules and two ClO_4^- anions in the molecular unit of the title compound. Six N atoms from six DAT molecules coordinate with the central cadmium(II) cation and form a six-coordinated uncentrosymmetric complex cation.

The bond lengths of the central Cd^{2+} to the six N coordination atoms are almost the same [2.371(1) Å]. However, the bond angles for N(1)#1–Cd(1)–N(1), N(1)#2–Cd(1)–N(1)#4 and N(1)#3–Cd(1)–N(1)#5 all deviate from 180° and they are 170.44(6), 170.44(6) and 170.43(6)°, respectively. The bond angles around the central Cd^{2+} all deviate from 90°, which are 82.58(6)° for N(1)#1–Cd(1)

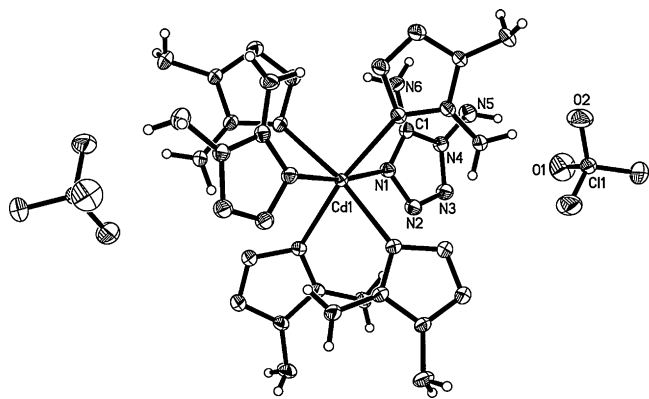


Fig. 1. Molecular unit and labeling scheme for $[\text{Cd}(\text{DAT})_6](\text{ClO}_4)_2$.

–N(1)#2, N(1)#3–Cd(1)–N(1) and N(1)#4–Cd(1)–N(1)#5; $91.02(4)^\circ$ for N(1)#1–Cd(1)–N(1)#3, N(1)#2–Cd(1)–N(1), N(1)#1–Cd(1)–N(1)#4, N(1)#3–Cd(1)–N(1)#4, N(1)#2–Cd(1)–N(1)#5 and N(1)–Cd(1)–N(1)#5; as well as $96.17(7)^\circ$ for N(1)#2–Cd(1)–N(1)#3, N(1)–Cd(1)–N(1)#4 and N(1)#1–Cd(1)–N(1)#5. All of the above demonstrate that each cadmium(II) center is coordinated to form a distorted octahedron.

The triangle composed of the three coordination atoms N1, N1A and N1B is equilateral and the three corresponding DAT ligands are located symmetrically on vertexes of the triangle. The bond angles between each tetrazole-ring plane of the above three DAT ligands and the triangle plane are all 17° . The bond angles between the tetrazole-ring planes of the above three DAT are all 29.4° . The same thing happens on the other three coordination atoms N1C, N1D and N1E as well as the three related DAT ligands. This kind of arrangement facilitates the H-bond interactions between the DAT ligands as well as between DAT ligands and the outer ClO_4^- anions, and at the same time it can ease the steric hindrance caused by the six big-sized DAT ligands in the title coordination compound.

N(6)–H(6A) of $\text{NH}_2(\text{C})$ -group of one DAT ligand can form intramolecular hydrogen bond with N(2) atom of the adjacent DAT ligand which is located symmetrically on vertexes of the above-mentioned equilateral triangles, N(6)–H(6A) . . . N(2). The three DAT ligands are linked together by these hydrogen bonds to form a circular structure, and the other three DAT ligands also form such a structure (Fig. 2). Hydrogen bonds can also be formed between ClO_4^- anions and amino-groups of DAT ligands. Each O atom of ClO_4^- anion can form hydrogen bonds with three amino-groups of three DAT ligands from three different molecular units. It can be seen from the packing diagram (Fig. 3) that di-dimension layer structure was formed by the intermolecular hydrogen bonds between DAT ligands and ClO_4^- anions. The layers were linked together by the above hydrogen bonds to form the crystal structure. Therefore, it can be said that ClO_4^- anions play vital roles for the formation of the crystal structure of the title compound.

