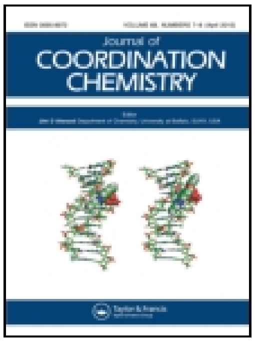

Journal of Coordination Chemistry

ISSN: 0095-8972 (Print) 1029-0389 (Online) Journal homepage: http://www.tandfonline.com/loi/gcoo20

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To cite this article: Xin Jin, Cai-Xia Xu, Xin Yin, Piao He & Jian-Guo Zhang (2015) A 1D cadmium complex with 3,4-diamino-1,2,4-triazole as ligand: synthesis, molecular structure, characterization, and theoretical studies, Journal of Coordination Chemistry, 68:11, 1913-1925, DOI: 10.1080/00958972.2015.1029465

To link to this article: http://dx.doi.org/10.1080/00958972.2015.1029465

Journal of Coordination Chemistry, 2015
Vol. 68, No. 11, 1913–1925, http://dx.doi.org/10.1080/00958972.2015.1029465

A 1D cadmium complex with 3,4-diamino-1,2,4-triazole as ligand: synthesis, molecular structure, characterization, and theoretical studies

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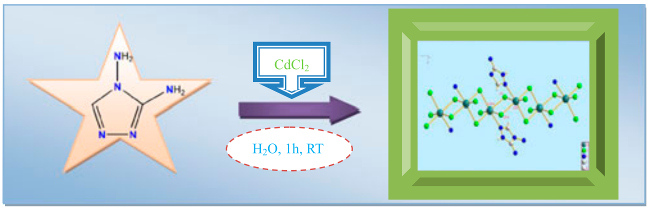
(*Received 30 October 2014; accepted 30 January 2015*)



A new 1D Cd complex based on 3,4-diamino-1,2,4-triazole was synthesized and structurally characterized. Its thermal stability, non-isothermal kinetics analysis, and theoretical calculation were studied, and energy of combustion was also measured.

An energetic complex, $[Cd_2(\mu\text{-}Cl)_4Cl_2(DATr)_2]_n$ (**1**) (DATr = 3,4-diamino-1,2,4-triazole), was synthesized from DATr·HCl and cadmium(II) chloride. The product was characterized by Fourier transform infrared spectroscopy analysis, elemental analysis, X-ray diffraction analysis, and differential scanning calorimeter (DSC) analysis. The central cadmium(II) ions in **1** are six-coordinate twisted octahedral structures, which are made up of 1D chains linked by bridging chlorides. The results of the DSC analysis suggest the temperature of decomposition to be above 503.15 K. Furthermore, the kinetic properties of decomposition are studied by Kissinger's and Ozawa–Doyle's methods, and the calculated average activation is 166.5 kJ M^{-1}, which means the complex is stable under normal conditions. In addition, the energy of combustion was measured by oxygen bomb calorimetry. The critical temperature of thermal explosion and parameters of thermodynamics of **1** were calculated. The periodic structure of **1** has been calculated based on the density functional theory. The theoretical results explain the electronic structure and thermal dynamic properties.

Keywords: Energetic complex; 3,4-Diamino-1,2,4-triazole ligand; Molecular structure; Thermal decomposition; Quantum chemical calculation

1. Introduction

To meet a variety of future military and civilian applications, many researchers attempt to make new energetic materials [1–4]. Recently, considerable attention has been paid to the

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*Corresponding author. Email: zjgbit@bit.edu.cn study of nitrogen-rich azole compounds as potential energetic materials. Azole-based heterocyclic compounds contain several advantages, such as smokeless combustion, good thermal stability, and positive heat of formation [5–8], which could be due to the existence of a large number of N–N and C–N bonds [9–16].

Azole-based compounds, 1,2,4-triazole, and its derivatives [11, 17–24] are versatile ligands, forming various compounds with interesting catalytic, magnetic, and explosive properties. Metal–organic frameworks involving 1,2,4-triazole and derivatives as ligands also have potential application in gas storage [25, 26]. The triazole 3,4-diamino-1,2,4-triazole (DATr) has high nitrogen content and is rich in lone pairs of electrons, being able to coordinate with transition metal ions. DATr can be coordinated as monodentate and as bidentate usually using N1 and N2 of the triazole ring. Compared to other triazole derivatives of only one amino substituent (e.g. 4-amino-1,2,4-triazole [13, 17, 27–29]), DATr increases nitrogen content and improves the possibility for hydrogen bonding to favor enhancing stabilities of complexes.

