Supporting Information

The Combined Effect of Pyrazole and Amino: Preparation of the Novel Energetic Coordination Compounds with High ClO₄⁻ Content

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Experimental Section

Caution!

The new substances and raw materials used in the article are all potentially explosive materials. Although we did not encounter any danger in the process of handling these compounds during the synthetic procedure, the necessary protective equipment (leather gloves, face mask) is strongly recommended.

Materials and Equipment

During the experiment, the reagents (analytical grade) used were purchased from Aladdin and Azov and used without further purification. Single crystal X-ray diffraction data was collected by using Rigaku supernova single X-ray diffractometer area detector ($Mo_{K\alpha'}$, 0.71073 Å). Powder X-ray diffraction (PXRD) data of the product was tested using a Bruker D8 ADVANCE X-ray powder diffractometer (Cu_{Ka}, 1.5418 Å). The thermal behavior of the compound was analyzed by differential scanning calorimeter (TGA/DSC2, METTLER TOLEDO STAR e system), with the heating rate was 5 K min⁻¹, and the gas atmosphere was N₂. Infrared (IR) spectra were measured on a Nicolet Is10 spectrometer (Equipped with KBr discs) with a measurement range of 4000 - 400 cm ⁻¹. Elemental analyses (C,H,N or C,H,N,S) were carried out on an elemental analyzer (Vario EL Cube, Germany). The mechanical sensitivities (including impact sensitivity and friction sensitivity) of the material were determined by the standard step method of the drop weight device with a BAM DFH-10 device with a weight drop of 10 kg. The constant pressure reaction heat is measured by High Pressore Oxygen Calorimeter (BCA@ 500), with the standard molar combustion enthalpy can be converted by the combustion equation. The experimental density is obtained by the powder densitometer test (Micromeritics AccuPyc II 1340). The laser performance test is measured by Diode Laser (Changchun laser technology co., LTD. LR-ISP-980/1~1000mW. Spectral Line width (nm): < 3, Output Power (mW): 1~1000, Beam Diameter at Aperture (mm): 5.0 x 5.0, Modulating Repetition: 100KHz TTL / 10KHz Analogue. Operating parameters: theoretical maximal output power $P_{\text{max}} = 30.15$ W; theoretical pulse length $\tau_{\text{max}} = 49571$ µs. wavelength $\lambda = 915$ nm. Frequency F = 1Hz.).

Synthesis of compound 3

At 0 °C, DMF (500 ml), methyl cyanoacetate (0.5 mol), trichloroacetonitrile (0.5 mol), and sodium oxalate (0.875 mol) were sequentially added to the reaction flask. The reaction mixture was stirred at this temperature for 3 hours, followed by slow heating to room temperature and allowed to react for 2 days. After completion of the reaction, sodium oxalate (0.875 mol) was added, and hydrated hydrazine (0.5 mol) was slowly added simultaneously. The reaction mixture was slowly heated to 115 °C and refluxed for 12 hours. After the reaction was complete and cooled to room temperature, the solid precipitate was filtered off and the solvent was distilled off to obtain a brown solid. The final target product was obtained with a yield of 73 % through hot water recrystallization. Yield: 53 %.

IR (KBr, v/cm⁻¹): 3409(m), 3367(m), 3191(m), 1691(s), 1618(s), 1578(s), 1497(s), 1435(s), 1383(s), 1340 (s), 1187(s), 1124(s),1033 (m). MS (ESI), m/z: 155.03 [$C_5H_7N_4O_2^{-1}$]. Elemental analysis (%) for $C_5H_8N_{54}O_2$ (Mr = 156.15 g mol⁻¹): calcd. C 38.5, H 5.2, N 35.9; found C 38.2, H 5.3, N 36.1. ¹³C NMR (400 MHZ, D₂O/NaOH- d_6): δ 174.4, 167.3, 156.5, 50.5.

Synthesis of HDAPZCA

Add hydrated hydrazine (50 ml), methanol (50 ml), and 3,5-diamino-1*H*-pyrazole-4-carboxylate (0.1 mol) to a 250 ml reaction flask. Slowly heat the mixture to 90 °C and reflux for 12 hours. Once the reaction is complete, place it in a refrigerator overnight to obtain a large amount of white solid. Yield: 81 %.

