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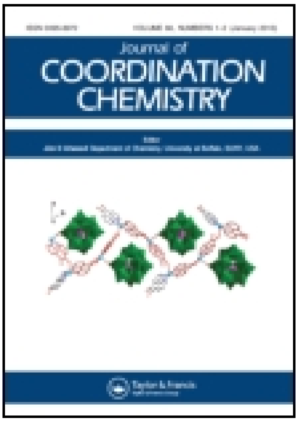

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Preparation, crystal structure, and thermal decomposition of an azide energetic compound $[Cd(IMI)_2(N_3)_2]_n$ (IMI=imidazole)

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Accepted author version posted online: 03 Jun 2013.Published online: 02 Aug 2013.

To cite this article: Bi-Dong Wu , Yan-Gang Bi , Zun-Ning Zhou , Li Yang , Jian-Guo Zhang & Tong-Lai Zhang (2013) Preparation, crystal structure, and thermal decomposition of an azide energetic compound $[Cd(IMI)_2(N_3)_2]_n$ (IMI=imidazole), Journal of Coordination Chemistry, 66:17, 3014-3024, DOI: 10.1080/00958972.2013.810733

To link to this article: http://dx.doi.org/10.1080/00958972.2013.810733

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Journal of Coordination Chemistry, 2013
Vol. 66, No. 17, 3014–3024, http://dx.doi.org/10.1080/00958972.2013.810733

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Preparation, crystal structure, and thermal decomposition of an azide energetic compound $[Cd(IMI)_2(N_3)_2]_n$ (IMI = imidazole)

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(*Received 27 November 2012; in final form 2 April 2013*)

Cadmium(II) imidazole (IMI) azide $[Cd(IMI)_2(N_3)_2]_n$ (**1**) was synthesized using imidazole and azide, and was characterized by the elemental analysis and FTIR spectrum. The crystal structure was determined by X-ray single crystal diffraction, and the crystallographic data show that the crystal belongs to *orthorhombic*, *Pba2* space group, $\alpha = 10.780(4)$ Å, $b = 13.529(5)$ Å, and $c = 3.6415(12)$ Å. Its crystal density is $2.080\ g \cdot cm^{-3}$. Cd(II) is a six-coordinate with six nitrogens from four imidazoles and two azides with μ–1,1 coordination. The thermal decomposition mechanism was determined based on differential scanning calorimetry (DSC) and thermogravimetry-derivative thermogravimetry (TG-DTG) analysis, and the kinetic parameters of the first exothermic process were studied using Kissinger's method and Ozawa's method, respectively. The energy of combustion, enthalpy of formation, critical temperature of thermal explosion, entropy of activation ($\Delta S^{\neq}$), enthalpy of activation ($\Delta H^{\neq}$), and free energy of activation ($\Delta G^{\neq}$) were measured and calculated. In the end, impact sensitivity was also determined by standard method.

Keywords: Cadmium(II); Imidazole; Crystal; Thermal; Sensitivity

1. Introduction

Energetic materials as controllable storage systems for relatively large amounts of chemical energy are widely applied in civil and military applications. In order to meet the requirements of modern high-energy-density materials (HEDMs), the synthesis of energetic heterocyclic compounds has attracted considerable interest due to their rather large densities, good oxygen balance, high performance, and environmental compatibility [1, 2]. Klapötke and Shreeve groups and other chemists have studied nitrogen-rich energetic compounds and salts on the basis of imidazole [3–12], triazole [13–22], tetrazole [23–41], and other energetic compounds [42–45].

Azides (N_3^-) are widely used as bridging groups in the reported compounds because of their effective exchange interactions with versatile coordination modes (figure 1), enabling compounds of great diversity depending on the reaction environment. Many scientists have researched azide salts and compounds with potential application as energetic materials [17, 44, 46–49]. Ma *et al.* synthesized and structurally characterized the azide compound