DATr has been described in the literature [30, 31]. However, DATr as a ligand has seldom been studied. The synthesis and crystal structure of $Zn(DATr)_2Cl_2$ was investigated, and the complex is biologically relevant [32]. Our group reported the synthesis and some energetic properties of several metal complexes based on 3,4-diamino-1,2,4-triazole [33]. For energetic materials, incorporating metals can both improve the sensitivities and increase classes of materials. In order to develop energetic compounds, we study complexes with chloride as counterions. Herein, we present a 1D Cd(II) complex based on DATr, $[Cd_2(\mu\text{-}Cl)_4Cl_2(DATr)_2]_n$ (**1**). We study preparation, crystal structure and discuss other characteristics of **1**. Furthermore, theoretical calculations of **1** are investigated.

2. Experimental

Caution: *The title compound could have energetic properties. Proper protective measures should be taken.*

2.1. *Materials*

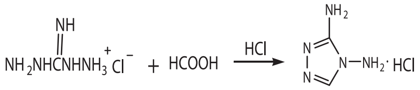
All reagents and solvents were of analytical grade and used as commercially obtained. 3,4-Diamino-1,2,4-triazole (DATr) was prepared as described in the literature [34].

2.2. *General methods*

Elemental analysis was performed with a Flash EA 1112 full automatic trace element analyzer. Fourier transform infrared (FT-IR) spectra were recorded with a Bruker Equinox 55 infrared spectrometer (KBr pellets) from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1}. Differential scanning calorimeter (DSC) analyses were carried out by heating from room temperature to 773.15 K with a Pyris-1 DSC in dry nitrogen with flow rate of 20 mL min^{-1}.

2.3. *Synthesis*

3,4-Diamino-1,2,4-triazolium chloride was synthesized by starting from the reaction of the diamino-guanidinium chloride with formic acid and hydrochloric acid as catalytic agent under reflux.



Synthesis of $[Cd_2(\mu\text{-}Cl)_4Cl_2(DATr)_2]_n$ (**1**): After a solution of lithium hydroxide (5 mmol) was used to neutralize the solution of 3,4-diamino-1,2,4-triazole (5 mmol), a solution of cadmium chloride (5 mmol) in water (10 mL) was added dropwise. The mixture was stirred for 1 h at room temperature. Subsequently, a white precipitate was obtained and filtered, and the solid was washed two times with water, then left to dry in ambient air. After several days, plates of **1** from the mother liquor, suitable for X-ray analysis, were obtained. The synthesis route of **1** is shown in figure 1. Yield: 1.4 g (87.5%). IR (KBr, cm^{-1}): $\tilde{\upsilon} = 3441$ (s), 3318(s), 3067(w), 1660(s), 1614(w), 1544(m), 1336(s), 1205(s), 1105(w), 1030(w), 997 (s), 962(w), 836(m), 727(s), 634(s), 502(w). $C_4H_{12}N_{10}Cl_6Cd_2$ ($M_W = 637.74$): Calcd (%): C, 7.53; H, 1.88; N, 21.95. Found: C, 7.41; H, 2.04; N, 21.41.

2.4. *X-ray data collection and structure refinement*

Single crystals with suitable dimensions were selected for X-ray diffraction analysis. The data collection was performed with a Rigaku AFC-10/Saturn 724 + CCD detector diffractometer with graphite monochromated Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å) at 153(2) K with multi-scan modes. The structures were solved by direct methods using SHELXS-97 (Sheldrick, 1990) [35] and refined by full-matrix least-squares methods on F^2 with SHELXL-97 [36]. All non-hydrogen atoms were obtained from the difference Fourier map and refined anisotropically. The hydrogens were treated geometrically and a constrained refinement.

