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## Preparation, Crystal Structure, and Thermal Decomposition of the Energetic Compound [Co(IMI)<sub>4</sub>(PA)](PA) (IMI = Imidazole and PA = Picrate)

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Keywords: Cobalt; Imidazole; Crystal structure; Thermal decomposition; Sensitivity

**Abstract.** The novel multi-ligand coordination compound  $[Co(IMI)_4(PA)](PA)$  (1) was synthesized by using imidazole (IMI) and picrate (PA) and characterized by elemental analysis and FT-IR spectroscopy. The crystal structure was determined by X-ray single crystal diffraction and the crystallographic data showed that the compound crystallizes in the triclinic space group  $P\overline{1}$  (a = 8.839(2) Å, b = 13.550(3) Å, c = 13.840(3) Å,  $a = 68.386(6)^{\circ}$ ,  $\beta = 88.349(9)^{\circ}$ , and  $\gamma = 87.494(9)^{\circ}$ ). Furthermore, the Co<sup>II</sup> ion is six-coordinated by four nitrogen atoms from four imidazole ligands and two oxygen atoms from a PA group. Its thermal decomposition mechanism was deter-

#### Introduction

Nitrogen-rich energetic compounds are among the most recent and exiting area in the development of modern high energy density materials (HEDMs) with higher performance and environmental compatibility.<sup>[1,2]</sup> This is mostly derived from their high positive heats of formation from the large number of inherently energetic N–N (160 kJ·mol<sup>-1</sup>), N=N (418 kJ·mol<sup>-1</sup>), and C–N bonds. *Klapötke* and other chemists have done lots of studies about nitrogen-rich energetic compounds on the basis of imidazoles, triazoles, tetrazoles, tetrazines, and their derivatives.<sup>[3–31]</sup>

Imidazoles (IMI) are nitrogen-rich compounds, covering a wide range of their derivatives, 2-azidoimidazole,<sup>[32]</sup> imidazole-4-acetic acid,<sup>[33,34]</sup> nitroimidazole,<sup>[35–41]</sup> trinitroimidazole,<sup>[42–44]</sup> and so on. Imidazoles are pentacyclic heterocyclic compounds containing two nitrogen atoms and three carbon atoms with relatively small volume, which may reduce steric hindrance. The advantages of imidazoles include high-nitrogen content, ready availability, high positive heat of formation, and good thermal stability. What is particularly important, the decomposition of imidazole results in the generation of large volumes of environmentally friendly nitrogen, which makes them promising candidates for applications requiring environmentally friendly highly energetic materials. The role of the imidazole ring as metal-binding site in compounds is well-known,

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Fax: +86-10-68911202 E-Mail: ztlbit@bit.edu.cn and, therefore, studies of the coordination properties of this

mined based on differential scanning calorimetry (DSC) and thermo-

gravimetry-derivative thermogravimetry (TG-DTG) analysis. The ki-

netic parameters of the first exothermic process were studied by using

Kissinger's and Ozawa's method, respectively. The energy of combus-

tion and the enthalpy of formation were measured and calculated. They

showed good combustion performance of the compound. Additionally,

the sensitivity properties were determined with standard methods. The

results of all these studies showed that [Co(IMI)<sub>4</sub>(PA)](PA) has poten-

tial application as ignition composition.

molecule and its derivatives are of interest. In previous studies,<sup>[45,46]</sup> the nitrogen-rich materials Cu(IMI)<sub>4</sub>(N<sub>3</sub>)<sub>2</sub>, Ni(IMI)<sub>4</sub>(N<sub>3</sub>)<sub>2</sub>, [Ni(IMI)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub>, [Ni(IMI)<sub>6</sub>]-(NO<sub>3</sub>)<sub>2</sub>, and [Cu(IMI)<sub>4</sub>](PA)<sub>2</sub> with nitrogen contents of 46.70%, 47.27%, 25.23%, 33.17%, and 24.74% were reported. They have potential application as energetic materials in the near future. Especially,  $Ni(IMI)_4(N_3)_2$  has a combustion heat, which is higher 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 it is regarded as an energy additive, which can improve the explosion performance of the traditional explosives and propellant formulations. In order to deepen the studies on the imidazole compounds, [Co(IMI)<sub>4</sub>(PA)](PA) was synthesized and its crystal structure, the thermal decomposition mechanism, and sensitivity properties were studied in the presented work.

