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# A novel cocrystal composed of CL-20 and energetic ionic salt

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#### SI 1. Experimental

Caution: Although no unplanned detonations were encountered during this work, CL-20 and 1-AMTN are both dangerous high explosives. Proper safety practices and equipment were used to prevent an explosion due to friction, heat, static shock or impact. Be aware that the potential for severe injury exists if these materials are handled improperly.

Energetic compounds 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) was provided by Liaoning Qingyang Chemical Industry Group and 1-amino-3-methyl-1,2,3-triazolium nitrate (1-AMTN) was received from Gansu Yinguang Chemical Industry Group.

A 1:1 mixture of  $\varepsilon$ -CL-20 (438mg 1mmol) and 1-AMTN (161mg 1mmol) was added to 10 ml of ethanol / ethyl acetate (1:1 volume ratio) and mildly heated to all the pure components dissolution. The solution was allowed to evaporate slowly at room temperature over several days. Colorless prisms of 1:1 CL-20/1-AMTN cocrystal explosive were obtained. Alternative solvents reliably producing this cocrystal form include ethanol / acetonitrile (1:1 volume ratio), ethanol / ethyl acetate (1:1 volume ratio), methanol / ethyl acetate (1:1 volume ratio), methanol / acetonitrile (1:1 volume ratio), methanol / acetonitrile (1:1 volume ratio).

#### SI 2. Raman Spectroscopy of ADNP Cocrystal

Raman spectra were collected by a LabRAM HR Evolution Raman microscope using 514.5 nm laser and 1 cm<sup>-1</sup> resolution. Spectra in the range of 4000-100 cm<sup>-1</sup> were collected and analyzed by the LabSpec 6 software package.



Figure S2. Raman spectra of cocrystal 1,  $\epsilon$ -CL-20 and 1-AMTN.

# SI 3. Powder X-ray Diffraction

Powder X-ray diffraction patterns were obtained at ambient temperature by a Bruker D8 Advance with a Cu-K $\alpha$  radiation ( $\lambda$ =1.5406Å) at 40 kV and 40 mA. The sample was placed onto a glass circular sample holder and revelled with a glass slide. The sample was scanned within the scan range of 2 $\theta$  from 5° to 50° continuous san with a step size of 0.015° and a scan speed of 0.2 s per step.



Figure S3a. PXRD patterns of cocrystal 1, ɛ-CL-20 and 1-AMTN.



Figure S3b. PXRD patterns of cocrystal 1 (Experimental and Calculated).



Figure S3c. PXRD patterns of of CL-20 polymorphs from ref.1.

### SI 4. Single Crystal X-ray Diffraction

Single crystal X-ray diffraction data for cocrystal **1** was collected using a Rigaku AFC10K Saturn. Single crystal of suitable quality was chosen and purged with a cooled nitrogen gas stream at 170 K throughout the data collection. X-ray reflections were collected on a Xcalibur Eos CCD detector with graphite-monochromated Ga-K $\alpha$  radiation ( $\lambda$ =1.34139 Å). Data were collected and processed using Olex-2 software. Structure was solved by direct methods and SHELX was used for structure solution and least-squares refinement. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using the riding model. The solvent-masking routine in Olex-2 [equivalent to SQUEEZE in PLATON] was used to remove the contributions of unspecified disordered components from the structure factor list in the CIF. With Z = 4 in this case, this is equivalent to the removal of 58/4 = 14.5 electrons from the formula unit. If the disordered component was ethanol, this could correspond with ~ 0.6(C~2~H~6~O) being added to the formula unit. If the disordered component was ethanol to the formula unit.



Figure S4 . OPTEP diagram for cocrystal **1** with 50% probability ellipsoids. Table S4. Crystallographic Data for cocrystal **1** (Collected at 170 K)

Material	Cocrystal 1	
Stoichiometry	1:1	
Empirical formula	$C_9H_{13}N_{17}O_{15}$	
Formula weight	599.36	
Temperature	170.01 K	
Wavelength	1.34139 Å	
Crystal system	Monoclinic	
Space group	P121/n1	
Unit cell dimensions	$a = 7.70210(10) \text{ Å}  \alpha = 90^{\circ}$	
	$b = 25.8034(4) \text{ Å}  \beta = 91.9310(10)^{\circ}$	
	$c = 11.7215(2) \text{ Å}  \gamma = 90^{\circ}$	
Volume	2328.21(6) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.71 g/cm <sup>3</sup>	
Absorption coefficient	0.913 mm <sup>-1</sup>	
F(000)	1224	
Crystal size	0.1 x 0.08 x 0.05 mm <sup>3</sup>	
Theta range for data collection	3.605 to 54.906°.	
Index ranges	-9<=h<=9, -31<=k<=31, -14<=l<=12	
Reflections collected	31959	
Independent reflections	4398 [R(int) = 0.0373]	
Completeness to theta = $53.594^{\circ}$	99.1 %	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7508 and 0.5766
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	4398 / 0 / 372
Goodness-of-fit on F <sup>2</sup>	1.049
Final R indices [I>2sigma(I)]	R1 = 0.0402, wR2 = 0.1004
R indices (all data)	R1 = 0.0419, wR2 = 0.1017
Extinction coefficient	n/a
Largest diff. peak and hole	0.473 and -0.410 e.Å <sup>-3</sup>

## SI 5. Infrared spectroscopy

IR Spectra were recorded on a Shimadzu FTIR 8400s infrared Spectrophotometer, using KBr pellets. 1-2 mg sample was mixed with 180 mg KBr. The mixture was triturated in an agate mortar and pressed into slice of KBr with sample in a mole. The IR spectra were collected for 64 scans at 4 cm<sup>-1</sup> resolution..



Figure S5. IR spectra of cocrystal 1,  $\epsilon$ -CL-20 and 1-AMTN (a). IR spectra of of CL-20 polymorphs from ref.2 (b).

# SI 6. Differential Scanning Calorimetry

The differential scanning calorimeter (DSC) was performed on a TA Q100 instrument. The test sample was manually ground to obtain fine powder. 2-5 mg of sample was placed in sample pan. The sample was heated from 50 to 300  $^{\circ}$ C at a heating rate of 10  $^{\circ}$ C / min. The sample was purged with a stream of flowing nitrogen at 50 ml / min.



Figure S6. Typical DSC traces of cocrystal 1, ε-CL-20 and 1-AMTN.

### SI 7. Morphology

The morphologies of the co-formers and the cocrystal **1** were carried out using a TESCAN (Czech Republic) MIRA3XMU Scanning Electron Microscope (SEM) at 5 kV and 10 mA.



Figure S7. SEM of cocrystal 1 (c and d),  $\epsilon$ -CL-20 (a) and 1-AMTN (b).

## SI 8. Detonation Property Evaluation

The detonation properties for the co-formers and the cocrystal **1** at theroretical maximum desity (TMD) were calculated by the linear output thermodynamic user-friendly software code<sup>3</sup> following equations:

 $D(km/s) = 1.6439 + 3.5933\rho_0 - 0.1326a - 0.0034b + 0.1206c + 0.0442d - 0.2768n_{-NRR}$ 

where  $\rho_0$  is the loading density, a, b, c, d and -NRR' are the number of moles of carbon,

hydrogen, oxygen, nitrogen and specific group in explosives. The specific group -NRR includes

 $-NH_2$ ,  $NH_4^+$  and  $\bigvee_N^N$  groups.

### SI 9. References

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