Crystallographic data (excluding structure factors) for the structures in this article have been deposited with the Cambridge Crystallographic Data Center, CCDC, 12 Union

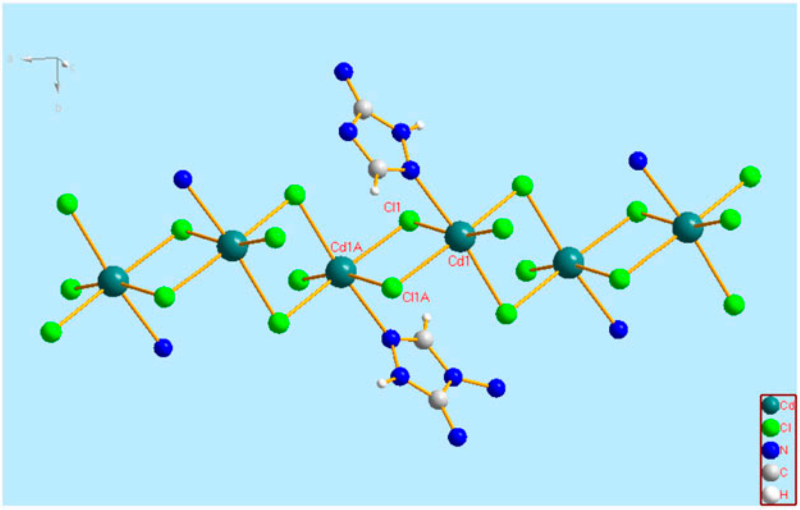


Figure 1. The molecular structure of **1**.

Road, Cambridge CB2 1EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC-971263 (Fax:+44–1223-336–033; E-mail: deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

3. Results and discussion

3.1. *Crystal description*

Complex **1** crystallizes in the monoclinic space group $P2_1/c$ with two molecular moieties in the unit cell. The calculated density is 2.477 g cm^{-3}. A view of the molecular structure and a view of the detailed crystallographic data of **1** are depicted in figure 1 and table 1. Each cadmium is six-coordinate linked by five chlorides and one DATr; this coordination number is the same as that of the central metal of those complexes based on DATr as ligands [33] and other Cd(II) energetic complexes [37, 38]. Two central Cd ions are bridged by two chlorides, but adjacent metal ions of similar complexes are connected by three DATr molecules [33]. N1 of DATr is the coordination site of the five-membered ring. Meanwhile, the C1 of triazole ring in DATr has been protonated.

Cd–Cl bond distances (between 2.5618(9) and 2.6856(10) Å) are slightly longer than Cd–Nl distance (2.502(2) Å). Both Cd–Cl1 and Cd1A–Cl1A bond lengths are 2.6856(10) Å for the weakest bonds with Cd, while Cd–Cl1A and Cd1A–Cl1 bonds (2.5618(9) Å) are stronger among all the Cd–Cl bonds. These distances are much longer than those found in similar coordination compounds [39]_ENREF_22. Metal coordination has slightly changed the bond lengths of N–N and C–N bonds of the triazole ring [31].

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

Formula	$[CdC_2H_6Cl_3N_5]_2$
Mr [g·M^{-1}]	637.74
Crystal system	Monoclinic
Space group	*P*2(1)/*c*
a [Å]	6.494(2)
b [Å]	11.616(4)
c [Å]	11.599(4)
β [°]	102.305(4)
V [$Å^3$]	854.9(5)
Z	2
ρ [g·cm^{-3}]	2.477
μ [mm^{-1}]	3.434
F(0 0 0)	608
T [K]	153(2)
θ range [°]	3.21–31.50
Data-set [*h*, *k*, *l*]	$-9 \le h \le 9$, $-17 \le k \le 10$, $-17 \le l \le -17$
R_{int}	0.0300
Absorption	Semi-empirical
R_1 (obsd)	0.0311
wR_2 (all data)	0.0631
Refinement	Full-matrix
Max(trans)	0.5056
Min(trans)	0.3515

Bond angles of two *trans* chlorides and cadmium ions as well as the bond angles of N–Cd–Cl (the *trans* chloride to 1,2,4-triazole ring) deviate from 180°, which results in a distorted octahedral configuration. The torsion angle of Cl(1A)–Cd(1)–Cl(1)–Cd(1A) is 0°, which suggests that Cd1, Cd1A, Cl1, and Cl1A form a rhombus geometry with the equation of plane A: $4.083x - 8.946y + 1.813z = 18.485$. Similarly, the four-membered ring is formed by Cd1A, the other Cd and bridged Cl^- corresponding to the equation of plane B: $4.590x + 2.542y - 8.513z = -24.105$. The dihedral angle between A plane and B plane (in figure 2) is 78.792°. The 1,2,4-triazole ring also forms a plane with the equation of $5.564x + 6.976y - 4.514z = -38.609$.

