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Preparation, Crystal Structure, and Thermal Decomposition of the Intriguing Five-coordinated Compound $[Cu(IMI)_4Cl]Cl$ (IMI = Imidazole)

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Abstract. The intriguing multi-ligand compound $[Cu(IMI)_4Cl]Cl$ (**1**) with the ligand imidazole (IMI) was synthesized 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 belongs to the monoclinic $P2_1/n$ space group [a = 8.847(2) Å, b = 13.210(3) Å, c = 13.870(3) Å, and β = 90.164(3)°]. Furthermore, the Cu^{II} ion is five-coordinated by four nitrogen atoms from four imidazole ligands and a chlorine atom. The thermal decomposition mechanism was determined based on differential scanning calorimetry (DSC) and thermogravimetric (TG-DTG) analysis. The non-isothermal kinetics parameters were calculated by the 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.

Introduction

The heterocyclic compounds have attracted considerable interest due to their rather large densities, good oxygen balance, high performance and environmental compatibility.[1,2] *Klapötke*, *Shreeve* and other chemists have done studies about high energy density materials (HEDMs) on the basis of imidazole,[3–16] triazole,[17–21] and tetrazole[22–32].

Imidazole (IMI) is a pentacyclic heterocyclic compound containing two potential nitrogen coordination atoms. The advantages of imidazole include the high nitrogen content (N = 41.15 %), ready availability, high positive heat of formation and good thermal stability. What is particularly important, decomposition of imidazole results in the generation of large volumes of environmentally friendly nitrogen (N_2). Imidazole derivative compounds can be obtained in three different ways. Firstly, a new compound was synthesized by introducing azido or nitro explosive groups in the imidazole group, such as 2-azido-imidazole,[11] nitro-imidazole,[9,10,13] and so on. Secondly, the preparation of a salt by neutralization or metathesis reaction.[11,33]. Furthermore, the role of the imidazole ring as metal binding site in compound is well-known. A series of compounds have been developed in our laboratory based on the imidazole and azide compounds. $Cu(IMI)_4(N_3)_2$,[16] $Ni(IMI)_4(N_3)_2$,[16] $[Ni(IMI)_6](ClO_4)_2$,[15] $[Ni(IMI)_6](NO_3)_2$,[15] and $[Cu(IMI)_4](PA)_2$[14] are the nitrogen-rich materials and their nitrogen contents are 46.70 %, 47.27 %, 25.23 %, 33.17 %, and 24.74 %, respectively.

In order to deepen the studies on the imidazole compound, $[Cu(IMI)_4Cl]Cl$ (**1**) was synthesized. The intriguing five-coordinated crystal structure and the thermal decomposition mechanism were studied in the presented work.

Results and Discussion

Crystal Structure Description

In our previous study, the electronic density of the highest occupied molecular orbitals (HOMOs) at the N(1) atom of the imidazole group is relatively higher compared with the lowest unoccupied molecular orbitals (LUMOs).[15,16] It is easy to understand the coordination bond formation between the nitrogen atom and the Cu^{II} ion with unoccupied 3*d* orbitals.

In **1**, there are one copper(II) cation, four imidazole molecules, a coordination chlorine atom, and an external chlorine atom (Figure 1). The four basically equivalent Cu–N bonds are approximately equal (2.0 Å) (see Table 1). The angles between two nitrogen atoms from two contraposition imidazole ligands and Cu^{II} cations are 174.75(8)° (N1–Cu1–N3) and 158.33(8)° (N5–Cu1–N7), whereas the bond angles between nitrogen (or chlorine) atoms from two borders upon ligands and Cu^{II} cations are all close to 90°. Therefore, all data of the above demonstrate that the Cu^{II} cation exhibits a distorted pentahedron configuration (Figure 2). From the packing diagram, all of these intermolecular hydrogen bonds are to extend the structure into the 3D super-molecular structure, and make an important contribution to enhance the thermal stability of the compound (see Supporting Information).