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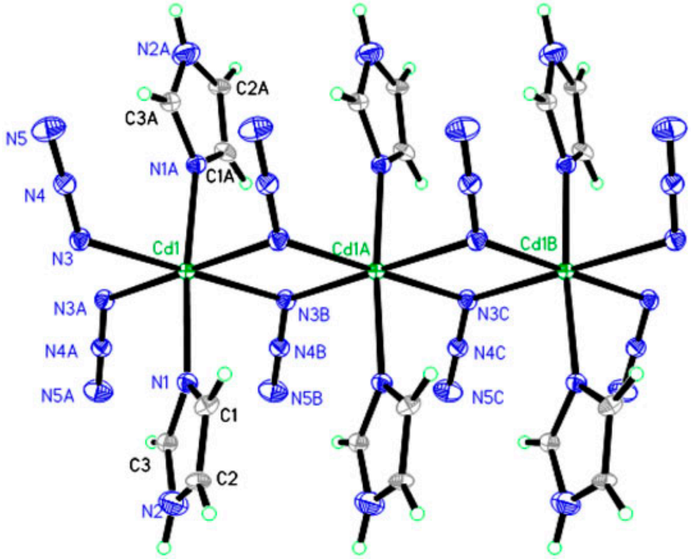

Figure 1. The molecule structure of **1**; thermal ellipsoids drawn at 50% probability level.

$[Mn_3(N_3)_6(admtrz)_4]_n$ (admtrz = 4-amino-3,5-dimethyl-1,2,4-triazole) [17]. The azides have three different coordination modes: μ–1, μ–1,3 and μ–1,1 modes [17].

Imidazole (IMI) is a heterocyclic compound containing two potential nitrogens for coordination and three carbons, with a nitrogen content of 41.15%. Imidazole derivative compounds can be obtained through the following ways. First, a new compound was synthesized by introducing azido or nitro explosive groups in IMI group, such as 2-azido-imidazole [3], nitro-imidazole [8], dinitro-imidazole [50], trinitro-imidazole [6, 51], etc. [7]. Second, the preparations of energetic salts are by neutralization or metathesis reactions. The role of the imidazole ring as a metal binding site is well-known. A series of energetic compounds as a class of high energetic materials have been developed in our laboratory based on the imidazole and azide; $Cu(IMI)_4(N_3)_2$ [11], $Ni(IMI)_4(N_3)_2$ [11], $[Ni(IMI)_6](ClO_4)_2$ [52], $[Ni(IMI)_6](NO_3)_2$ [52], and $[Cu(IMI)_4](PA)_2$ [53] are nitrogen-rich materials and their nitrogen contents are 46.70%, 47.27%, 25.23%, 33.17%, and 24.74%, respectively. Especially, $Ni(IMI)_4(N_3)_2$ had higher combustion heat than that of TNT (2,4,6-trinitrotoluene), RDX (1,3,5-trinitro-1,3,5-triaza-cyclohexane), and HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazocane), and was regarded as an energy additive, which can improve the explosion performance of the traditional explosives and propellant formulations.

In order to deepen the study on imidazole azide compounds, $[Cd(IMI)_2(N_3)_2]_n$ (**1**) was synthesized and its crystal structure, thermal decomposition mechanism and impact sensitivity were studied in the present work.

2. Experimental

General caution: The title compound is an energetic material and tends to explode under certain conditions. Appropriate safety precautions (safety glasses, face shields, leather coat, and ear plugs) should be taken, especially when the compound is prepared on a large scale and in a dry state.

2.1. *Materials and physical techniques*

All reagents and solvents were of analytical grade and were used as commercially obtained. Elemental analysis was performed on a Flash EA 1112 full-automatic trace element analyzer. The FTIR spectra were recorded on a Bruker Equinox 55 infrared spectrometer (KBr pellets) from 4000∼400 cm^{-1} with a resolution of 4 cm^{-1}. DSC and TG measurements were carried out using a Pyris–1 differential scanning calorimeter and Pyris–1 thermogravimetric analyzer (Perkin–Elmer, USA). The combustion heat was measured by an oxygen bomb calorimetry (Parr 6200, USA) in an atmosphere of oxygen at a pressure of 3.10 MPa.