The cadmiums in **1** make up a 1D chain linked by bridging chlorides. Hydrogen bonds extend the solid into a 3D supramolecular structure, which is similar to the crystal structure of the zinc complex with DATr [32]. The packing diagram of **1** and detailed hydrogen-bond information are shown in figure 3 and table 2, respectively. Hydrogen bonds are formed between amino groups of a 1,2,4-triazole and the NH_2 groups of the other 1,2,4-triazole ligand (N–H···N) as well as chlorides. The extensive hydrogen bonds play an important role in the thermal stability of **1**.

3.2. *Vibration spectroscopy*

FT-IR spectrum [40] of **1** is shown in figure 4. The sharp, strong band at 3318 cm^{-1}, which corresponds to NH_2 stretch [41], is present in the IR spectrum. C–N stretching vibrations at 1100–1010 cm^{-1} are in the spectrum of **1**. The band at 502 cm^{-1} may be due to the Cl–Cd vibration [42, 43]. At 700–600 cm^{-1}, there are characteristic deformation bands of the triazole ring. The band at 1545 cm^{-1} is assigned to the 1,2,4-triazole ring stretching vibration for DATr.

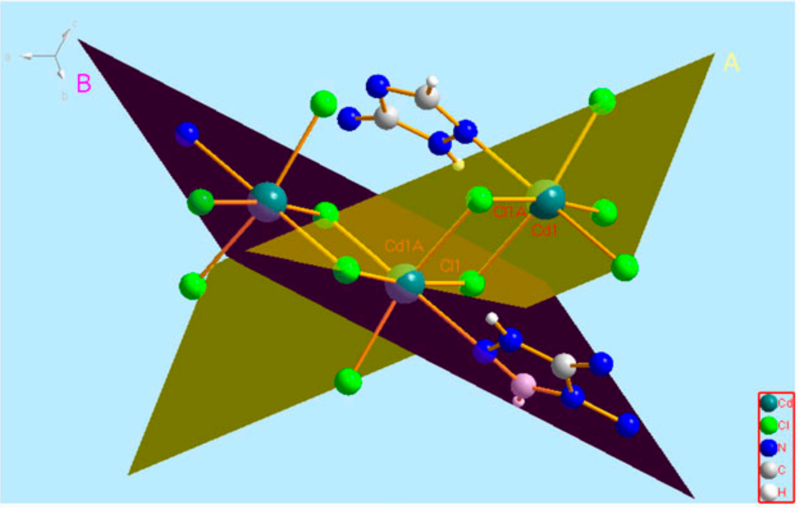


Figure 2. The two planes A and B in **1**.

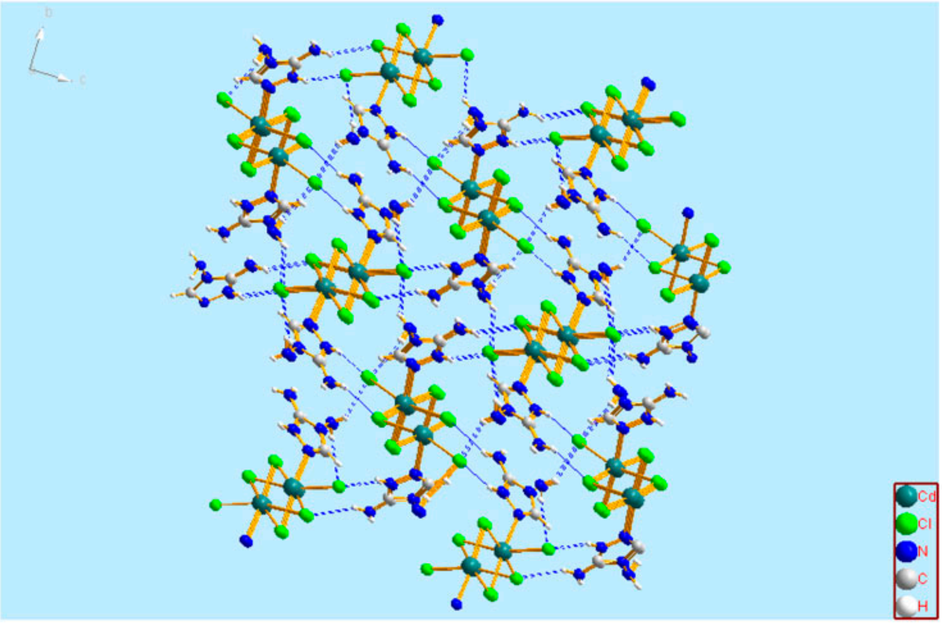


Figure 3. The packing diagram of **1**.

