Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

The Novel Strategies about Synthesizing Energetic Materials Based BTO with Satisfactory Performances

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Experimental Section

Safety Precautions! Although we experienced no difficulties in the synthesis and characterization of these materials, small-scale syntheses are strongly encouraged. All of the compounds should be handled with extreme care, and eye protection and gloves must be worn at all times.

General Methods. Chemical reagents and solvents were purchased from Aladdin (Shanghai, China) and used as supplied without further purification. ^{1}H NMR and ^{13}C NMR spectra were obtained using a JEOL GSX 600 MHz nuclear magnetic resonance (NMR) spectrometer in a DMSO solution by using tetramethylsilane as an internal standard. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet-5700 FTIR spectrometer by using pressed KBr pellets to evaluate the chemical bonding of the samples from 4000 cm^{-1} to 400 cm^{-1}. Elemental analyses (C, H, and N) were conducted using a Vario EL CUBE device. DSC was performed by a Q200 DSC instrument (TA Instruments, United States) at a heating rate of 10 ^{o}C min^{-1} in flowing high-purity nitrogen. TGA was performed with an SDT Q600 TGA instrument (TA Instruments, United States) at a heating rate of 10 ^{o}C min^{-1} in flowing high-purity nitrogen.

X-ray Crystallography.

The single crystals of **2-** were cultured via a slow solvent evaporation method. Data were collected using a three-circle Bruker platform diffractometer equipped with a SMART APEX II CCD detector. All calculations were performed using the Crystal Structure crystallographic software package except for refinement, which was performed using SHELXL2. [1] Hydrogen atoms were added theoretically and refined with riding model position parameters and fixed isotropic thermal parameters. The details of the data collection and refinement are presented in Table S1.

Synthesis of 1*H*,1′*H*-5,5′-bistetrazole-1,1′-diolate Dihydrate: 1*H*,1′*H*-5,5′-bistetrazole-1,1′-diolate dihydrate was synthesized according to a procedure reported in the literature.

3-amino-1,2,4-triazolium 1*H*,1′*H*-5,5′-bistetrazole-1,1′-diolate (2): 1*H*,1′*H*-5,5′-bistetrazole-1,1′-diolate dihydrate (206 mg, 1 mmol) was dissolved in a few milliliters of distilled water, and previously added 3-amino-1,2,4-triazole (84.1 mg, 1 mmol). The mixture was heated and filtered. After cooling to room temperature, **2** crystallized as colorless blocks to yield 190.6 mg (0.75 mmol, 75%). DSC (10 ^{o}C min^{-1}): 261 ^{o}C (dec). IR (KBr) ν/cm^{-1}: 3456, 3319, 3170, 1688, 1568, 1427, 1312, 1262, 954, 863, 769, 714, 496. ^{1}H NMR (600 MHz, [D6] DMSO, 25 ^{o}C) δ/ppm: 8.24. ^{13}C NMR (150 MHz, [D6] DMSO, 25 ^{o}C) δ/ppm: 151.89, 140.50, 135.61. Elemental analysis (%) calcd for $C_4H_6N_{12}O_2$ (254.21): C 18.90, H 2.38, N 66.13; found: C 18.68, H 2.56, N 66.45. BAM drop hammer: >20 J; friction tester: 252 N.

Aminoguanidinium 1*H*,1′*H*-5,5′-bistetrazole-1,1′-diolate (3): 1*H*,1′*H*-5,5′-bistetrazole-1,1′-diolate dihydrate (206 mg, 1 mmol) was dissolved in a few milliliters of distilled water, and previously added aminoguanidine hemisulfate (123.13 mg, 1 mmol). The mixture was heated and filtered. After cooling to room temperature, 2 crystallized as colorless blocks to yield 190.6 mg (0.75 mmol, 75%). DSC (10 °C min^{-1}): 246 °C (dec). IR (KBr) ν/cm^{-1}: 3435, 3357, 2973, 2916, 1672, 1635, 1477, 1375, 1290, 1090, 993, 762, 712, 625, 512, 444. ^{1}H NMR (600 MHz, [D6] DMSO, 25 °C) δ/ppm: 8.24. ^{13}C NMR (150 MHz, [D6] DMSO, 25 °C) δ/ppm: 151.89, 140.50, 135.61. Elemental analysis (%) calcd for $C_3H_8N_{12}O_2$ (244.21): C 14.75, H 3.31, N 68.84; found: C 14.96, H 3.01, N 68.35. BAM drop hammer: >20 J; friction tester: 324 N.