## **Results and Discussion**

#### Crystal Structure Description

The highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) of the IMI group were exploited in our previous study<sup>[45]</sup> and they again are shown in Figure 1, the electronic density of the HOMO at N(1) atom of the imidazole group is relatively higher. This enables a better understanding of the coordination bond formation between the nitrogen atom and the Co<sup>II</sup> ion because of the unoccupied 3*d* orbitals of the metal ion.

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Figure 1. HOMO (left) and LUMO (right) of the imidazole group.<sup>[44]</sup>

Compound 1 crystallizes in the triclinic space group  $P\bar{1}$  with a cell volume of 1539.4(7) Å<sup>3</sup> and only two molecular moieties in the unit cell (Table 1). In 1 (Figure 2), there are one co-

**Table 1.** Crystal data and structure refinement for  $[Co(IMI)_4(PA)](PA)$  (1).

	$[Co(IMI)_4(PA)](PA)$ (1)
Empirical formula	CoC <sub>24</sub> H <sub>20</sub> N <sub>14</sub> O <sub>14</sub>
Formula mass	787.47
Temperature /K	153(2)
Crystal shape	prismatic
Crystal dimensions /mm	$0.56 \times 0.18 \times 0.07$
Crystal system	triclinic
Space group	ΡĪ
Ζ	2
<i>a</i> /Å	8.839(2)
b /Å	13.550(3)
c /Å	13.840(3)
a /°	68.386(6)
β /°	88.349(9)
γ /°	87.494(9)
h k l	-11 to 11, -17 to 18, -18 to
п, к, і	18
Unit cell dimensions V /Å <sup>3</sup>	1539.4(7)
$D_{\rm c}$ /g·cm <sup>-3</sup>	1.699
$\mu \text{ (Mo-}K_{\alpha}) / \text{mm}^{-1}$	0.653
F(000)	802
$\theta$ Range /°	2.77-29.13
Max. and min. transmission	0.9557, 0.7103
Measured reflections	17089
Unique data	$8059 \ (R_{int} = 0.0332)$
$R_1, wR_2 [I > 2\sigma(I)]^{a)b}$	0.0483, 0.1020
$R_1$ , $wR_2$ (all data) <sup>a)b)</sup>	0.0775, 0.1118
Goodness of fit	1.002
$\delta p_{ m max}$ , $\delta p_{ m min}$ /e·Å <sup>-3</sup>	0.570, -0.536

a)  $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$ ,  $P = (F_o^2 + 2F_c^2)/3$ . b)  $w = 1/[\sigma^2(F_o^2) + (0.0510P)^2 + 0.1600P]$ .

Table 2. Selected bond lengths //	A and bond angles /°	for $[Co(IMI)_4(PA)](PA)$ (1).
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Figure 2. Molecular structures of  $[Co(IMI)_4(PA)](PA)$  (1), thermal ellipsoids drawn at 30% probability level.



Figure 3. Octahedral coordination structure of cobalt and its coplanar structure.

balt(II) cation, four imidazole molecules, and two PA groups. The six basically equivalent Co–N and Co–O bonds are approximately equal (2.1 nm) (see Table 2). The bond angle of the two nitrogen atoms from two contra-positioned imidazole ligands and the Co<sup>II</sup> cation, N1–Co1–N5, is 172.54(7)°. The bond angles of the nitrogen atoms of imidazole group and the contra-positioned oxygen atoms of the PA group and the Co<sup>II</sup> cation are 172.41(7)° and 169.87(6)° (N3–Co1–O2 = 172.41(7)° and O1–Co1–N7 = 169.87(6)°). In addition, the bond angles of the nitrogen (or oxygen) atom from two border ligands and the Co<sup>II</sup> cation are all close to 90°. Therefore, all of the above data demonstrates that the Co<sup>II</sup> cation exhibits a distorted octahedral configuration (Figure 3).

Bond		Bond		Bond	
Co1–N1	2.111(2)	Co1–N5	2.1321(19)	Co1-O1	2.1068(16)
Co1–N3	2.0931(18)	Co1–N7	2.125(2)	Co1–O2	2.1896(16)
Angle		Angle		Angle	·
N1-Co1-N5	172.54(7)	N(3)-Co1-O1	93.93(7)	01-Co1-N(5)	86.73(7)
N3-Co1-O2	172.41(7)	N(3)-Co1-N1	93.59(7)	N(5)-Co1-O(2)	88.45(7)
01-Co1-N7	169.87(6)	N(3)-Co1-N(7)	95.19(7)	N(7)-Co1-O(2)	92.12(7)
N1-Co1-O(2)	84.32(7)	N(3)-Co1-N(5)	93.81(7)	N(7)-Co1-N(5)	88.27(8)
N1-Co1-N(7)	90.17(8)	01-Co1-N1	93.65(7)	O1–Co1–O(2)	78.95(6)