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2.2. *Synthesis of $[Cd(IMI)_2(N)_2]_n$*

$Cd(NO_3)_2 \cdot 6H_2O$ (10 mmol) was dissolved in distilled water (30 mL) and then charged into a glass reactor with a water bath. It was mechanical stirred and heated to 60∼70 °C. Imidazole (20 mmol) and sodium azide (20 mmol) were dissolved in distilled water (20 mL) and adjusted to pH 7.0 and 8.0∼9.0 with dilute nitric acid, respectively. Subsequently, they were added to Cd(II) aqueous solution during 25∼30 min with continuous stirring and the solution was allowed to cool to room temperature. The yield was 58%. The resulting solution was filtered and evaporated slowly at room temperature for a week. Colorless prism crystals suitable for X-ray analysis were obtained. FTIR (KBr, cm^{-1}) v: 3134, 2944, 2037, 1631, 1536, 1490, 1429, 1067, 780, 652, 617. Elemental analysis for $CdC_6H_8N_{10}$ (molar mass: 332.62 $g \cdot mol^{-1}$), Calcd (%): C 21.67 N 42.11 H 2.42. Found (%): C 21.76 N 42.17 H 2.38.

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

A crystal was chosen for X-ray determination. The X-ray diffraction data were collected on a Rigaku AFC−10/Saturn 724$^+$ CCD detector diffractometer with graphite monochromated Mo K_α radiation ($\lambda = 0.071073$ nm). The structure was solved by direct methods using *SHELXS–97* [54] (Sheldrick, 1990) and refined by full-matrix least-squares on F^2 with *SHELXL–97* [55] (Sheldrick, 1997). All nonhydrogen atoms were obtained from the difference Fourier map and were subjected to anisotropic refinement by full-matrix least-squares on F^2. Detailed information concerning crystallographic data collection and structure refinement are summarized in table 1.

Further information regarding the crystal structures determination has been deposited with the Cambridge Crystallographic Data Center as supplementary publication. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223–336,033; E-mail: deposit@ccdc.cam.ac.uk).

3. Results and discussion

3.1. *Crystal structure description*

In our previous study, the electron density of the highest occupied molecular orbitals (HOMOs) at N(1) of the imidazole is relatively higher than the lowest unoccupied molecular orbitals (LUMOs) [11, 52]. It is easy to understand the coordination bond formation between N and Cd(II).

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

Compound	**1**
CCDC	910442
Empirical formula	$CdC_6H_8N_{10}$
Formula mass	332.62
Temperature (K)	153(2)
Color	prism
Crystal dimensions (mm)	0.36 × 0.13 × 0.13
Crystal system	*Orthorhombic*
Space group	*Pba2*
Z	2
a (Å)	10.780(4)
b (Å)	13.529(5)
c (Å)	3.6415(12)
h, k, l	–15∼15, –14∼19, –5∼5
Unit cell dimensions V (Å^3)	531.1(3)
D_c (g cm^{-3})	2.080
μ (Mo K$_\alpha$) (mm^{-1})	2.052
F (0 0 0)	324
θ Range (°)	3.01∼31.48
Max. and min. transmission	0.7835, 0.5294
Measured reflections	4241
Unique data	1612 ($R_{int}=0.0242$)
R_1, wR_2 [$I>2\sigma(I)$]	0.0277, 0.0744[a]
R_1, wR_2 (all data)	0.0308, 0.0776[a]
Goodness of fit	1.001
δp_{max}, δp_{min} (e Å^{-3})	1.132, −0.664

$wR_2=[\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)]^{1/2}$, $P=(F_o^2+2F_c^2)/3$; [a]$w=1/[\sigma^2(F_o^2)+(0.0468P)^2+0.3860P]$.

In **1**, there are one cadmium(II), two imidazoles, and two azides as the bidentate bridging ligands (μ–1,1, EO) (figure 1). The six basically equivalent Cd–N bonds are approximately equal, 2.26∼2.44 Å from table 2. The two contraposition azides and Cd(II) bond angles are 179.39(16)° (<N3–Cd1–N3B). The Cd(II) bond angles are close to 90°. There is a plane A (Cd1–N3–N3A–N3B) formed by four N3 of azido groups and Cd(II) (plane equation is $-2.533\ x+13.150\ y+0\ z=11.884$ ($R=0.000$)). All data demonstrate that Cd(II) exhibits a distorted octahedral configuration (figure 2).

