Peroxosolvate Discovery Method Leads to First Cocrystal with Three Energetic Components

Supplementary Information

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SI 1. Experimental

Caution: Although no unplanned detonations were encountered during this work, 3,4-diaminofurazan and 3,4dinitropyrazole are dangerous explosive materials and hydrogen peroxide is a powerful oxidizing agent. Proper safety practices and equipment was used to prevent an explosion due to friction, heat, static shock, impact, or flame. Be aware that the potential for severe injury exists if these materials are handled improperly.

3,4-Dinitropyrazole (DNP) was received from Lawrence Livermore National Labs. 3,4-Diaminofurazan (DAF), 97% purity, was received from Sigma Aldrich. 98% Hydrogen peroxide (H₂O₂) was received from PeroxyChem LLC. Acetonitrile (MeCN) was obtained from Fisher Scientific, passed through an activated alumina column, and stored over 4Å molecular sieves prior to use. Hexanes, certified ACS grade, was obtained from Fisher Scientific and stored over 4Å molecular sieves prior to use. Urea hydrogen peroxide, 97% purity, and 5-aminotetrazole monohydrate (5-AtH), 97% purity, were received from Sigma Aldrich. Sodium thiosulphate pentahydrate (NaTS), certified ACS grade, was received from Fisher Scientific. 2-Methylquinoline-N-oxide (MQNO), 98% purity, was received from TCI America. 4-(3-Phenylpropyl)pyridine-N-oxide (3PNO), 95% purity, was received from MilliporeSigma. Disposable syringe filters were obtained from Macherey-Nagel (0.45 µm, polytetrafluoroethylene). Disposable filter funnels were obtained from Sigma Aldrich (10 µm, polytetrafluoroethylene, 8 mL capacity). Microcentrifuge tubes were obtained from Fisher Scientific (1.5 mL, MCT Graduated Natural).

Synthesis

Urea:H₂O₂-MeCN solution (UHPA)

Urea hydrogen peroxide (344 mg, 3.66 mmol) and MeCN (20 mL) were combined in a 20 mL glass scintillation vial with a magnetic stir bar. The slurry was shielded from light and left stirring at ambient temperature for 4h. The vial was then tightly sealed and placed in a freezer for 12h at which time the solution was syringe filtered.

2-methylquinoline-N-oxide peroxosolvate from UHPA

MQNO (3.20 mg, 0.0201 mmol) was placed in a 1.5 mL microcentrifuge tube and 750 μ L UHPA was added. The solution was briefly sonicated and syringe filtered into a fresh 1.5 mL microcentrifuge tube. The tube was then placed in a desiccator with Drierite to evaporate (24h). The obtained solid was a physical mixture which contained 2-methylquinoline-N-oxide peroxosolvate.

4-(3-phenylpropyl)pyridine-N-oxide peroxosolvate from UHPA

3PNO (3.41 mg, 0.0160 mmol) was placed in a 1.5 mL microcentrifuge tube and 750 μ L UHPA was added. The tube was then placed in a desiccator with Drierite to evaporate (24h). The obtained solid was a physical mixture which contained 4-(3-phenylpropyl)pyridine-N-oxide peroxosolvate.

5-aminotetrazole (5-At)

5-AtH (2.30 g, 22.3 mmol) was placed in a 50 mL round bottom flask which was then heated to 60 °C and placed under high-vacuum for 16h resulting in 5-At.

5-aminotetrazole peroxosolvate (5-AtP) from UHPA

5-At (5.09 mg, 0.0598 mmol) was placed in a 4 mL vial and dissolved with 2 mL UHPA. This solution was slowly (16h) evaporated to dryness under an N₂ stream. The obtained solid was a physical mixture which contained 5-AtP.