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In compound **1**, the plane A (Co1–N1–N2–N5–N6) is formed by two contra-positioned imidazole rings and the cobalt(II) cation with a plane equation of -3.059x + 7.417y +12.380z = 4.2935 (R = 0.0274). Furthermore, a second plane B with the benzene ring is made up; the plane equation is 7.071x-7.198y-0.025z = 1.7719 (R = 0.0300). The angle between plane A and B is 116.6° (see Figure 3)

From the packing diagram it can be seen that all of these intermolecular hydrogen bonds extend the structure into a 3D supermolecular structure, which makes an important contribution to enhance the thermal stability of the compound (Figure 4).



Figure 4. Packing of the unit cells view along the *a* axis.

#### **Thermal Decomposition Mechanism**

In order to investigate the thermal behavior of 1, the DSC and TG curves with the linear heating rate of 5 K·min<sup>-1</sup> in a nitrogen gas flow at the rate of 20 mL·min<sup>-1</sup> are shown in Figure 5 and Figure 6, respectively.



Figure 5. DSC curve in a nitrogen atmosphere with a heating rate of 5  $K \cdot min^{-1}$ .



**Figure 6.** TG-DTG curve in a nitrogen atmosphere with a heating rate of 5 K $\cdot$ min<sup>-1</sup>.

In compound 1, the melting point with an endothermic process was observed in the temperature range of 450-510 K and the peak temperature in the DSC curve was at 480 K. The TG-DTG curves showed that in the first stage a mass loss of 14.6% occurred in this temperature range, which reached the largest rate at 462 K with a mass loss percentage of 2.8 % min<sup>-1</sup>. Afterwards, two successive exothermic processes appeared in the temperature range from 580 K to 850 K with peak temperatures of 627 K and 727 K, respectively. Corresponding to the exothermic processes, the TG-DTG curves showed two consecutive mass losses stages in a tardigrade process and the mass loss is 74.7%, where the largest mass loss percentage was 7.2% min<sup>-1</sup> at 603 K. The mass of the final residue was 10.7 %, which is coincident with the calculated value of  $Co_3O_4$ (10.19%). The absorption band in the FT-IR spectrum of the residue at 850 K proved that the final residue is Co<sub>3</sub>O<sub>4</sub>.

#### Non-Isothermal Kinetics Analysis

In the presented work, Kissinger's method <sup>[47]</sup> and Ozawa's method <sup>[48]</sup> are widely used to determine the apparent activation energy ( $E_a$ ) and the pre-exponential factor (A). The Kissinger Equation (1) and Ozawa equation (Equation 2) are as follows, respectively:

$$\ln \beta / T_{\rm p}^{\ 2} = \ln \left[ RA / E_{\rm a} \right] - E_{\rm a} / RT_{\rm p} \tag{1}$$

$$\lg \beta = \lg \left[ AE_a / RG(a) \right] - 2.315 - 0.4567E_a / RT_p$$
(2)

 $T_{\rm p}$  is the peak temperature (in K), A is the pre-exponential factor (s<sup>-1</sup>),  $E_{\rm a}$  is the apparent activation energy (kJ·mol<sup>-1</sup>) R is the gas constant (8.314 J·K<sup>-1</sup>·mol<sup>-1</sup>),  $\beta$  is the linear heating rate (K·min<sup>-1</sup>), and G(a) is reaction mechanism function.

Based on the first exothermic peak temperatures measured with four different heating rates of 5, 10, 15, and 20 K·min<sup>-1</sup>, Kissinger's method and Ozawa's method were applied to study the kinetic parameters of the title compound. From the original data, the apparent activation energy  $E_k$  and  $E_o$ , pre-exponential factor  $A_k$ , and linear coefficients  $R_k$  and  $R_o$  were determined and showed in Table 3. Accordingly, the Arrhenius Equation of 1 can be expressed as follows (*E* is the average of  $E_k$  and  $E_o$ ):

$$\ln k = 3.759 - 76.27 \times 10^{3} / (RT)$$

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

	[Co(IMI) <sub>4</sub> (PA)](PA) (1)
Heating rates $\beta$ /K·min <sup>-1</sup>	Peak temperatures $T_p$ /K
5	594.45
10	618.85
15	631.05
20	649.05
Kissinger's method	
$\overline{E_k / \text{kJ} \cdot \text{mol}^{-1}}$	73.16
$ln(A_k/s^{-1})$	3.759
Linear correlation coefficient $(R_k)$	-0.992
Standard deviation	0.0815
Ozawa's method	
$\overline{E_{\rm o}}$ /kJ·mol <sup>-1</sup>	79.38
Linear correlation coefficient $(R_0)$	-0.994
Standard deviation	0.03499