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

Bond		Bond		Bond	
Cd1–N1#1	2.258(2)	Cd1–N3	2.408(4)	Cd1–N3#4	2.438(4)
Cd1–N1	2.258(2)	Cd1–N3#2	2.438(4)	N3–N4	1.198(4)
Cd1–N3#1	2.408(4)	Cd1–N3#3	2.438(4)	N4–N5	1.156(4)
Angle		Angle		Angle	
N1#1–Cd1–N1	174.74(19)	N3–Cd1–N3#2	179.39(16)	N5–N4–N3	178.0(4)
N1#1–Cd1–N3#1	91.50(10)	N1#1–Cd1–N3#3	88.48(10)	C1–N1–C3	106.1(3)
N1–Cd1–N3#1	92.44(10)	N1–Cd1–N3#3	87.55(10)	C1–N1–Cd1	125.9(2)
N1#1–Cd1–N3	92.44(10)	N3#1–Cd1–N3#3	179.39(16)	C3–N1–Cd1	128.0(2)
N1–Cd1–N3	91.50(10)	N3–Cd1–N3#3	97.43(8)	N1–C1–C2	109.8(3)
N3#1–Cd1–N3	83.18(18)	N3#2–Cd1–N3#3	81.96(17)	N2–C2–C1	108.9(3)
N1#1–Cd1–N3#2	87.55(10)	N4–N3–Cd1	130.0(6)	C2–N2–C3	106.0(3)
N1–Cd1–N3#2	88.48(10)	N4–N3–Cd1#4	115.5(6)	N2–C3–N1	109.2(3)
N3#1–Cd1–N3#2	97.43(8)	Cd1–N3–Cd1#4	97.43(8)		

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

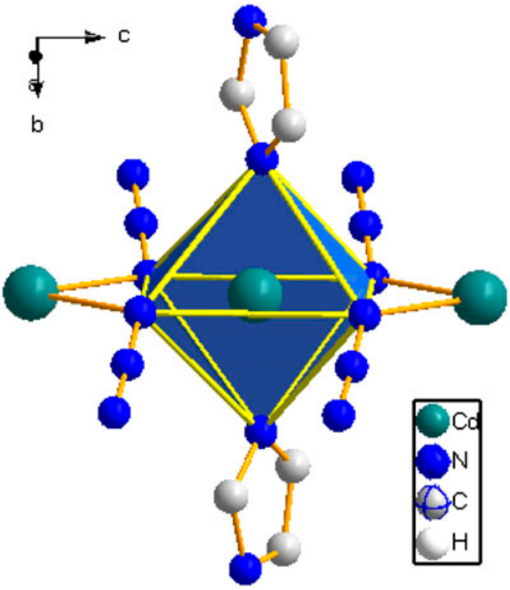

Figure 2. Cd octahedral coordination of **1**.

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A one-dimensional chain runs along the *c*-axis of the unit cell with alternate four-membered Cd_2–N_2 rings (figure 3). Intermolecular hydrogen bonds (C2–H2···N5) extend the structure into the 3-D super-molecular structure and make an important contribution to the thermal stability of the compound.

3.2. *Thermal decomposition mechanism*

To investigate the thermal behavior of **1**, it was analyzed by DSC and TG-DTG with a linear heating rate of $10\,\mathrm{K\,min^{-1}}$ in flowing N_2 (flow rate $20\,\mathrm{mL\,min^{-1}}$). The data curves from these analyses are shown in figures 4 and 5.

In the DSC curve of **1**, a melting point peak (457.45 K) with a corresponding endothermic stage can be seen at 430~475 K. TG-DTG curves showed that the first mass loss occurred very slowly and the total mass loss was 24.63%. The exothermic fast decomposition stage was seen in the DSC data and a peak was observed at 690.85 K. The TG-DTG curves showed a mass loss of 42.26% in the second stage of decomposition that occurred over this temperature range and reached the highest rate of mass loss at 626.35 K when the mass loss percentage equaled $8.43\%\,\mathrm{min^{-1}}$.