5-aminotetrazole peroxosolvate (5-AtP) from 98% H₂O₂

5-At (85.7 mg, 1.01 mmol) was placed in a 4 mL vial and dissolved with 2 mL 98% H_2O_2 . This solution was slowly (24h) concentrated under an N_2 stream. An aqueous solution of NaTS (2.31 g, 9.31 mmol, 25 mL H_2O) was then loaded into the reservoir of a 125 mL filter flask. The 5-AtP crystals were collected from the residual 98% H_2O_2 solution via vacuum filtration through a disposable polytetrafluoroethylene filter into the neutralizing NaTS solution followed by rinsing with hexanes (3 × 3 mL). The crystallization vial, with residual material, was quenched in the NaTS solution. Yield after air drying (0.25h): 62.5 mg, 0.525 mmol, 52%.

DAF-DNP-H2O2 (DDP) from UHPA

DAF (10.0 mg, 0.100 mmol) and DNP (15.8 mg, 0.100 mmol) were placed in a 20 mL vial and dissolved with 10 mL UHPA. This solution was slowly (48h) evaporated to dryness under an N_2 stream providing a physical mixture containing DDP.

DAF-DNP-H₂O₂ (DDP) from 98% H₂O₂

DAF (10.0 mg, 0.100 mmol) and DNP (15.8 mg, 0.100 mmol) were placed in a 4 mL vial and dissolved with 1.1 mL 98% H_2O_2 . This solution was slowly (48h) evaporated to dryness under an N_2 stream. yield: 28.7 mg, 0.0983 mmol, 98%.

DAF-DNP-H₂O (DDH)

DAF (9.99 mg, 0.100 mmol) and DNP (15.8 mg, 0.100 mmol) were placed in a 4 mL vial and dissolved with 0.1 mL H_2O with gentle heating. This solution was slowly (16h) evaporated to dryness under an air stream. yield: 27.7 mg, 0.100 mmol, 100%.

Characterization

Single-Crystal X-Ray Structure Determination

Single-crystal X-ray diffraction data were collected using a Rigaku XtaLAB Synergy-S X-ray diffractometer in a kappa goniometer geometry configuration. The X-ray source is a PhotonJet-S microfocus Cu source ($\lambda = 1.54187$ Å) operated at 50 kV and 1 mA. X-ray intensities were measured with a HyPix-6000HE detector held 34.00 mm from the sample. The data were processed using CrysAlisPro v38.46 (Rigaku Oxford Diffraction) and were corrected for absorption. The structures were determined using OLEX2^[1] as well as SHELXT^[2] and refined with SHELXL.^[3] All non-hydrogen atoms were refined anisotropically with hydrogen atoms placed at idealized positions.

Powder X-Ray Diffraction

All powder pattern data were collected using a Panalytical Empyrean system utilizing Cu-K α radiation (λ = 1.54187 Å) and operating at 45 kV and 40 mA. The system uses a Bragg-Brentano HD X-ray optic and an X'Celerator Scientific detector operating in a continuous 1D scan mode. Scans were conducted according to the following parameters: 2 θ = 3° to 50°, step size = 0.008°, and step speed = 19.7 seconds. The data were worked up using OriginPro 2017.

Raman Spectroscopy

Raman spectra were collected using a Renishaw inVia Raman Microscope equipped with a Leica microscope in the following configuration: a 633nm laser, 1800 lines/mm gratings, 50 μ m slit size, and a Renishaw Centrus detector. Spectra were collected in extended scan mode with a range of 1750 - 400 cm⁻¹. All spectra were analyzed using the WiRE 5.3 software package (Renishaw). Calibration was performed using a silicon standard in static mode.

Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) thermograms were recorded on a TA Instruments Q10 DSC. All experiments were carried out at a heating rate of 5 °C/min, covering a minimum temperature range of 30 °C to 350 °C. Samples were analyzed in Tzero[™] hermetic aluminum DSC pans. The instrument was calibrated using an indium standard and all DSC thermograms were analyzed using TA Universal Analysis 2000, V4.5A, build 4.5.0.5.