Table 2. Hydrogen bonding (Å, °) information for **1**.

D−H⋯A	d(H⋯A) (Å)	d(D⋯A) (Å)	<(DHA) (°)	Symmetry code A
N3−H3N⋯Cl3	2.2600	3.0542	151.00	$x, 1/2-y, 1/2+z$
N4−H4A⋯Cl3	2.6400	3.4867	161.00	$-1+x, y, z$
N4−H4B⋯Cl3	2.6500	3.2772	138.00	$1-x, 1/2+y, 1/2-z$
N5−H5A⋯N4	2.6100	2.9011	102.00	$-x, 1-y, 1-z$
N5−H5B⋯Cl1	2.5800	3.2646	140.00	$1-x, 1/2+y, 3/2-z$

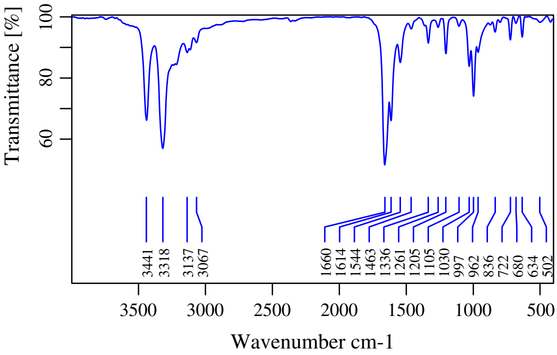


Figure 4. The FT-IR spectrum of **1**.

3.3. *Thermal behavior*

The melting point and decomposition temperatures are used to investigate the thermal properties of **1** with the DSC measurements. DSC curve of **1** under the linear heating rate of 10 K min^{-1} is illustrated in figure 5. In the DSC curve of **1**, a melting point was at 530.7 K and there was an exothermic process at 613.2–643.2 K. The exothermic peak occurred at 633.6 K, and DSC curve of **1** showed that the decomposition temperature based on its onset DSC peak was 628.2 K. No endothermic peak for the loss of crystal water or coordinated water was found from the DSC curve, which is in agreement with the obtained crystal structure of **1**.

Complex **1** is thermally stable (decomposing above 503.2 K), which may be attributed to the symmetry of crystal unit and a large number of hydrogen bonds in **1**. Metal coordination compounds based on DATr are heat resistant.

Energy of combustion is important to assess energetic properties of a complex. Constant volume energy of combustion (Qv) of 5.94 MJ kg^{-1} was measured by oxygen bomb calorimetry in an oxygen atmosphere. The data imply that the complex has good energetic characteristics.

3.4. *Non-isothermal kinetics analysis*

Kissinger's methods [44] and Ozawa's methods [45] are widely used to determine the Arrhenius equation for a given material. The Kissinger [Equation (a)] and Ozawa equations [Equation (b)] are as follows:

$$\ln \beta / {T_\mathrm{p}}^2 = \ln[RA/E_\mathrm{a}] - E_\mathrm{a}/(RT_\mathrm{p}) \tag{a}$$

$$\lg \beta = \lg[AE_\mathrm{a}/RG(\alpha)] - 2.315 - 0.4567 E_\mathrm{a}/(RT_\mathrm{p}) \tag{b}$$

T_p is the temperature (K) at which the first exothermic peak occurs in the DSC curve; A is the pre-exponential factor [s^{-1}]; E_a is the apparent activation energy [kJ M^{-1}]; R is the gas

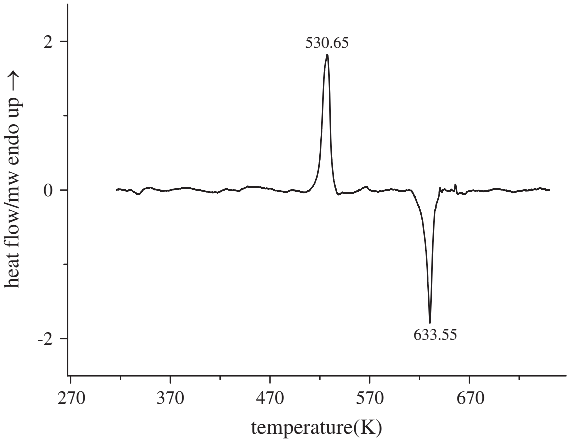


Figure 5. The DSC curve of **1** at heating rate of 10 K min^{-1}.

constant (8.314 J K^{-1} M^{-1}); β is the linear heating rate [K min^{-1}]; and $G(\alpha)$ is the reaction mechanism function.

