Electronic Supplementary Information

A Highly Stable Octa-coordinated Energetic Complex

Wenchao Tong,[a] Mei Bian,[a] Yongan Feng,[ab]* Tonglai Zhang,[a] Shuangqi Hu,[b] and Li Yang*[a]

[a] State Key Laboratory of Explosion Science and Technology
School of Mechatronical Engineering
Beijing Institute of Technology
5 South Zhongguancun Street, Beijing 100081, P. R. China

[b] National Defense Key Laboratory of Underground Damage Technology
School of Environmental and Safety Engineering
North University of China
3 Xueyuan Road, Taiyuan 030051, P. R. China

* Corresponding authors: Dr. Li Yang and Yongan Feng

E-mail:
Dr. Li Yang: yanglibit@bit.edu.cn
Dr. Yongan Feng: fengyongan0918@126.com

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S1. Materials and instruments

All reagents (analytic grade) were commercially available and used without further purification. Elemental analyses were 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 4000-400cm^{-1}with a resolution of 4cm^{-1}. The crystal structure determination was performed on a Rigaku AFC-10/Saturn 724+ CCD detector diffractometer with graphite monochromated Mo-Kα radiation (λ=0.071073 nm) with φ and ω modes. The structure was solved by direct methods using SHELXS-97 and refined by SHELXL-97 and OLEX-2.[1-3] The X-ray powder diffraction (XRPD) measurement was performed on a Bruker D8 advance diffractometer at 60 kV, 300 mA and Cu Kα radiation (λ=1.5406 Å), with a scan speed of 5°·min^{-1} and a step size of 0.02° in 2θ.All non-hydrogen atoms were obtained from the difference Fourier map and subjected to anisotropic refinement by full-matrix least squares on F2. DSC measurement was performed with a Pyris-1 differential scanning calorimeter in a dry nitrogen atmosphere (flowing rate of 20mL·min^{-1}) with a linear heating rate of 10^{o}C·min^{-1}from 50^{o}C to 500^{o}C.

S2. Synthesis and characterization

$Cd_2(SCZ)_4(TNR)_2$ (**Octa-HECs**): Cadmium carbonate (10mmol, 1.72g) was added to 60mL methanol solution of stephen acid (10mmol, 2.45g), and the mixture was stirred at 60-65°C until a clear solution appeared. Semicarbazide hydrochloride (30 mmol, 3.33 g) was dissolved in 20mL distilled water, then adjusted the pH of the solution to 6-7 using solid NaOH. Adding the semicarbazide solution to above methanol solution and keeping this mixture at 60-65°C for 15 minutes. Then the mixture was cooled to room temperature. An orange precipitation was collected after filtration. Washing the orange precipitation with ethanol, and drying under vacuum to achieve target compound. Yield: 87% (4.40 g). Elemental analysis (%) for $C_{16}H_{22}Cd_2N_{18}O_{20}$: C 19.00, H 2.19, N 24.93; Found: C 19.10, H 2.14, N,24.89. IR (cm^{-1}, KBr): 3292, 3188, 2920, 1633, 1583, 1501, 1461, 1396, 1324, 1224, 1183, 1074, 941, 783, 709, 530.

S3. X-ray diffraction

Table S1. Crystallographic data and structure refinement details for **Octa-HECs**.

Items	Octa-HECs
CCDC	1013947
Formula	$C_{16}H_{22}Cd_2N_{18}O_{20}$
Formula weight	1011.29
T/K	183(2)
Crystal system	*Triclinic*
Space group	*P-1*
a, b, c /nm	0.77293(17), 1.0047(2), 1.0550(3)
A, β, γ /(°)	114.942(3), 91.849(2), 95.634(3)
V/nm^3	0.7369(3)
Z	1
D_c/(g·cm^{-3})	2.2788
θ/(°)	2.66-31.53
h, k, l	-11-11,-14-14,-15-15
Reflections collections	4370
R_{int}	0.0262
S	0.9992
R_1,wR_2[$I>2\sigma(I)$][a]	0.0285, 0.0673
R_1,wR_2(all data)[a]	0.0325, 0.0692
μ(MoKα)/mm^{-1}	1.569
F(000)	498.6763

Table S2. Bond lengths (Å) for **Octa-HECs.**

Bond	Bond length / Å	Bond	Bond length / Å
Cd1-O1	2.3698(18)	N5-C2	1.360(3)
Cd1-O2	2.3586(17)	N6-C2	1.342(3)
Cd1-O3	2.3135(18)	N7-C4	1.421(2)
Cd1-O4	2.7282(19)	N8-C6	1.447(3)
Cd1-N1	2.3522(19)	N9-C8	1.426(3)
Cd1-N4	2.3552(17)	N1-H1B	0.920(3)
Cd1-O3	2.4175(16)	N1-H1A	0.920(2)
Cd1-O10	2.5391(17)	N2-H2	0.880(2)
O1-C1	1.254(2)	N3-H3A	0.880(2)
O2-C2	1.248(3)	N3-H3B	0.880(2)
O3-C3	1.271(3)	N4-H4A	0.920(3)
O4-N7	1.248(3)	N4-H4B	0.920(3)
O5-N7	1.246(2)	N5-H5	0.880(2)
O6-N8	1.223(3)	N6-H6A	0.880(3)
O7-N8	1.231(3)	N6-H6B	0.880(2)
N3-C1	1.336(3)	C7-C8	1.445(3)
N4-N5	1.410(3)	C5-H5A	0.950(3)