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) thermograms for each sample were recorded on a TA Instruments Q50 TGA. All experiments were conducted on platinum TGA sample pans under a nitrogen purge of 50 mL/min with a heating rate of 5 °C/min, covering a minimum temperature range of 30 °C to 350 °C. The instrument was calibrated using the Curie points of alumel and nickel standards and all TGA thermograms were analyzed using TA Universal Analysis 2000, V4.5A, build 4.5.0.5.

Sensitivity to mechanical stimuli

Impact sensitivities were determined using an in-house apparatus ^[4] whereby a 2.380 Kg stainless-steel impactor impinges samples of 2 mg \pm 10% inside aluminum DSC pans resting on an anvil from varying heights. 20 samples of each material were tested with D_{h50} measured as the dropping height at which there was a 50% probability of detonation.

SI 2. Crystallographic Data

Table 1. Room temp. and 100 K crystal structure data

	DDP	DDH	5-AtP
Stoichiometry	1:1:1	1:1:1	1:1
Space Group	C2	P212121	Pmna
Temperature (K)	293(2)	293(2)	293(2)
a (Å)	25.6236(2)	5.36177(4)	9.9196 (2)
b (Å)	5.46400(10)	8.07141(5)	6.44705(16)
c (Å)	8.13850(10)	25.18846(16)	8.1105(2)
α (°)	90	90	90
β (°)	96.7550(10)	90	90
γ (°)	90	90	90
Volume (ų)	1131.54(3)	1090.081(13)	518.68(2)
$ ho_{ m calc}$ (g cm ⁻³)	1.715	1.683	1.525
R_1/wR_2	2.44/6.17	3.15/9.04	3.41/10.05
GOF	1.083	1.079	1.115
Deposition number	2157430	2157431	2157429

SI 3. Thermal ellipsoid plots



Figure S1. Thermal ellipsoid plot of DDP at 293(2) K



Figure S2. Thermal ellipsoid plot of DDH at 293(2) K



Figure S3. Thermal ellipsoid plot of 5-AtP at 293(2) K



Figure S4. Raman spectra of MQNO:H₂O₂ synthesized using the UHPA method (MQNO:H₂O₂/urea:H₂O₂), the reported MQNO:H₂O₂ Raman spectrum,^[5] 3PNO:H₂O₂ synthesized using the UHPA method (3PNO:H₂O₂/urea:H₂O₂), the reported 3PNO:H₂O₂ Raman spectrum,^[5] and urea hydrogen peroxide.

SI 4. Raman Spectra



Figure S5. Raman spectra of 5-At, 5-AtH, 5-AtP, 5-AtP synthesized using the UHPA method, and urea hydrogen peroxide.



Figure S6. Raman spectra of DAF, DNP, DDH, DDP, DDP synthesized using the UHPA method, and urea hydrogen peroxide.





Figure S7. PXRD data for the 5-At solvate/hydrate system. Experimental diffractogram provided for 5-AtP, powder patterns predicted using the room temp. single crystal structures for 5-AtH, 5-At, 5-AtP, and urea:H₂O₂.



Figure S7. PXRD data the DAF-DNP solvate/hydrate system. Experimental diffractograms provided for DNP and DPP, powder patterns predicted using the room temp. single crystal structures for DPP, DAF, DDH, and urea:H₂O₂.

SI 6. Thermal analysis of the 5-At and DAF-DNP hydrate/solvate systems



Figure S8. TGA traces and DSC thermograms, A) and B) respectively, for 5-At (black), 5-AtH (red), and 5-AtP (blue), as well as TGA traces and DSC thermograms, C) and D) respectively, for DAF (orange), DNP (black), DDH (red), and DDP (blue).

SI 7. Performance calculations and impact sensitivity

Cheetah 7.0 calculations were performed using the Sandia JCZS product library revision 32. The heat of formation and density for DNP were taken from the literature.^[6]

With regard to impact sensitivity, the d_{h50} for DDH was determined to be 116 cm while 5-AtH did not detonate at the limit of our apparatus. The d_{h50} values for DDP and 5-AtP are 38 cm and 14 cm, respectively.