Based on the first exothermic peaks measured with four different heating rates of 5, 10, 15, and 20 K min^{-1}, Kissinger's and Ozawa's methods are applied to study the kinetic parameters of **1**. From these data, the apparent activation energies E_k and E_o, the pre-exponential factor A_k, and linear correlation coefficients R_k and R_o were determined and are listed in table 3. Accordingly, the Arrhenius equation of **1** can be expressed as follows (E is the average of E_k and E_o): $\ln k = 11.43–166.5 \times 10^3/(RT)$.

Comparison of the value of the average activation energy of 166.5 kJ M^{-1} for **1** with literature data for energetic cobalt(II) complex [46] shows that the values are analogous.

3.5. *Calculation of critical temperature of thermal explosion and parameters of thermodynamics (ΔS≠, ΔH≠, and ΔG≠)*

According to equation [47] (c), the value of the peak temperature corresponding to $\beta \rightarrow 0$ is 665.25 K, where a, b, and c are coefficients.

$$T_{\mathrm{pi}} = T_{\mathrm{p0}} + a\beta_{\mathrm{i}} + b\beta_{\mathrm{i}}^2 + c\beta_{\mathrm{i}}^3 \qquad \text{(c)}$$

The corresponding calculated critical temperature of thermal explosion is 688.53 K, according to equation (d), where R is the gas constant (8.314 J K^{-1} M^{-1}). E_o is the value of activation energy calculated by Ozawa's method.

$$T_{\mathrm{bp}} = \frac{E_o - \sqrt{E_{\mathrm{o}}^2 - 4E_{\mathrm{o}}RT_{\mathrm{p0}}}}{2\mathrm{R}} \qquad \text{(d)}$$

The entropy of activation ($\Delta S^{\neq}$), enthalpy of activation ($\Delta H^{\neq}$), and free energy of activation ($\Delta G^{\neq}$) of the decomposition reaction of **1** corresponding to $T = T_{p0}$, $E_a = E_k$, and $A = A_k$ (obtained by Kissinger's method), calculated by the following equations [48] (e)–(g) are –156.55 J K^{-1} M^{-1}, 159.97 kJ M^{-1}, and 264.08 kJ M^{-1}, respectively.

Table 3. The temperature of the first main exothermic peak at different heating rates and chemical kinetic parameters of **1**.

	$[Cd_2(\mu\text{-}Cl)_4Cl_2(DATr)_2]_n$
Heat rates	Peak temperature Tp/K
5	631.05
10	633.55
15	648.75
20	652.55
Kissinger's method	
E_k [kJ·M^{-1}]	165.5
ln A_k	11.43
R_k	0.9119
Standard deviation	0.2866
Ozawa's method	
E_o	167.5
R_o	0.9211
Standard deviation	0.1245

$$A = \frac{k_{\mathrm{B}}T}{h} e^{\frac{\Delta S^{\neq}}{R}} \tag{e}$$

$$\Delta H^{\neq} = E - \mathrm{RT} \tag{f}$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \tag{g}$$

where k_{B} is the Boltzmann constant and h is the Plank constant.

The calculated critical temperature of thermal explosion is higher than that of some alkali [49] and alkaline-earth [50, 51] metal energetic compounds, which indicate that **1** is fairly stable and safe under general conditions.

3.6. *Theoretical calculation analysis*

The structure was calculated using the Dmol^3 [52] code of Materials Studio 5.0 program package. Perdew Burke Ernzerhof (PBE) [53] variant of the generalized gradient approximation [54] has been used to calculate the exchange–correlation energy. The total energy of the system was converged in 1.0×10^{-5} Ha, while the remaining forces on the atoms were <0.002 Ha/Å. The displacement of atoms is <0.005 Å. The smearing width was set at 0.05 eV for easier converge. In the calculation, all the electrons are included in the orbital basis set of DNP (double numerical plus polarization). We have used 4 × 2 × 2 *k*-points to sample the Brillouin zone. The smearing width was set at 0.05 Ha in the simulation experiments. The optimized molecular structure is shown in figure 6, and selected bond lengths and angles of theoretical calculations are listed in tables 4 and 5.