Diammonium 1*H*,1′*H*-5,5′-bistetrazole-1,1′-diolate (4): 1*H*,1′*H*-5,5′-bistetrazole-1,1′-diolate dihydrate (206 mg, 1 mmol) was dissolved in a few milliliters of water, and diammone 61μL, 1 mmol) was added. After boiling and stirring the mixture for a few minutes, **6** precipitated as thin, colorless plates upon cooling the solution to room temperature, yield 172.1 mg (0.63mmol, 63%). DSC (10 °C min^{-1}): 241 °C (dec). IR (KBr) ν/cm^{-1}:3435, 2974, 2897, 1622, 1504, 1425, 1412, 1350, 1232, 1174, 1117, 1047, 1043, 999, 881, 733, 714, 677, 586, 499. ^{1}H NMR (600 MHz, [D6] DMSO, 25 °C) δ/ppm: 9.54. ^{13}C NMR (150 MHz, [D6] DMSO, 25 °C) δ/ppm: 144.48, 135.65. Elemental analysis (%) calcd for $C_2H_6N_{10}O_2$ (202.17): C 11.88, H 3.00, N 69.30; found: C 12.10, H 2.79, N 69.68. BAM drop hammer: 15.5 J; friction tester: 144 N.

Co-crystal of 4-amino-pyrazole and 1*H*,1′*H*-5,5′-bistetrazole-1,1′-diolate (5): 1*H*,1′*H*-5,5′-bistetrazole-1,1′-diolate dihydrate (206 mg, 1 mmol) and 4-amino-pyrazole (84.08 mg, 1 mmol) were added in a few milliliters of water, and apace dissolved. The mixture was briefly heated to reflux and filtered. After cooling to room temperature, **4** crystallized as colorless needles, yield 204.3 mg (0.81 mmol, 81%). DSC (10 °C min^{-1}): 212 °C (dec). IR (KBr) ν/cm^{-1}: 3417, 3300, 3149, 1662, 1504, 1477, 1410, 1350, 1329, 1286, 1126, 1039, 997,939, 889, 815, 754, 592, 512. ^{1}H NMR (600 MHz, [D6] DMSO, 25 °C) δ/ppm: 8.55. ^{13}C NMR (150 MHz, [D6] DMSO, 25 °C) δ/ppm: 135.76, 132.81. Elemental analysis (%) calcd for $C_5H_6N_{11}O_2$ (252.21): C 23.81, H 2.40, N 61.10; found: C 24.02, H 2.61, N 60.73. BAM drop hammer: >20 J; friction tester: 216 N.

Co-crystal of 2-methylimidazolium 1*H*,1′*H*-5,5′-bistetrazole-1,1′-diolate and 1*H*,1′*H*-5,5′-bistetrazole-1,1′-diolate (6·2H_2O): 2-methylimidazole (82.10 mg, 1 mmol) and 1*H*,1′*H*-5,5′-bistetrazole-1,1′-diolate dihydrate (206 mg, 1 mmol) were added in a few milliliters of water, and apace dissolved. The mixture was briefly heated to reflux and filtered. After cooling to room temperature, **6·2H$_2$O** crystallized as colorless needles, yield 204.3 mg (0.81 mmol, 81%). DSC (10 °C min^{-1}): 266 °C (dec). IR (KBr) ν/cm^{-1}: 3429, 3008, 2925, 1622, 1423, 1390, 1375, 1311, 1290, 1250, 1124, 1086, 1047, 989, 924, 881, 784, 714, 656, 517, 457. ^{1}H NMR (600 MHz, [D6] DMSO, 25 °C) δ/ppm: 7.47, 4.36. ^{13}C NMR (150 MHz, [D6] DMSO, 25 °C) δ/ppm: 144.56, 135.55, 119.22, 11.66. Elemental analysis (%) calcd for $C_{12}H_{20}N_{20}O_6$ (540.48): C 26.67, H 3.74, N 51.84; found: C

26.25, H 3.98, N 51.39. BAM drop hammer: 19 J; friction tester: 120 N.