SI 8. CSD Search

Search conducted using ConQuest^[7] version 5.42, on March 3, 2022. The search was conducted with the following requirements:

Must include: $H_O^{O_H}$, as drawn.

Only single crystal structures.

Only organics.

This search provided 125 hits meeting these criteria which were then individually inspected to ensure the criteria were met. Some instances of protonated water cluster containing structures (PANZEK, PANZIO, SOXVUX) were identified and excluded from further analysis. Of the remaining "hits" one entry (ROLPAJ) was excluded from analysis as access to the publication was unavailable. An additional four structures (OJOCOH, UDUWEX, UDUWIB, VAYGUY) were excluded from analysis as they were deposited as "private communications" without experimental details available. Each publication related to the remaining crystallographic data were then inspected to identify the synthesis conditions employed. In no instance was urea: H_2O_2 (or that by any other name) employed. The figure below details the full (125 hit) data set providing CSD reference code and publication year.

NAME	Publication Year		NAME	Publication Year	NAME	Publication Year		NAME	Publication Year	NAME	Publication Year
QAGXAB	2020	l	EKULUR	2002	LIOXPH	1969	1	TANCES	2011	WINSA001	2017
RUXLAA	2020		FURFIH	1987	MAQRIH	2012		TANCIW	2011	WUTKUT	2003
AMOXPH10	1972		GADOXP10	1976	MEXTIU	2013		TANCOC	2011	WUTKUT01	2003
ANIMUH	2013		GUDPYQ	1978	MEXTIU01	2013		TANCUI	2011	WUTKUT02	2003
ANINAO	2013		GUPMEL	1979	MUXHIX	2010		TANDAP	2011	WUTKUT03	2003
ANINES	2013		GUPYML	1978	NAOXAP	1964		TANDET	2011	WUTKUT04	2003
AZAMIZ	2016		HMTOXH	1978	NAOXAP01	1984		TOYTEJ	2019	WUTKUT05	2003
AZAMIZ01	2016		HOJCAN	2019	NAOXAP11	1989		TPPOPH	1980	WUTKUT06	2003
BAFGOH	2015		HOQRUD	2019	OHIJEX	2020		TUBNUC	2018	WUTKUT07	2003
BAFJUQ	2015		HOQSAK	2019	ОЈОСОН	2016		TUBPOY	2018	WUTKUT08	1977
BAMXAR	2014		HOQSEO	2019	PANZEK	2002		TUPLUO	2020	WUTLEE	2003
BOHLOC	2018		HOQSIS	2019	PANZIO	2002		TUYJOP	2020	WUXSIT	2012
BONGES	2014		JELQOJ	2017	POMQEQ	2019		UDUROD	2018	WUXSOZ	2012
BONGIW	2014		JESXEN	2018	POMQIU	2019		UDUWEX	2009	XETSUK	2001
CAZHAN	2005		JOZZED	1992	POMQOA	2019		UDUWIB	2009	YAFFUJ	2017
CAZHAN01	2005		KELXAD	2017	POMQUG	2019		UKEFEV	2003	YAFGEU	2017
CAZHAN02	2005		KELXEH	2017	POMRAN	2019		UREXPO	1941	YECTOP	1994
CAZHER	2005		KOXPHY01	1984	QOHXUH	2008		UREXPO01	1980	YUHTAW	1995
CAZHIV	2005		KOXPHY10	1967	QUYRUA	2020		UREXPO11	1981	ZUWCIG	2020
CAZHOB	2005		KOXPHY11	1990	RBOXPH10	1967		VANVOX	2012	ZUWCIG01	2020
CAZHUH	2005		KULMOU	2009	RIKJAW	1994		VAYGUY	2003	AVUDAZ	2021
CAZJAP	2005		KULMOU01	2011	ROLPAJ	1996		VAYGUY01	2006	AYAQEZ	2021
DATHIQ	2005		KULMUA	2009	SEMXIU	2017		VILFUU	2018	AYAQID	2021
DOJMIZ	2008		KULMUA01	2011	SOXVUX	2009		VILGAB	2018	IPAFUD	2021
DOSPOT	2016		KUMRER	2015	TANCAO	2011		WINSAO	2007	TANCIW01	2021

Figure S9. The data set resulting from the CSD search as implemented in the description above. Note that this data set includes structures which were not included in the analysis; excluded structures and explanations for their exclusion are provided above.