Table S3. Hydrogen Bonds for **Octa-HECs.**

Hydrogen Bond	Bond length / Å	Bond Angles / Å
N1-H1B···O6	2.480(3)	105.96(19)
N2-H2···O7	2.551(2)	127.9(2)
N2-H2···O8	1.946(3)	143.7(2)
N3-H3A···O1	2.129(2)	170.9(2)
N3-H3B···O8	2.019(2)	144.5(2)
N3-H3B···O9	2.252(3)	142.6(2)
N4-H4A···O10	2.504(3)	128.4(2)
N4-H4A···O9	2.408(3)	118.3(2)
N4-H4B···O7	2.258(3)	140.5(2)
N5-H5···O4	2.263(2)	169.3(2)
N6-H6A···O5	2.356(3)	144.9(2)
N6-H6B···O5	2.169(3)	160.5(2)

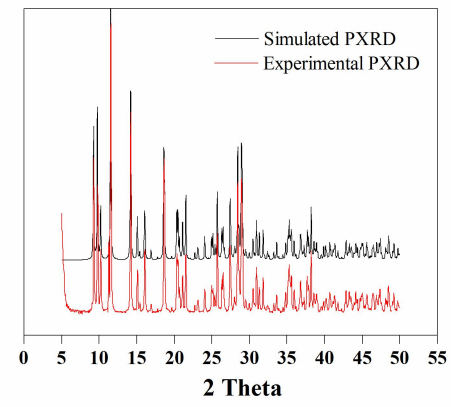

Figure S1 The PXRD curves of **Octa-HECs.**

S4.Differential scanning calorimetry (DSC)

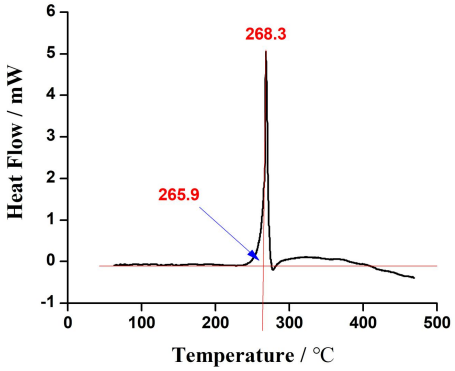

Figure S2 The DSC curve of **Octa-HECs**.

S5. Non-isothermal kinetics analysis

The commonly used Kissinger's method and Ozawa-Doyle's method were employed to determine the apparent activation energies.[4-6] The Kissinger and Ozawa-Doyle equations are as follows:

$$\ln\beta/T_p^2=\ln[RA/E]-E/(RT_p) \quad \text{(eq. S1)}$$

$$\lg\beta=\lg[AE/RG(\alpha)]-2.315-0.4567E/RT_p \quad \text{(eq. S2)}$$

Where T_p is the peak temperature [K], A is the pre-exponential factor [s^{-1}], E 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 exothermic peak temperatures measured at different heating rates of 5, 10, 15 and 20 $^{o}C\cdot min^{-1}$, the apparent activation energy E, pre-exponential factor A, linear coefficient R_c and standard deviations S were calculated and shown in Table S4.

Table S4. Thermal and kinetic data for **Octa-HECs.**

β / $^{o}C\cdot min^{-1}$	T_p / ^{o}C	Parameter	Kissinger's method	Ozawa's method
5	263.7	E / kJ mol^{-1}	187.4	186.9
10	268.5	lgA	16.12	
15	273.5	R_c	-0.9568	-0.9605
20	280.7	S	0.2051	0.0890

S6. Sensitivity

Impact sensitivity (IS) and friction sensitivities(FS) were measured according to the BAM method. Electrostatic sensitivities(EDS)are tested on a JGY-50 (III) Electrostatic test apparatus, the high voltage was supplied through an EST806F Electrostatic Power Generator. Test conditions: 25°C(temperature); 32% (relative humidity).

S7. Reference

1 G. M. Sheldrick, SHELXS97, Program for the Solution of Crystal Structures; University of Göttingen: Germany, 1997.
2 G. M. Sheldrick, SHELXL97, Program for Crystal Structure Refinement from Diffraction Data; University of Göttingen: Germany, 1997.
3 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. J. Puschmann, *Appl. Cryst.* 2009, **42**, 339.
4 H. E. Kissinger, *Anal. Chem.* 1957, **29**, 1702.
5 T. Ozawa, *Bull. Chem. Soc. Jpn.* 1965, **38**, 1881.
6 C. D. Doyle, *J. Appl. Polym. Sci.* 1961, **5**, 285.