In $[\text{Cd}(\text{DAT})_6](\text{ClO}_4)_2$, most of the bond angles and bond lengths for DAT ligand are similar with the corresponding ones of DAT molecule and only $\text{NH}_2(\text{N})$ -group differs slightly from the ones of

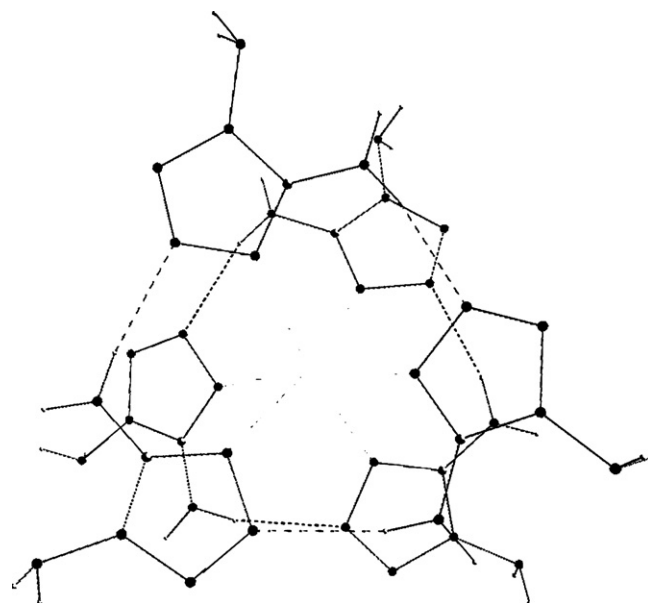


Fig. 2. Circular structure formed by the intramolecular hydrogen bonds between DAT ligands of $[\text{Cd}(\text{DAT})_6](\text{ClO}_4)_2$ (the central Cd is omitted).

DAT molecules [38]. It may be caused by the hydrogen-bond interactions in the crystal structure of the title coordination compound.

3.2. Thermal decomposition

In order to investigate the thermal decomposition of $[\text{Cd}(\text{DAT})_6](\text{ClO}_4)_2$, the DSC and TG experiments were carried out. DSC curve of the title compound at the heating rate of $5^\circ\text{C}/\text{min}$ is illustrated in Fig. 4. TG-DTG curves of the title compound at the heating rate of $5^\circ\text{C}/\text{min}$ in N_2 gas flowing at the rate of $20\text{ mL}/\text{min}$ are illustrated in Fig. 5.

It can be seen from the DSC curve, the decomposition of the title compound occurs in the temperature range of $197.9\text{--}600.0^\circ\text{C}$ with three exothermic stages. The first exothermic stage occurs in the range of $197.9\text{--}276.2^\circ\text{C}$ with the peak temperature at 243.5°C . Corresponding to this process, there is a mass loss of 59.16% in the TG-DTG curves. The cleavage of the amino-groups and the breaking of the tetrazole ring can be confirmed by the disappearance of the characteristic absorption bands of ν_{NH} at 3406 and 3381 cm^{-1}

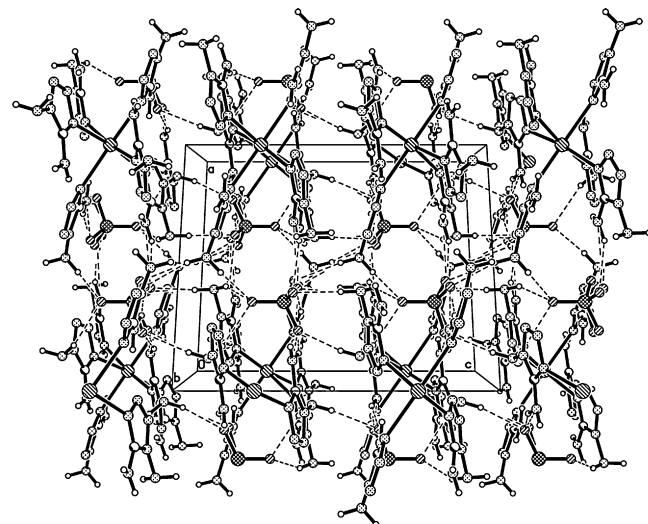


Fig. 3. Packing diagram of $[\text{Cd}(\text{DAT})_6](\text{ClO}_4)_2$ in crystal.

Table 3
Hydrogen bond lengths (\AA) and bond angles ($^\circ$) for $[\text{Cd}(\text{DAT})_6](\text{ClO}_4)_2^a$

D–H . . . A	d(D–H)	d(H . . . A)	d(D . . . A)	<(DHA)
N(5)–H(5A) . . . O(1)	0.9000	2.3400	3.171(2)	154.00
N(5)–H(5B) . . . O(2)#6	0.8900	2.2800	3.170(3)	173.00
N(6)–H(6B) . . . O(2)#7	0.8800	2.2900	3.115(2)	156.00
N(6)–H(6A) . . . N(2)#8	0.8800	2.1400	2.998(2)	164.00

^a Symmetry transformations used to generate equivalent atoms—#6: $1 - y, 1 - x, -1/2 + z$; #7: $y, x, 3/2 - z$; #8: $2 - y, 1 + x - y, z$.