SI 9. Structural Similarity Calculations

Mercury software^[8] was used to perform structural similarity calculations using the "packing similarity" option within the "search" option found in the drop-down tab under "CSD materials". After selecting the DDH and DDP crystal information files for the comparison, the following restrictions were applied:

- size of molecular cluster set to "15"
- distance tolerance "20%"
- angle tolerance "50°"
- allow molecular differences was selected
- ignore hydrogen positions was selected
- ignore bond types was selected
- allow structure inversion was selected
- show only the highest similarity result was selected

The result was a 96% similarity.

The comparison was done in the same way for the 5-AtH/5-AtP system and that resulted in a 77% similarity.

SI 10. Density changes in isostructural peroxosolvate/hydrate systems

Peroxosolvate ref. code	d(g/cm³)	Temp. (<i>K</i>)	Hydrate ref. code	d(g/cm³)	Temp. (<i>K</i>)	$\Delta d(g/cm^3)$		tetrahedron vol. (Å ³)
AMOXPH10	1.537	RT	AMOXAL03	1.501	RT	0.036	2.398	5.915
KULMOU	1.571	150	LSERMH21	1.512	12*	0.059	3.902	8.298
MEXTIU	1.326	100	KICCOO03	1.279	RT	0.047	3.674	8.390
WINSAO	1.542	120	THYMMH	1.486	RT	0.056	3.768	NA
TPPOPH	1.287	RT	JEDTOB	1.253	RT	0.034	2.713	7.336
CAZHAN	1.325	120	VADVEC01	1.264	173	0.061	4.825	10.159
CAZHOB	1.431	120	WEYMIV	**	* *	**	* *	**
CAZJAP	1.437	120	SATSEL01	1.288	100	0.149	11.56	10.902
CAZHER	1.431	120	VAXFAB	1.359	RT	0.072	5.298	10.747
CAZHIV	1.399	120	VAXFAB	1.359	RT	0.040	2.943	10.747

Table S1. Crystallographic density data from reported isostructural peroxosolvate/hydrate systems.^[9]

*LSERMH21 was deposited with the CSD as a private communication, this is the reported collection temp. and the details cannot be verified.

**WEYMIV, though included as an isomorphous structure in the original report,^[9] is no longer accessible.

The isostructural pair UDUWIB/TANCIW were also included in the original report^[9] but were excluded here as both structures contain peroxide.

The crystallographic densities for the isostructural peroxosolvate/hydrate systems reported in reference 9*** were tabulated and compared. The limited number of systems collected at the same temperature preclude definitive conclusions. Qualitatively, however, peroxosolvate formation appears to improve the density of a material (relative to the hydrate); it should be noted that this statement is valid even in instances where the peroxosolvate structure was determined at a higher temperature than the hydrate structure. The average density increase from peroxosolvate formation is 4.56%. The density increase associated with the 5-AtH/5-AtP system is 3.50% and the DDH/DDP system is 1.90%.

The tetrahedral volume for each hydrate structure was calculated using the online calculator available at: <u>https://keisan.casio.com/exec/system/1329962711</u> accessed on 5/26/2022, using measurements taken from the cifs. For THYMMH the arrangement around the water molecules is not tetrahedral thus precluding this analysis. The average tetrahedral volume is 9.062 Å³. ***In ref. [9], these materials are referred to as isomorphous rather than isostructural.

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