Co-crystal of imidazolium 1*H*,1′*H*-5,5′-bistetrazole-1,1′-diolate and 1*H*,1′*H*-5,5′-bistetrazole-1,1′-diolate (7): 1*H*,1′*H*-5,5′-bistetrazole-1,1′-diolate dihydrate (206 mg, 1 mmol) was dissolved in a few milliliters of water, and imidazole (81.4 mg, 1 mmol) was added. After boiling and stirring the mixture for a few minutes, **7** precipitated and as thin, colorless plates upon cooling the solution to room temperature, yield 172.1 mg (0.63mmol, 63%).DSC (10 ^{o}C min^{-1}): 256/273 ^{o}C (dec). IR (KBr) ν/cm^{-1}: 3433, 2976, 2920, 1635, 1433, 1375, 1311, 1284, 1165, 1083, 1051, 881, 621. ^{1}H NMR (600 MHz, [D6] DMSO, 25 ^{o}C) δ/ppm: 8.57. ^{13}C NMR (150 MHz, [D6] DMSO, 25 ^{o}C) δ/ppm: 144.48, 135.65. Elemental analysis (%) calcd for $C_{10}H_{12}N_{20}O_4$ (476.40): C 25.21, H 2.54, N 58.82; found: C 25.55, H 2.98, N 58.16. BAM drop hammer: 15 J; friction tester: 168N.

Table S1. Crystal data and structure refinement parameters of **2-7**

Compound	**2**	**3**	**4**	**5**	**6·2H$_2$O**	**7**
Empirical formula	$C_4H_6N_{12}O_2$	$C_3H_8N_{12}O_2$	$C_2H_6N_{10}O_2$	$C_5H_6N_{11}O_2$	$C_{12}H_{20}N_{20}O_6$	$C_{10}H_{12}N_{20}O_4$
Formula weight	254.21	244.21	202.17	252.21	540.48	476.40
CCDC number	1840941	1879814	1878638	1872564	1840856	1850642
Crystal size/mm^3	0.19×0.18×0.17	0.17×0.16×0.15	0.16×0.14×0.12	0.28×0.18×0.12	0.19×0.18×0.17	0.19×0.18×0.17
Crystal system	Monoclinic	Monoclinic	triclinic	Monoclinic	Triclinic	Triclinic
Space group	$P\ 2_1/\ C$	$P\ 2_1/\ m$	$P\ \bar{1}$	$C2/\ c$	$P\ \bar{1}$	$P\ \bar{1}$
a [Å]	3.79910(10)	7.3674(7)	4.7590(13)	7.4215(5)	3.7719(4)	7.2291(7)
b [Å]	12.3968(4)	6.5154(6)	5.9153(15)	9.2025(6)	10.4109(10)	9.8660(9)
c [Å]	19.5608(6)	20.4844(18)	6.7057(18)	13.7986(9)	14.7027(19)	13.8595(12)
α [Å]	90	90	98.682(8)	90	105.675(10)	89.590(7)
β [Å]	90.308(3)	98.532(2)	90.720(8)	98.745(2)	95.669(9)	82.374(7)
γ [Å]	90	90	109.044(7)	90	98.072(8)	68.567(8)
V [Å^3]	921.24(5)	972.40(15)	176.01(8)	931.44(11)	544.69(11)	911.08(15)
Z	4	4	1	4	1	2
T [K]	150	293	293	298	150	150
ρ [g cm^{-3}]	1.833	1.668	1.907	1.799	1.648	1.737
Mu [mm^{-1}]	1.323	0.140	0.163	0.147	1.171	1.226