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

Bond		Bond		Bond	
Cu1–N1	1.997(2)	Cu1–N7	2.0089(19)	Cu1–Cl1	2.6154(7)
Cu1–N3	2.005(2)	Cu1–N5	2.0148(19)	Cu1···Cl2	4.1249(9)
Angle		Angle		Angle	
N1–Cu1–N3	174.75(8)	N7–Cu1–N5	158.33(8)	N1-Cu1···Cl2	87.78(6)
N1–Cu1–N7	88.97(8)	N1–Cu1–Cl1	92.31(6)	N3–Cu1···Cl2	87.03(6)
N3–Cu1–N7	89.37(8)	N3–Cu1–Cl1	92.91(6)	N7–Cu1···Cl2	79.81(6)
N1–Cu1–N5	90.12(7)	N7–Cu1–Cl1	103.58(6)	N5–Cu1···Cl2	78.52(6)
N3–Cu1–N5	89.59(7)	N5–Cu1–Cl1	98.09(6)	Cl1–Cu1···Cl2	176.604(17)

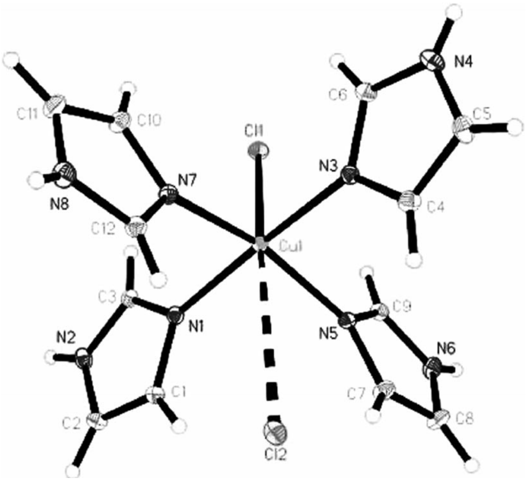

Figure 1. Molecular structure of **1**, thermal ellipsoids drawn at 30 % probability level.

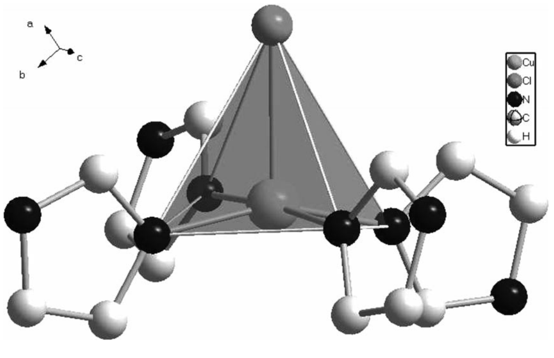

Figure 2. Pentahedral coordination around the copper atom in **1**.

Thermal Decomposition Mechanism

In order to investigate the thermal behavior, compound **1** was analyzed by DSC and TG-DTG, with a linear heating rate of 10 K·min^{-1} in a flowing nitrogen atmosphere (flow rate 20 mL·min^{-1}). The data curves from these analyses are shown in Figure 3 and Figure 4.

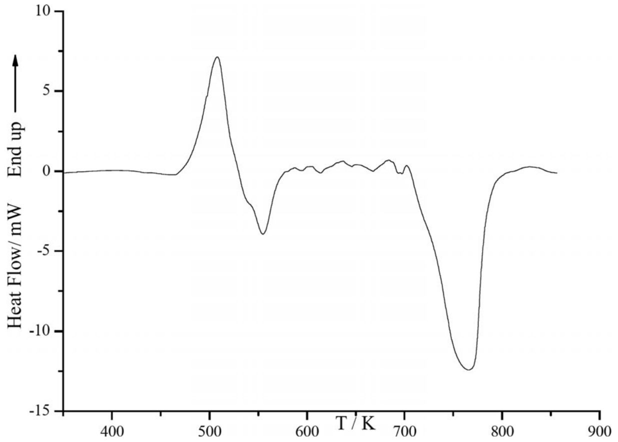

Figure 3. DSC curve of **1** in a nitrogen atmosphere with a heating rate of 10 K·min^{-1}.