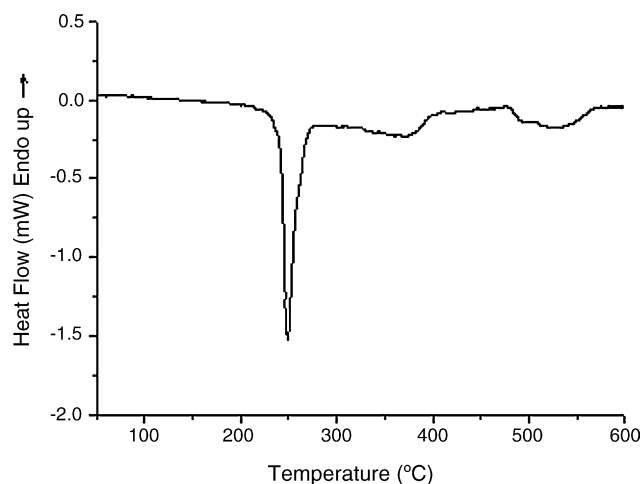


Fig. 4. The DSC curve of $[\text{Cd}(\text{DAT})_6](\text{ClO}_4)_2$ at a heating rate of $5^\circ\text{C}/\text{min}$.

and the characteristic absorption bands of $\nu_{\text{C}=\text{N}}$ at 1677, $\nu_{\text{N}=\text{N}}$ at 1626, along with $\nu_{\text{C}=\text{N}}$ at 1337 cm^{-1} in the FT-IR spectra of the residue at 276°C . The absorption bands at 1086 and 625 cm^{-1} indicate that there are $\text{Cd}(\text{ClO}_4)_2$ in the solid residue at 276°C . New bands at 1620, 1514, 1318, 1423 and 780 cm^{-1} prove the existence of $[-\text{CO}-\text{NH}-]$ polymer and $\text{Cd}(\text{CO}_3)_2$ in the solid residue.

The DSC curve shows that the title coordination compound undergoes further decomposition in the range of $295.9\text{--}471.1^\circ\text{C}$. During this process, the $\text{Cd}(\text{ClO}_4)_2$, $[-\text{CO}-\text{NH}-]$ polymer and $\text{Cd}(\text{CO}_3)_2$ decompose. This can be confirmed by the disappearance of the characteristic absorption bands of these groups in the FT-IR spectra of the residue at 471°C . New band at 2117 cm^{-1} prove the possible existence of $\text{Cd}(\text{NCO})_2$ [39] in the residue at 471°C .

The last exothermic process occurs in the range of $471.1\text{--}600.0^\circ\text{C}$. It can be seen from the TG-DTG curves that the mass of the final residue is 20.63% of the initial mass, coincident with the calculating value of CdCl_2 , 20.10%. The bands at 423 cm^{-1} in the FT-IR spectrum of the residue at 600°C prove that the final residue is CdCl_2 [40].

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

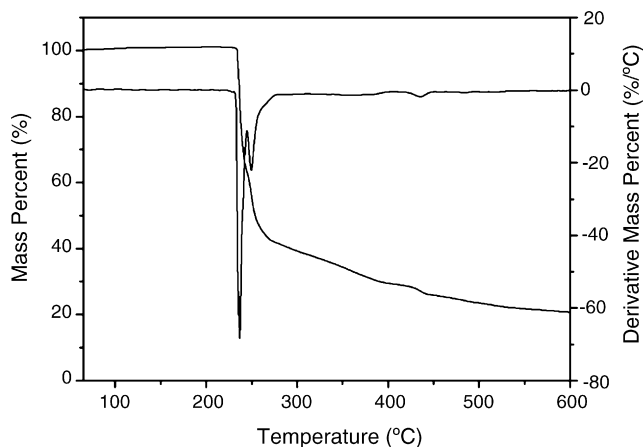
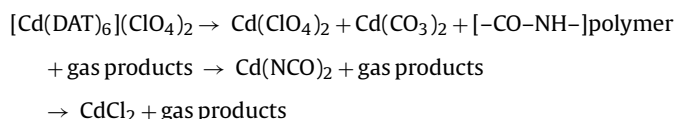


Fig. 5. The TG-DTG curves of $[\text{Cd}(\text{DAT})_6](\text{ClO}_4)_2$ at a heating rate of $5^\circ\text{C}/\text{min}$.