#### Energy of Combustion and Enthalpy of Formation

In order to study the energy of combustion and the enthalpy of formation of 1, the constant volume energy of combustion  $(Q_v)$  was measured by oxygen bomb calorimetry and was determined to have a value of  $-14.36 \text{ MJ} \cdot \text{kg}^{-1}$ .

The bomb equation is as follows:

$$\operatorname{CoC}_{24}\operatorname{H}_{20}\operatorname{N}_{14}\operatorname{O}_{14} + \frac{32}{3}\operatorname{O}_2 \to \frac{1}{3}\operatorname{Co}_3\operatorname{O}_4 + 10\operatorname{H}_2\operatorname{O} + 12\operatorname{CO}_2 + 7\operatorname{N}_2$$
 (3)

And the energy of combustion is as follows (T = 298.15 K):

 $\Delta H = Q_{\rm p} = Q_{\rm v} + \Delta nRT = -11329 \text{ kJ} \cdot \text{mol}^{-1} = -14.39 \text{ MJ} \cdot \text{kg}^{-1}$ (4)

It was reported in the literature<sup>[49]</sup> that the energies of combustion of RDX, HMX, and TNT were  $-9.60 \text{ MJ} \cdot \text{kg}^{-1}$ , -9.44 to  $-9.88 \text{ MJ} \cdot \text{kg}^{-1}$ , and  $-15.22 \text{ MJ} \cdot \text{kg}^{-1}$ , respectively. Consequently, the energy of combustion of **1** was equal to that of TNT.

The metal coordination compound should have relatively thermodynamically stable structures. The standard enthalpies of formation was back calculated from the energy of combustion on the basis of Equation (3), and Hess's Law as applied in thermochemical Equation (5). With the known enthalpies of formation of cobalt(II,III) oxide  $[\Delta_{\rm f} H^{\circ}_{298}({\rm Co}_3{\rm O}_4,{\rm s}) = -891.0 \text{ kJ}\cdot\text{mol}^{-1}]$ , carbon dioxide  $[\Delta_{\rm f} H^{\circ}_{298}({\rm CO}_2,{\rm g}) = +393.5 \text{ kJ}\cdot\text{mol}^{-1}]$  and water  $[\Delta_{\rm f} H^{\circ}_{298}({\rm H}_2{\rm O},{\rm I}) = -285.8 \text{ kJ}\cdot\text{mol}^{-1}]$ , the enthalpy of formation of 1 can now be calculated as:

$$\Delta_{f}H^{\circ}(1,s) = 1/3\Delta_{f}H^{\circ}(Co_{3}O_{4},s) + 10\Delta_{f}H^{\circ}(H_{2}O,l) + 12\Delta_{f}H^{\circ}(CO_{2},g) - \Delta_{c}H^{\circ}(s)$$
(5)

 $\Delta_{\rm f} H^{\circ}_{298}(1,{\rm s}) = +12896 \,{\rm kJ} \cdot {\rm mol}^{-1} = +16.38 \,{\rm MJ} \cdot {\rm kg}^{-1}.$ 

#### Sensitivity Tests

On the basis of the China National Military Standard, the impact and friction sensitivities as well as the flame sensitivity were determined.<sup>[50]</sup>

Impact sensitivity was determined using a Fall Hammer Apparatus. Compound 1 (50 mg) was placed between two steel

poles and was hit by a 5.0 kg drop hammer at 25 cm height. The test result showed that the firing rate was 0%.

Friction sensitivity was determined on a MGY-1 pendular friction sensitivity apparatus by a standard procedure using 20 mg of the sample. Compound **1** was compressed between two steel poles with mirror surfaces at the pressure of 1.96 MPa, and was hit horizontally with a 1.5 kg hammer from 90° angle, the firing rate was 0%.