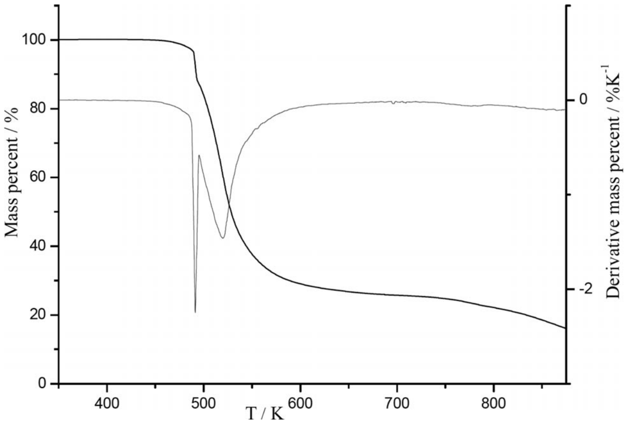

Figure 4. TG-DTG curve of **1** in a nitrogen atmosphere with a heating rate of 10 K·min^{-1}.

In the DSC curve of **1**, a melting point peak (506.25 K) with a corresponding endothermic stage can be seen in the range of 460–530 K. TG-DTG curves showed the first mass-loss stage occurred very slowly (total mass loss 13.12 %). The exothermic decomposition stages were seen in the DSC data, and peaks were observed at 555.05 K and 765.15 K. The TG-DTG curves showed a mass loss of 70.61 %, and reached the highest rate of mass loss at 519.88 K when the mass loss percentage has a value 14.21 %·min^{-1} in the first stage of decomposition.

Non-isothermal Kinetics Analysis

Kissinger's method and Ozawa's method, respectively, are widely used to determine the Arrhenius equation for a given material. The Kissinger Equation (1)[34] and Ozawa Equation (2)[35] are as follows:

$$\ln \beta / T_p^2 = \ln [RA / E_a] - E_a / (RT_p) \quad (1)$$

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

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 ($kJ \cdot mol^{-1}$). R is the gas constant ($8.314\ J \cdot K^{-1} \cdot mol^{-1}$). β is the linear heating rate ($K \cdot min^{-1}$), and $G(\alpha)$ is the reaction mechanism function.

Based on the first and second exothermic peak temperatures measured with four different heating rates of 5, 10, 15, and 20 $K \cdot min^{-1}$, Kissinger's method and Ozawa's method were applied to study the kinetics parameters of the title compound. From the original data, the apparent activation energy E_k and E_o, the pre-exponential factor A_k, and the linear coefficients R_k and R_o were determined and are showed in Table 2. Accordingly, the Arrhenius Equation of the different thermal decomposition reaction stages can be expressed as follows (E is the average of E_k and E_o):

$\ln k_1 = 3.145 – 60.865 \times 10^3 / (RT)$ and $\ln k_2 = 2.743 – 80.755 \times 10^3 / (RT)$

Table 2. Peak temperatures of the first exotherm at different heating rates and kinetic parameters.

	1	
Heating rates β /$K \cdot min^{-1}$	Peak temperatures T_p /K	
5	519.55	718.45
10	555.05	765.15
15	561.15	767.15
20	564.35	791.85
Kissinger's method		
E_k /$kJ \cdot mol^{-1}$	58.02	76.70
ln (A_k/s^{-1})	3.145	2.743
Linear correlation coefficient (R_k)	–0.9348	–0.9569
Standard deviation	0.2301	0.1859
Ozawa's method		
E_o /$kJ \cdot mol^{-1}$	63.71	84.81
Linear correlation coefficient (R_o)	–0.9496	–0.9675
Standard deviation	0.1002	0.0808

Energy of Combustion and Enthalpy of Formation

In order to study the energy of combustion and the enthalpy of formation of **1**, constant volume energy of combustion (Q_v) was measured with an oxygen bomb calorimeter and showed a value of –18.16 $MJ \cdot kg^{-1}$.