Table 4
Peak temperatures of the first exothermic stage at different heating rates and the kinetic parameters

Heating rates (K/min)	Peak temperatures (K)
2	505.45
5	516.65
10	522.45
20	530.35
The calculation results by Kissinger's method	
E_k (kJ/mol)	199.7
$\ln(A_k/s^{-1})$	18.12
Linear correlation coefficient (R_k)	-0.9968
The calculation results by Ozawa-Doyle's method	
E_o (kJ/mol)	198.1
Linear correlation coefficient (R_o)	-0.9971

3.3. Non-isothermal kinetics analysis

From the DSC and TG curve of $[\text{Cd}(\text{DAT})_6](\text{ClO}_4)_2$, we can infer that the first exothermic process make a dominant effect on the decomposition of the title compound. Kissinger's and Ozawa-Doyle's method were applied to study the kinetic parameters of the first exothermic process of the title compound, based on the DSC curve obtained under the condition of static air at heating rates of 2, 5, 10 and 20 K/min. The Kissinger and Ozawa-Doyle equations are as follows:

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

$$\log \beta + \frac{0.4567E}{RT_p} = C$$

where T_p is the peak temperature, K; R is the gas constant, $8.314\text{ J}/(\text{mol K})$; β is the linear heating rate, K/min; C is a constant.

The peak temperatures T_p (K) of the first exothermic process at different heating rates, the apparent activation energy E_k and E_o (kJ/mol), pre-exponential factor A_k (s^{-1}) and linear coefficient R_k and R_o were determined and listed in Table 4. The calculated results using both methods are similar and they are all in the normal range of kinetic parameters for the thermal decomposition reaction of solid materials [41].

The Arrhenius equation can be expressed by using the calculated E_a (the average of E_k and E_o) and $\ln A_k$ (Table 4) as follows: $\ln k = 18.12 - 198.9 \times 10^3/RT$ for the first-step exothermic decomposition. This equation can be used to estimate the rate constants of the initial thermal decomposition process of $[\text{Cd}(\text{DAT})_6](\text{ClO}_4)_2$.

3.4. Sensitivity test

Impact sensitivity was determined by using a Fall Hammer Apparatus. 20 mg $[\text{Cd}(\text{DAT})_6](\text{ClO}_4)_2$ was compacted to a copper cap under the press of 39.2 MPa, and was hit by 800 g drop hammer. The 50% firing high is 15.17 cm, which corresponds to the impact energy of 1.19 J. The impact sensitivity of the title compound is higher than that of lead azide [42].

Friction sensitivity was determined by a Pendulum Apparatus. When 20 mg $[\text{Cd}(\text{DAT})_6](\text{ClO}_4)_2$ was compressed between two steel poles with mirror surfaces at the pressure of 0.64 MPa, and was hit horizontally with a 1 kg hammer from 50° angle, the firing rate is 40%, which is higher than that of $\text{K}_2(\text{HTNPG})\cdot\text{H}_2\text{O}$ and $\text{K}_3(\text{TNPG})\cdot 2\text{H}_2\text{O}$ and much less than that of $\text{K}(\text{H}_2\text{TNPG})\cdot\text{H}_2\text{O}$ [43].

Flame sensitivity was tested according to the literature method [44]. 20 mg $[\text{Cd}(\text{DAT})_6](\text{ClO}_4)_2$ was compacted to a copper cap under the press of 39.2 MPa and was ignited by black powder pellet

which was situated right above the sample. The 50% firing high is 33.93 cm, which is higher than that of lead azide [42] and lower than that of RbDNBF [45].

4. Conclusions

An energetic coordination compound $[\text{Cd}(\text{DAT})_6](\text{ClO}_4)_2$ has been synthesized and structurally characterized. Its crystal structure belongs to trigonal system and the crystal structure data are as follows: $P\bar{3}c1$ space group, $a = 11.9445(7) \text{ \AA}$, $b = 11.9445(7) \text{ \AA}$, $c = 13.2162(14) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 120^\circ$ and $Z = 2$. The results show that the central cadmium(II) cation coordinates with six N atoms of six bulky DAT molecules. The molecular units of the title complex are linked together by the extensive intermolecular hydrogen bonds between DAT ligands and ClO_4^- anions. ClO_4^- anions play vital roles for the formation of the crystal structure of the title compound. Thermal analyses results show there are one intense and two mild exothermic decomposition stages in the temperature range of 197.9–600.0 °C in the DSC curve of the title complex, and the final residue at 600 °C is CdCl_2 . The sensitivity test results indicate that $[\text{Cd}(\text{DAT})_6](\text{ClO}_4)_2$ has sensitive nature toward impact, friction and heat. However, Cd is one kind of toxic heavy metal and perchlorate may be a possible teratogen and has adverse effects on thyroid function. All of those may limit the utilization of the title compound as energetic materials to some extent.

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Appendix A. Supplementary material

CCDC 671286 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033).

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