3.3. *Nonisothermal kinetics analysis*

Kissinger's method and Ozawa's method are widely used to determine the Arrhenius equation for a given material. The Kissinger equation (1) [56] and Ozawa equation (2) [57] are as follows:

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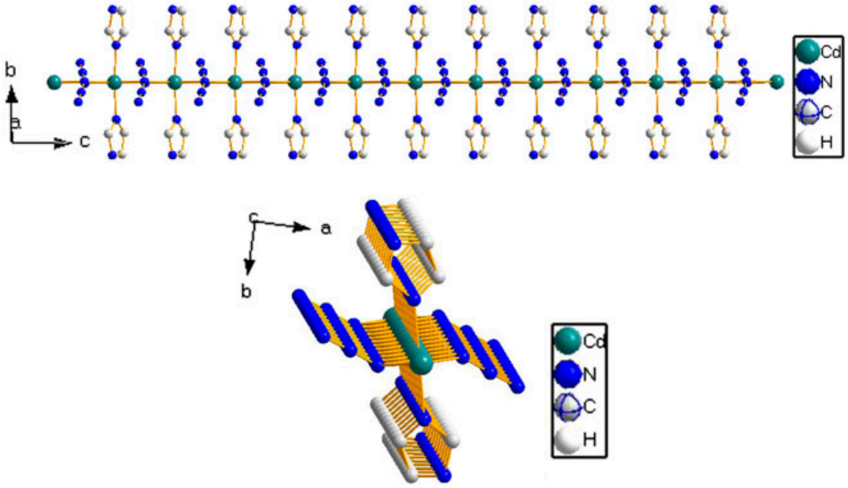

Figure 3. A one-dimensional chain of **1**.

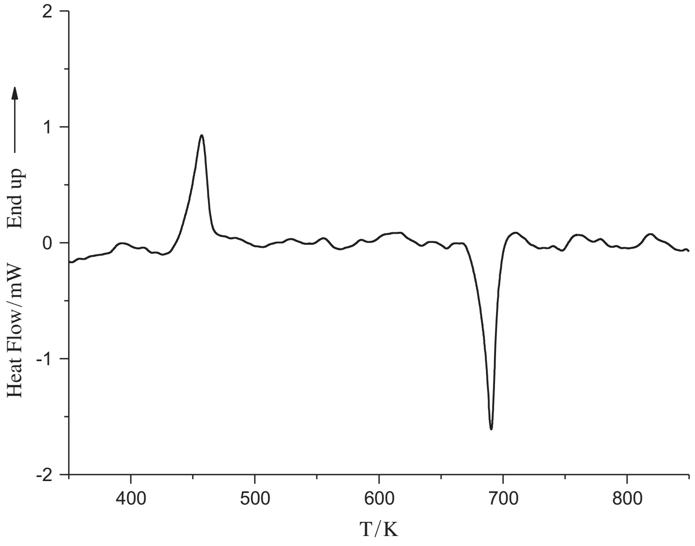

Figure 4. The DSC curve under N_2 with a heating rate of $10\,\mathrm{K\,min^{-1}}$.

$$\ln\frac{\beta}{T_p^2} = \ln[RA/E_a] - E_a/(RT_p) \tag{1}$$

$$\lg\beta = \lg[AE_a/RG(\alpha)] - 2.315 - 0.4567E_a/RT_p \tag{2}$$

where T_p is the peak temperature (K) at which the exothermic peak occurs in the DSC curve, A is the pre-exponential factor (s^{-1}), E_a is the apparent activation energy ($\mathrm{kJ\,mol^{-1}}$), R is the gas constant ($8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}$), β is the linear heating rate ($\mathrm{K\,min^{-1}}$), and $G(\alpha)$ is the reaction-mechanism function.