IR (KBr, v/cm⁻¹): 3405(m), 3362(m), 3191 (m), 3146 (m), 1654 (s), 1598(s), 1560(s), 1500(s), 1343(s) 1214(s), 1150(s), 960(s), 876(s). Elemental analysis (%) for C₄H₈N₆O (Mr = 156.08 g mol⁻¹): calcd. C 30.8, H 5.2, N 53.8; found C 30.4, H 5.5, N 53.7. ¹³C NMR (400 MHZ, D₂O/NaOH- d_6): δ 166.7, 154.6, 87.4.

Synthesis of EIsCCs-1·2H₂O and EIsCCs-1

In a 100 ml beaker, add HDAPZCA (50 mmol) to methanol (50 ml), and slowly heat the reaction mixture to 60 °C. At this temperature, slowly add HClO₄ until the solution becomes clear. Then add $Cu(ClO_4)_2 \cdot 5H_2O$ solid and continue stirring for 5 minutes until the solid dissolves. While stirring, cool the mixture down and after about 30 minutes, a large amount of blue solid **EIsCCs-1**·2H₂O can be obtained. Yield:82%. To obtain the anhydrous **EIsCCPs-1**, the blue solid needs to be dried in a vacuum oven at 50 °C for 12 hours. Yield:82%.

EIsCCs-1·2H₂O: IR (KBr, v/cm⁻¹): 3567(m), 3449(s), 3352 (m), 3266 (s), 1669 (s), 1582(s), 1432(s), 1247(s), 1109(s), 923(s), 889(s), 739(s), 625(s), 590(s). Elemental analysis (%) for $C_8H_{22}Cl_4CuN_{12}O_{20}$ (Mr = 811.67 g mol⁻¹): calcd. C 11.8, H 2.7, N 20.7; found C 11.5, H 2.8, N 20.8.

EIsCCs-1: IR (KBr, v/cm⁻¹): 3447(m), 3130(m), 3260 (m), 1651 (s), 1612 (m), 1582(s), 1432(s), 1247(s), 1109(s), 923(s), 889(s), 739(s), 625(s), 590(s). Elemental analysis (%) for $C_8H_{18}Cl_4CuN_{12}O_{18}$ (Mr = 775.64 g mol⁻¹): calcd. C 12.4, H 2.3, N 21.7; found C 12.1, H 2.5, N 21.9.

Oxygen bomb calorimetry

The constant pressure reaction heat $(\Delta_C U)$ was measured by an oxygen bomb calorimeter, and the average value was obtained by three measurements independently. The standard molar combustion enthalpy $(\Delta_C H^{\theta}_m)$ can be obtained from the constant pressure reaction heat $(\Delta_C U)$ according to the equation 1. According to the principle of Hess' law, the complete combustion reaction equation was shown in equation 2, and the standard molar generation enthalpy $(\Delta_f H^{\theta}_m)$ can be obtained based on

the formulas 1, 2 and 3 [CO₂(g): -393.51 kJ mol⁻¹; CuCl₂(s): -220.1 kJ mol⁻¹; H₂O(l): -285.85 kJ mol⁻¹]. The experimental results showed that the combustion heat of **ECPs-1** is -7390 kJ mol⁻¹.

$$\Delta c H^{\theta} m = \Delta c U + \Delta n R T \tag{1}$$

 $\Delta_n = n_g$ (products)- n_g (reactants), (n_g is the sum of the total moles of gas in the product or reactant, R = 8.314 J mol⁻¹ K⁻¹, T = 298.15 K)

$$C_8 H_{18} N_{12} O_{18} CuCl_4(s) + 3O_2(g) = 8CO_2(g) + 8H_2O(l) + 6N_2(g) + CuCl_2(s) + 2HCl(g)$$
(2)

$$\Delta_{f}H^{\theta}m(compound) = \sum \Delta_{f}H^{\theta}m(products) - \Delta_{c}H^{\theta}m(compound)$$
(3)