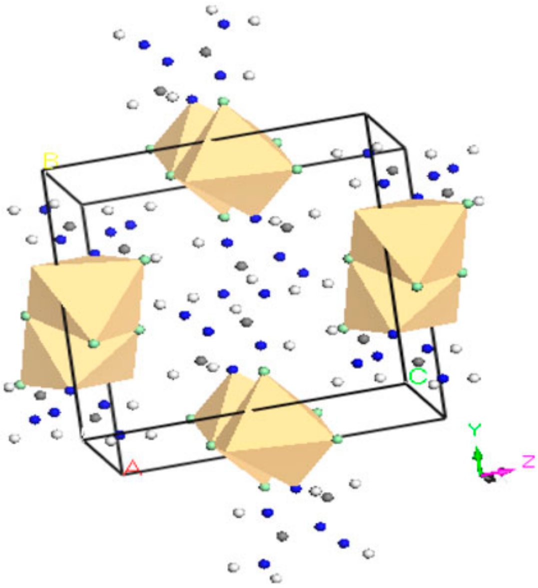


Figure 6. The optimized crystal structure of **1**.

Table 4. Select theoretical and experimental bond lengths/Å for **1**.

Bond	Exp.	Cal.	Bond	Exp.	Cal.
Cd(1)–N(2)	2.502(2)	2.498	Cd(1)–Cl(2C)	2.6336(9)	2.676
Cd(1)–Cl(1)	2.6856(10)	2.715	Cd(1)–Cl(3)	2.5688(9)	2.632
Cd(1)–Cl(1A)	2.5618(9)	2.615	N(1)–N(4)	1.409(3)	1.399
Cd(1)–Cl(2)	2.5682(8)	2.602	N(5)–C(2)	1.324(3)	1.327
Cl(1)–Cd(1A)	2.5618(9)	2.615	Cl(2)–Cd(1A)	2.6336(9)	2.676

Table 5. Select theoretical and experimental bond angles/° for **1**.

Bond angle	Exp.	Cal.	Bond angle	Exp.	Cal.
Cl(1A)–Cd(1)–Cl(2)	171.918(19)	172.220	N(2)–Cd(1)–Cl(2)	96.53(5)	98.379
N(2)–Cd(1)–Cl(2C)	172.97(5)	169.94	Cl(2)–Cd(1)–Cl(2C)	90.36(3)	91.631
Cl(3)–Cd(1)–Cl(1)	101.347(19)	105.131	Cd(1A)–Cl(1)–Cd(1)	92.35(3)	91.794
N(2)–Cd(1)–Cl(1A)	83.71(5)	84.320	Cd(1)–Cl(2)–Cd(1)#2	89.64(3)	88.369
N(5)–C(2)–N(1)	126.3(2)	126.153	C(2)–N(1)–C(1)	107.17(19)	107.204
N(3)–C(2)–N(1)	105.7(2)	105.559	C(2)–N(1)–N(4)	122.75(19)	122.752

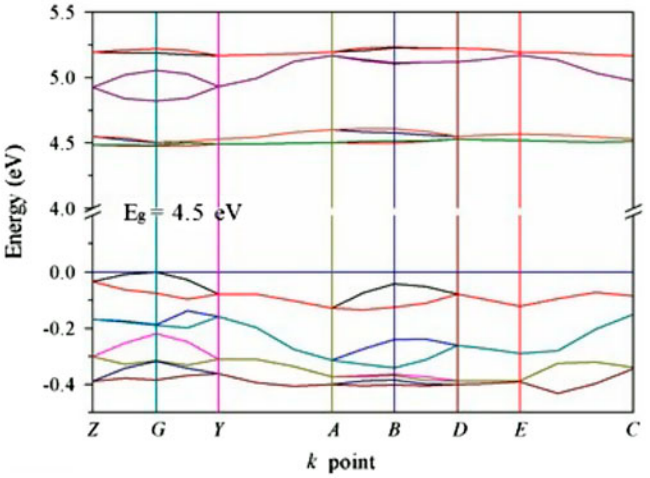


Figure 7. The electronic band structure of **1**.