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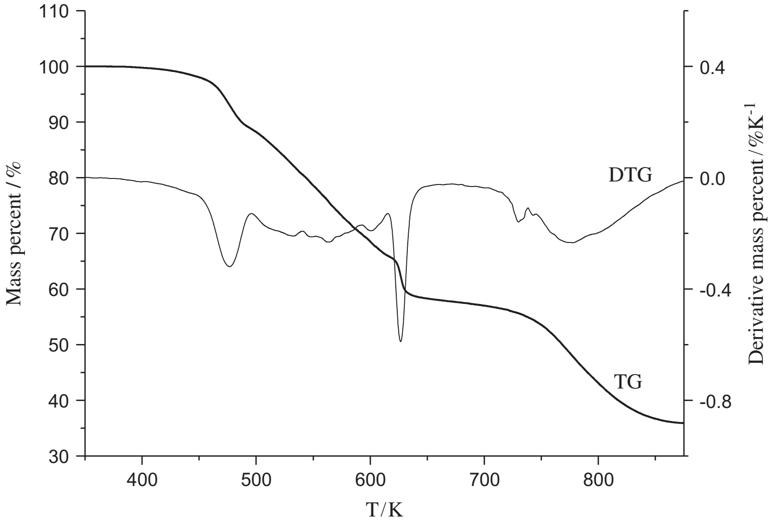

Figure 5. The TG–DTG curve under N_2 with a heating rate of $10\,\mathrm{K\,min^{-1}}$.

Based on the temperatures at which the first exothermic peaks occur in the DSC curves were measured with four different heating rates (5, 10, 15, and $20\,\mathrm{K\,min^{-1}}$), Kissinger's method and Ozawa's method were applied to study the kinetics parameters of **1**. From these data, the apparent activation energy E_k and E_o, pre-exponential factor A_k, and linear coefficient R_k and R_o were determined and 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): $\ln k = 10.84 – 171.7 \times 10^3/(RT)$.

3.4. *Energy of combustion and enthalpy of formation*

In order to study the energy of combustion (ΔH) and the enthalpy of formation ($\Delta_f H°_{298}$) of **1**, constant-volume energy of combustion (Q_v) was measured by oxygen bomb calorimetry as $-11.42\,\mathrm{MJ\,kg^{-1}}$.

Table 3. The peak temperatures of the first exotherm at different heating rates and chemical kinetics parameters.

Compound	**1**
Heating rates β ($\mathrm{K\,min^{-1}}$)	Peak temperatures T_p (K)
5	670.65
10	690.85
15	693.55
20	699.35
Kissinger's method	
E_k ($\mathrm{kJ\,mol^{-1}}$)	170.5
$\ln(A_k/\mathrm{s^{-1}})$	10.84
Linear correlation coefficient (R_k)	−0.9675
Standard deviation	0.1752
Ozawa's method	
E_o ($\mathrm{kJ\,mol^{-1}}$)	172.9
Linear correlation coefficient (R_o)	−0.9712
Standard deviation	0.07616

The bomb (equation (3)) is as follows:

$$CdC_6H_8N_{10} + 8.5O_2 \rightarrow CdO + 4H_2O + 6CO_2 + 5N_2 \tag{3}$$

and the energy of combustion is ($T = 298.15\,K$):

$$\Delta H = Q_p = Q_v + \Delta nRT = -3804.72 \text{ kJ mol}^{-1} = -11.44 \text{ MJ kg}^{-1} \tag{4}$$

The metal coordination compound should have a thermodynamically stable structure. The standard enthalpy of formation was back calculated from the energy of combustion on the basis of equation (3) and Hess's Law has been applied in the thermochemical equation (5). With the known enthalpies of formation of cadmium(II) oxide ($\Delta_f H°_{298}(CdO(s)) = -258.0\,kJ\,mol^{-1}$), carbon dioxide ($\Delta_f H°_{298}(CO_2(g)) = -393.5\,kJ\,mol^{-1}$), and water ($\Delta_f H°_{298}(H_2O(l)) = -285.8\,kJ\,mol^{-1}$), the enthalpy of formation of **1** can now be calculated as:

$$\begin{aligned} \Delta_f H^{\circ}(1, s) &= \Delta_f H^{\circ}(\text{Cdo}, s) + 4\Delta_f H^{\circ}(H_2O, \text{I}) + 6\Delta_f H^{\circ}(CO_2, g) - \Delta_c H^{\circ}(s) \\ \Delta_f H^{\circ}_{298}(1, s) &= +42.52\,\text{kJ mol}^{-1} = +54\,\text{kJ kg}^{-1} \end{aligned} \tag{5}$$

3.5. *Calculation of critical temperature of thermal explosion, ΔS≠, ΔH≠, and ΔG≠*

The value of the peak temperature corresponding to $\beta \rightarrow 0$ obtained according to the following equation (6) [58, 59] is 612.35 K, where a, b, and c are coefficients.