Flame sensitivity was determined by a standard method, in which the sample was ignited by standard black powder pellet. Compound 1 (20 mg) was pressed into a copper cap under a pressure of 58.8 Mpa and was ignited by a standard black powder pellet. The test result showed that the 50% firing height ( $h_{50}$ ) was 13 cm.

Therefore, the compound had higher flame sensitivity.

#### Conclusions

The novel environmental friendly cobalt(II) imidazole energetic compound, [Co(IMI)<sub>4</sub>(PA)](PA) (1), was synthesized and characterized. The crystal structure analysis showed that the Co<sup>II</sup> ion is six-coordinated in a slightly distorted octahedral arrangement with four imidazole molecules and the PA group. Surprisingly, the PA group is able to coordinate with the metal ion through the oxygen atoms. In 1, thermal analysis indicated that one endothermic process occurred between 450 K and 510 K and two main exothermic processes occurred in the temperature range from 580 K to 850 K as shown in the DSC curve corresponding to TG-DTG curves. The results of the non-isothermal kinetic analysis indicated that the Arrhenius Equation of 1 can be expressed as follows:  $\ln k = 3.759$ - $76.27 \times 10^{3}/(RT)$ . The experiment found the energy of combustion and the enthalpy of formation of 1 were -14.39 MJ·kg<sup>-1</sup> and +12896 kJ·mol<sup>-1</sup> (+16.38 MJ·kg<sup>-1</sup>), respectively. More importantly, compound 1 was regarded as the less toxic energy additive that can be applied to improve the explosion performance of the traditional explosives and propellant formulations. The results of the studies showed that  $[Co(IMI)_4(PA)](PA)$  has potential application as ignition composition in the near future.

#### **Experimental Section**

**General Caution**: The title compound is 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 dry state.

**Materials and Physical Techniques:** All the reagents and solvents were of analytical grade and used without further purification as commercially obtained.

Elemental analyse was performed on a Flash EA 1112 full automatic trace element analyzer. The FT-IR spectra was recorded with a Bruker Equinox 55 infrared spectrometer (KBr pellets) in the range of 4000–400 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>. DSC and TG measurements were carried out with a Pyris-1 differential scanning calorimeter and Pyris-

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1 thermogravimetric analyzer (Perkin-Elmer, USA) in a dry nitrogen atmosphere with flowing rate of 20 mL·min<sup>-1</sup>. The combustion heat was measured by oxygen bomb calorimetry (Parr 6200, USA).

**Synthesis of [Co(IMI)<sub>4</sub>(PA)](PA) (1):** The synthesis of **1** was as follows: Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (10 mmol) was dissolved in distilled water (30 mL), and charged into a glass reactor with a water bath. It was kept under mechanical stirring and heated to the temperature of 60–70 °C. Imidazole (40 mmol) and picric acid (20 mmol) were dissolved in distilled water (20 mL), respectively, and subsequently they were added to the Co<sup>II</sup> aqueous solution during 25–30 min with continuous stirring. In the end, the solution was cooled to room temperature naturally. **FT-IR** (KBr):  $\tilde{v} = 3315$ , 1613, 1361, 1067, 787, 656, 611 cm<sup>-1</sup>. CoC<sub>24</sub>H<sub>20</sub>N<sub>14</sub>O<sub>14</sub> (molar mass: 787.47 g·mol<sup>-1</sup>): calcd. C 36.61 N 24.90 H 2.56%; found C 36.60 N 24.91 H 2.54%.

**X-ray Data Collection and Structures Refinement:** The prism crystal was chosen for X-ray determination. The X-ray diffraction data collection were performed with a Rigaku AFC-10/Saturn 724<sup>+</sup> CCD detector diffractometer with graphite monochromated Mo- $K_{\alpha}$  radiation ( $\lambda = 0.71073$  Å) with *multi-scan* mode at the 153(2) K. The structures were solved by direct methods using SHELXS–97<sup>[51]</sup> (Sheldrick, 1990) and refined by full-matrix least-squares methods on  $F^2$  with SHELXL-97<sup>[52]</sup> (Sheldrick, 1997). And all non-hydrogen atoms were obtained from the difference Fourier map and subjected to anisotropic refinement by full-matrix least-squares on  $F^2$ . Detailed information concerning crystallographic data collection and structures refinement are summarized in Table 1.

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC-880778 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

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The Energetic Compound [Co(IMI)<sub>4</sub>(PA)](PA)



Preparation, Crystal Structure, and Thermal Decomposition of the Energetic Compound  $[Co(IMI)_4(PA)](PA)$  (IMI = Imidazole and PA = Picrate)



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