The electronic band structure and the total and partial density of states (DOS) of the complex are shown in figures 7 and 8, respectively. In figure 7, the band gap of the complex is 4.5 eV, which indicates that it is an insulator. According to the abovementioned statement, it is concluded that **1** is insensitive toward mechanical stimulation under normal conditions. From figure 7, the top part of the valence band of the total DOS in **1** has two peaks, mainly dominated by p states. The valence band and the conduction band are mainly composed of the overlap of ns and np states. External chlorides and DATr make important contribution to providing s and p states, which also suggests that the electronic transition of chlorides and DATr molecules may cause the chemical reaction of the Cd complex.

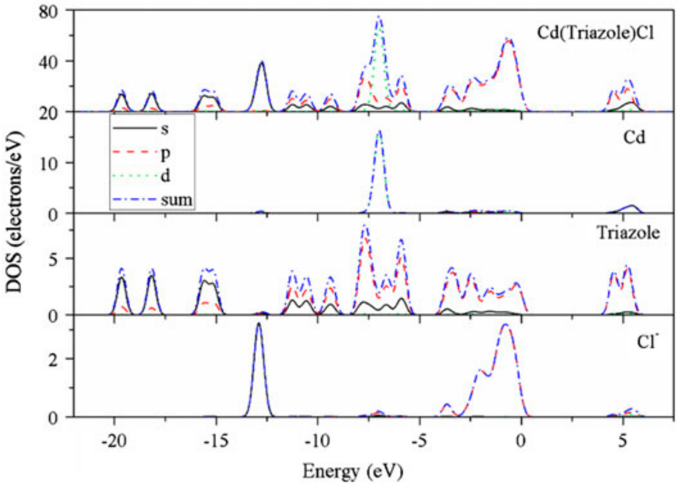


Figure 8. The total and partial densities of states of **1**.

To further analyze the structure, from total and partial DOS in figure 8, several energy band regions are distributed in the valence energy band structure. The main energy band region at –8.5 Ha to –5 Ha is dominated by the Cd ion and the p state of the triazole, which indicates that bonding of Cd with ligand is built through sharing lone pair electrons. A few electrons of Cl^- ions are also detected in this region, showing that Cl^- can form a coordination bond with Cd, which is consistent with the experimental results. The energy band regions of Cd and ligand near the Fermi level do not overlap, also illustrating that the bond between the Cd and ligand is coordination, not ionic bonds. Meanwhile, some electrons of Cl^- and DATr appear in the region (–5 Ha – 0 Ha), which demonstrates that Cl^- ions form hydrogen bonds with NH_2 groups of 3,4-diamino-1,2,4-triazole ligands as found in the crystal structure.

4. Conclusion

Complex **1** based on DATr was synthesized and characterized by FT-IR analysis, elemental analysis, and X-ray diffraction analysis. Cadmium is six-coordinate with one nitrogen and five chlorides, which are composed of 1D chains linked by bridging chlorides. Furthermore, the structure forms a 3D network construction connected by a variety of hydrogen bonds. Adjacent cadmium ions are bridged by two chlorides, and the N1 of 1,2,4-triazole ring in DATr is the coordination site. Chlorides are coordinated not only as monobidentate, but also as bidentate ligands. DSC analysis shows that **1** is thermally stable (decomposing above 503.2 K). The constant volume energy of combustion of **1** was determined experimentally as 5.94 MJ kg^{-1}. The critical temperature of thermal explosion and parameters of thermodynamics of **1** were calculated, T_{bp}, $\Delta S^{\neq}$, $\Delta H^{\neq}$, and $\Delta G^{\neq}$ as 688.53 K, –156.55 J K^{-1} M^{-1}, 159.97 kJ M^{-1}, and 264.08 kJ M^{-1}, respectively, which indicate that **1** is fairly stable and safe under general conditions. Theoretical studies show that **1** may depend on chlorides. According to experiment measurements and quantum chemical calculations, **1** is heat resistant and has good energetic properties. Therefore, compared to the common explosive RDX (T_{dec} = 483.2 K) [55] and energetic coordination compounds, such as CHP (T_{dec} = 467.2 K) and NHP (T_{dec} = 493.2 K) [56], **1** may be candidate as a thermally resistant energetic compound.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

The work was financially supported from the National Natural Science Foundation of China [grant number 10776002] and the project of State Key Laboratory of Science and Technology [grant number ZDKT12-03], [grant number YBKT16-04].

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