$$T_{pi} = T_{p0} + a\beta + b\beta^2 + c\beta^3 \tag{6}$$

The corresponding critical temperature of thermal explosion (T_b) obtained is 654.05 K by equation (7) [58, 59].

$$T_b = (E - \sqrt{E^2 - 4ERT_{p0}})/2R \tag{7}$$

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 $T = T_{p0}$ and $A = A_K$ (obtained by Kissinger's method), obtained by equations (8)–(10) [58, 59], are $-169.08\,kJ\,mol^{-1}$, $166.61\,J\,(K\,mol)^{-1}$, and $270.15\,kJ\,mol^{-1}$, respectively.

$$A = (k_B T/h)e^{\Delta S^{\neq}/R} \tag{8}$$

$$\Delta H^{\neq} = E - RT \tag{9}$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \tag{10}$$

where k_B is the Boltzmann constant and h is the Planck constant.

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Table 4. Physicochemical properties of **1**.

Compound	**1**
T_d (K)[a]	690.85
N (%)[b]	42.11
Ω (%)[c]	−81.77
E (kJ mol^{-1})[d]	171.7
$\Delta H°$ (kJ mol^{-1})[e]	−3804.72
$\Delta_f H°_{298}$ (kJ mol^{-1})[f]	+42.52
T_{p0} (K)	612.35
T_b (K)	654.05
$\Delta S^{\neq}$ (kJ mol^{-1})	−169.08
$\Delta H^{\neq}$ (J (K mol)$^{-1}$)	166.61
$\Delta G^{\neq}$ (kJ mol^{-1})	270.15
Impact sensitivity (J)	>12.25

[a] Thermal degradation/DSC main exothermic peak.
[b] Nitrogen content.
[c] Oxygen balance.
[d] Activation energy.
[e] Experimental energy of combustion.
[f] Molar enthalpy of formation.

3.6. *Physicochemical properties*

The physicochemical properties of **1** are tabulated in table 4. It has the worse oxygen balance than TNT ($\Omega = -74.0\%$). The nitrogen content is more than 42% by weight. More importantly, the energy of combustion was higher than RDX (−9.60 MJ kg^{-1}) and HMX (−9.44 to −9.88 MJ kg^{-1}) and lower than TNT (−15.22 MJ kg^{-1}). The high value of Tb shows that the transition from thermal decomposition to thermal explosion is easy compared to $[Mg(CHZ)_3](ClO_4)_2$ (CHZ = carbohydrazide) [42]. The positive value of $\Delta G^{\neq}$ indicates that the exothermic decomposition must proceed under heating. In the end, compared to Cu(HATZ)(PDA)(H_2O) (HATZ = 5-aminotetrazole, H_2PDA = pyridine-2,6-dicarboxylic acid) [23], $Cu(IMI)_4(N_3)_2$ [11], $Ni(IMI)_4(N_3)_2$ [11], and $[Bi(tza)_3]_n$ (tza = tetrazole acetic acid) [40], **1** shows lower impact sensitivity.

4. Conclusions

The energetic compound $[Cd(IMI)_2(N_3)_2]_n$ (**1**) was synthesized and characterized. The crystal structure shows that Cd(II) is six-coordinate in a slightly distorted octahedral geometry and two azides are the bridging ligands. In **1**, thermal analysis indicated that there was a melting point peak (457.45 K) and a main exothermic process as shown in the DSC curve. Nonisothermal kinetics analysis results indicated that the Arrhenius equation of **1** can be expressed as follows: $\ln k = 10.84–171.7 \times 10^3/(RT)$. The experiment found that the energy of combustion and the enthalpy of formation of **1** were to be −11.42 MJ kg^{-1} and +42.52 kJ mol^{-1} (+54 kJ kg^{-1}), respectively. **1** is a less toxic energy additive, which will be applied to improve the explosion performance of the traditional explosives and propellant formulations.

Acknowledgments

The projects were supported by the State Key Laboratory of Explosion Science and Technology (No. YBKT10–05 and ZDKT10–01b), Science and Technology on Applied Physical Chemistry Laboratory (9140C3703051105).

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