The bomb equation is as follows:

$$CuC_{12}H_{16}N_8Cl_2 + 16O_2 \rightarrow CuO + 7H_2O(l) + 12CO_2 + 4N_2 + 2HCl(g) \quad (3)$$

The energy of combustion is as follows ($T = 298.15$ K):

$$\Delta H = Q_p = Q_v + \Delta nRT = -7391.90\ kJ \cdot mol^{-1} = -18.17\ MJ \cdot kg^{-1} \quad (4)$$

So the energy of combustion **1** was –18.17 $MJ \cdot kg^{-1}$, which was higher than the energy of combustion of $Cu(IMI)_4(N_3)_2$ (–11.15 $MJ \cdot kg^{-1}$).[16]

The metal coordination compound should have relatively 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 as applied in thermochemical Equation (5). With the known enthalpies of formation of copper oxide [$\Delta_f H^\circ_{298}$ (CuO, s) = –155.2 $kJ \cdot mol^{-1}$], carbon dioxide [$\Delta_f H^\circ_{298}$ (CO_2, g) = –393.5 $kJ \cdot mol^{-1}$], water [$\Delta_f H^\circ_{298}$ (H_2O, l) = –285.8 $kJ \cdot mol^{-1}$], and hydrogen chloride [$\Delta_f H^\circ_{298}$ (HCl, g) = –92.3 $kJ \cdot mol^{-1}$], the enthalpy of formation of **1** can now be calculated as:

$$\Delta_f H^\circ (\mathbf{1}, s) = \Delta_f H^\circ (CuO, s) + 7\Delta_f H^\circ (H_2O, l) + 12\Delta_f H^\circ (CO_2, g) + 2\Delta_f H^\circ (HCl, g) - \Delta_c H^\circ (s) \quad (5)$$

$$\Delta_f H^\circ_{298} (\mathbf{1}, s) = +323.54\ kJ \cdot mol^{-1} = +0.41\ MJ \cdot kg^{-1}.$$

Calculation of Critical Temperature of Thermal Explosion, $\Delta S^{\neq}$, $\Delta H^{\neq}$, and $\Delta G^{\neq}$

The value of the peak temperature corresponding to $\beta \rightarrow 0$ obtained according to the following Equation (6)[36] is 428.15 K, where a, b, c, and d are coefficients:

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

The corresponding critical temperature of thermal explosion (T_b) obtained is 447.69 K by the following Equation (7):[36]

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

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 the following Equation (8), Equation (9), and Equation (10)[36] are –230.09 $kJ \cdot mol^{-1}$, 57.31 $J \cdot K^{-1} \cdot mol^{-1}$, and 155.82 $kJ \cdot mol^{-1}$, respectively.

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

$$\Delta H^{\neq} = E - RT \quad (9)$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \quad (10)$$

where k_B is the Boltzmann constant ($1.381 \times 10^{-23}\ J \cdot K^{-1}$) and h is the Planck constant ($6.626 \times 10^{-34}\ J \cdot s$).

Physicochemical Properties

The physicochemical properties of **1** are tabulated in Table 3.

Table 3. Physicochemical properties of **1**.

	1
T_d a) /K	555.05, 765.15
N b) /%	27.55
Ω c) /%	–125.9
E d) /kJ·mol^{-1}	60.865, 80.755
ΔH° e) /kJ·mol^{-1}	–7391.90
$\Delta_f H^\circ_{298}$ f) /kJ·mol^{-1}	+323.54
T_{p0} /K	428.15
T_b /K	447.69
$\Delta S^{\neq}$ /kJ·mol^{-1}	–230.09
$\mathit{\Delta} H^{\neq}$ /J·K^{-1}·mol^{-1}	57.31
$\Delta G^{\neq}$ /kJ·mol^{-1}	155.82
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.