Theoretical simulation based on K-J equations

Detonation speed (D) and explosion pressure (P) are the main indicators for measuring energetic materials. The various detonation characteristics of the EIsCCs-1 were predicted using the modified Kamlet-Jacbos (K-J) equations (eq 5-7) which is a commonly used equation for predicting the detonation velocity and pressure of high energy materials $[CO_2(g): -393.51 \text{ kJ mol}^{-1}; CuCl_2(s): -220.1 \text{ kJ mol}^{-1}; H_2O(g): -241.82 \text{ kJ mol}^{-1}; HCl(g): -92.31 \text{ kJ mol}^{-1}].$

$$C_8 H_{18} N_{12} O_{18} CuCl_4(s) = 6CO(g) + 2CO_2(g) + 8H_2O(g) + 6N_2(g) + CuCl_2(s) + 2HCl(g)$$
(4)

$$D = 1.01(NM^{1/2}Q^{1/2})^{1/2}(1+1.30\rho)$$
(5)

$$P = 1.55\rho^2 N M^{1/2} Q^{1/2} \tag{6}$$

$$Q = \frac{-\left[\Delta H_f(detonation \ production) - \Delta H_f(explosive)\right]}{-(\Delta H_f(explosive))}$$

D: detonation velocity, km s⁻¹); P: detonation pressure, GPa; ρ : density, g cm⁻³; ΔH_{f} : heat of formation, kJ mol⁻¹); Q: heat of detonation, J g⁻¹); N: moles of detonation gases per gram of explosive, mol g⁻¹); M: average molecular weight of gases, g mol⁻¹)

Improved hot noodle tests

Approximately 5 mg of the compound was dispersed on the filter paper in a powdered state. Light the filter paper, and then slowly ignite EIsCCs-1, while recording the deflagration process of the compound with a high-speed camera.

Detonation initiation

The test device used to breakdown of the lead plate, the material inside can be divided into two parts: the first part is filled with LA or EIsCCs-1 (80 mg, pressure of fixation is 25 MPa); the second component is RDX (500 mg, charge pressure is 40 MPa). The lead plate has a thickness of 5 mm.

Laser performance test

Weigh 3 mg samples (pressure of fixation is 0 MPa or 3 GPa), a total of 5 parts, and place them in sample tubes. Use a semiconductor laser to trigger the sample. Determine the minimum trigger energy by adjusting the action time and power. Take the average value as the final test value.

Supplementary Figures S1-S11



Figure S1 The IR spectra of methyl 3,5-diamino-1*H*-pyrazole-4-carboxylate.



Figure S2 IR spectra of 3,5-diamino-1*H*-pyrazole-4-carbohydrazide.





Figure S4 IR spectra of EIsCCs-1.







Figure S6 TG-DSC testing result of EIsCCs- $1.2H_2O$



Figure S7 Comparison of single crystal and powder X-ray diffraction of EIsCCs-1



Figure S8 Illustration of setup of Laser Initiation Tests.



Figure S9 ¹³C NMR of 3,5-diamino-1*H*-pyrazole-4-carboxylate



Figure S10 ¹³C NMR of 3,5-diamino-1*H*-pyrazole-4-carbohydrazide.



Figure S11 Laser comparative experimental test results.

Supplementary Table S1

Formula	$C_8H_{22}Cl_4CuN_{12}O_{20}$
Temperature [K]	298.15
$M_{\rm w}[{ m g mol}^{-1}]$	811.73
Crystal size [mm ³]	0.1 x 0.1 x 0.1
Crystal system	triclinic
Space group	<i>P</i> -1
unit cell dimensions	a= 7.8824(6) Å, b = 9.8098(9) Å, c [Å]= 10.0694(8) Å
	α [Å]= 69.274(8), β [Å]= 72.562(7), γ [Å]= 67.701(8)
<i>V</i> [[Å ³]	661,34(11)
Ζ	2
$\rho_{\rm calc}[\rm g\ cm^{-3}]$	2.038
μ [mm ⁻¹]	5.945
<i>F</i> (000)	411.0
2θ range[°]	9.568 - 155.296
Reflections collected	7198
Index ranges	$-9 \le h \le 9, -11 \le k \le 12, -10 \le l \le 12$
R _{int}	0.0338
Data/restraints/parameters	2659 / 0 / 1209
Final R index $[I > 2\sigma(I)]$	R1 = 0.0765, wR2 = 0.1923
Final <i>R</i> index [all data]	R1 = 0.0817, wR2 = 0.1958
GOF on F ²	1.067
CCDC	2270340

Table S1. Crystallographic data for EIsCCs-1