Conclusions

The novel copper(II) imidazole chloride compound, [Cu(IMI)$_4$Cl]Cl (**1**), was synthesized and characterized. The surprise is that the Cu^{II} ion was intriguing five-coordinated in a distorted pentahedron arrangement with four imidazole molecules and a coordination chlorine atom. In **1**, thermal analysis indicated that there were one endothermic process and two main exothermic processes, with peaks at 506.25 K, 555.05 K, and 765.15 K, respectively, as shown in the DSC curve corresponding to the TG-DTG curves. Non-isothermal kinetics analysis results indicated that the Arrhenius Equation of **1** can be expressed as follows: $\ln k_1 = 3.145–60.865 \times 10^3/(\mathrm{R}T)$ (the first exothermic process) and $\ln k_2 = 2.743–80.755 \times 10^3/(\mathrm{R}T)$ (the second exothermic process). The experiment found the energy of combustion and the enthalpy of formation of **1** are –18.17 MJ·kg^{-1} and +323.54 kJ·mol^{-1} (+0.41 MJ·kg^{-1}), respectively. It is more important, **1** was regarded as the less toxicity energy additive which will be applied to improve the explosion performance of the traditional explosives and propellant formulations.

Experimental Section

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

Elemental analysis was performed with a Flash EA 1112 full-automatic trace element analyzer. The FT-IR spectra were recorded with a Bruker Equinox 55 infrared spectrometer (KBr pellets) in the range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1}. DSC and TG measurements were carried out with a Pyris-1 differential scanning calorimeter and a Pyris-1 thermogravimetric analyzer (Perkin-Elmer, USA). The combustion heat was measured by oxygen bomb calorimetry (Parr 6200, USA).

Synthesis of [Cu(IMI)$_4$(Cl)]Cl (1): The synthesis of **1** was as follows: CuCl$_2$·2H$_2$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 ca. 60–70 °C. Imidazole (40 mmol) was dissolved in distilled water (20 mL), and subsequently it was added to the Cu^{II} aqueous solution during 25–30 min with continuous stirring. Finally the solution was cooled to room temperature naturally. **IR** (KBr): $\tilde{\nu}$ = 2948 (N–H), 1604 (C=N), 1531 (C=C), 1328 (C–N), 1255 (C–N), 1063 (C–N), 772 (C–H) cm^{-1}. CuC$_{12}$H$_{16}$N$_8$Cl$_2$: calcd. C 35.43; H 3.96; N 27.55 %; found: C 35.48; H 3.42; N 27.47 %.

X-ray Data Collection and Structures Refinement: A crystal was chosen for X-ray determination. The X-ray diffraction data collection were performed with a Rigaku AFC–10/Saturn 724$^+$ CCD detector diffractometer with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). The structure was solved by direct methods using SHELXS-97[37] (Sheldrick, 1990) and refined by full-matrix least-squares methods on F^2 with SHELXL-97[38] (Sheldrick, 1997). 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 4.

Table 4. Crystal data and structure refinement for **1**.

	[Cu(IMI)$_4$Cl]Cl (**1**)
Empirical formula	CuC$_{12}$H$_{16}$N$_8$Cl$_2$
Formula mass	406.77
Temperature /K	293(2)
Color	blue
Crystal dimensions /mm	0.40 × 0.38 × 0.16
Crystal system	monoclinic
Space group	$P2_1/n$
Z	4
a /Å	8.847(2)
b /Å	13.210(3)
c /Å	13.870(3)
β /°	90.164(3)
hkl-ranges	$-12 \le h \le 9$ $-17 \le k \le 18$ $-17 \le l \le 18$
Unit cell dimensions V /Å^3	1621.0(6)
D_c /g·cm^{-3}	1.667
μ (Mo-K_α) /mm^{-1}	1.688
F(000)	828
θ Range /°	2.77~29.00
Max. and min. transmission	0.7681, 0.5516
Measured reflections	11488
Unique data	4261 (R_{int} = 0.0348)
R_1, wR_2 [$I > 2\sigma(I)$]	0.0380, 0.0936 a)
R_1, wR_2 (all data)	0.0433, 0.0976 a)
Goodness of fit	0.999
$\delta p_{\max}$, $\delta p_{\min}$ /e·Å^{-3}	0.537, –0.575

a) $wR_2 = [\sum w(F_o^2–F_c^2)^2/\sum w(F_o^2)]^{1/2}$, $P = (F_o^2+2F_c^2)/3$; $w = 1/[\sigma^2(F_o^2)+(0.0485P)^2+1.3960P]$.

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-910441 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Supporting Information (see footnote on the first page of this article): Hydrogen bond lengths /Å and bond angles /° for **1**.

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