F (000)	520.0	504.0	104.0	516	280.0	488.0
Index range	$-3 \le h \le 4$ $-14 \le k \le 14$ $-23 \le l \le 23$	$-8 \le h \le 8$ $-7 \le k \le 7$ $-24 \le l \le 24$	$-5 \le h \le 5$ $-7 \le k \le 7$ $-7 \le l \le 7$	$-9 \le h \le 9$ $-11 \le k \le 11$ $-17 \le l \le 17$	$-4 \le h \le 4$ $-12 \le k \le 12$ $-15 \le l \le 17$	$-8 \le h \le 8$ $-10 \le k \le 11$ $-14 \le l \le 16$
Reflections collected	2899	9274	2990	8078	2586	4783
$R_{int.}$	0.0307	0.0485	0.0207	0.0168	0.0637	0.0539
Data/Restraints/Parameters	1608/0/164	1715/3/166	608/0/66	1066/1/84	1862/114/172	3126/0/308
GOF on F^2	1.060	1.095	1.175	1.123	1.055	1.154
R_1 [$I > 2\sigma$ (I)]	0.0451	0.0503	0.0256	0.0609	0.1073	0.1475
wR_2 [$I > 2\sigma$ (I)]	0.1197	0.1102	0.0700	0.1995	0.2296	0.3383
R_1 (all data)	0.0487	0.0868	0.0259	0.0623	0.1324	0.1536
wR_2 (all data)	0.1258	0.1233	0.0703	0.2009	0.2572	0.3408
Largest diff. peak and hole [e Å^{-3}]	0.28/-0.29	0.22/-0.31	0.24/-0.16	0.883/-0.576	0.66/-0.77	0.71/-0.74

Table S2. Selected bond lengths [Å] of **2-5**

Atoms 1–2	**d (1–2) [Å]**	**d (1–2) [Å]**	**d (1–2) [Å]**	**d (1–2) [Å]**
	2	**3**	**4**	**5**
O1–N1	1.327(2)			1.327(2)
N1–N2	1.332(2)		1.344(15)	1.339(3)
N1–C1	1.344(2)	1.318(3)	1.326 (16)	1.339(3)
N2–N3	1.317(2)	1.308(3)	1.306 (16)	1.302(3)
N3–N4	1.346(2)	1.327(3)	1.336(15)	1.345(3)
N4–C1	1.328(2)	1.338(3)	1.343(16)	1.328(3)
N5–N6	1.331(2)	1.330(3)		
N5–C2	1.344(2)	1.328(3)		1.312(4)
N6–N7	1.303(2)	1.307(3)		
N7–N8	1.358(2)	1.330(3)		
N8–C2	1.326(2)	1.335(3)		
C1–C2	1.437(3)	1.448(3)		
N9–C3	1.367(2)	1.317(3)		
N10–C3	1.291(2)	1.309(3)		
N11–C4	1.328(2)			
N12–C4	1.327(2)			
O1–N4		1.332(2)	1.320(13)	
O2–N8		1.325(2)		
N1–C2		1.343(3)		
N11 –N12		1.392(3)		
N11 –C3		1.320(3)		
N5–N5^{i}			1.437(2)	
C1–C1^{ii}			1.443(2)	1.440(4)

Symmetry transformations used to generate equivalent atoms:

i -x+2, -y+1, -z+1 ii -x+1, y, -z+3/2

Table S3. Selected bond angles [°] of 2-5

Atoms 1–2–3	**∢ (1–2–3) [°]**	**∢ (1–2–3) [°]**	**∢ (1–2–3) [°]**	**∢ (1–2–3) [°]**
	2	**3**	**4**	**5**
O1–N1–N2	122.5(15)	106.2(19)		123.3 (18)
O1–N1–C1	128.5(16)			127.5(18)
N2–N1–C1	109.0(16)		105.5(10)	109.2 (18)
N3–N2– N1	105.9(15)	111.0(19)	111.5(10)	105.9(18)
N2– N3–N4	111.1(15)	105.5(19)	105.8(10)	111.1(18)
N3–N4–C1	105.6(16)	109.7(2)	108.8(10)	106.1(17)
N6–N5–C2	109.7(15)	105.7(18)		
N7–N6–N5	106.2(15)	111.6(18)		
N6–N7–N8	110.6(15)	105.7(19)		
N1–C1–C2	124.3(17)	127.8(2)		
N4–C1–N1	108.4(17)	107.6(2)	108.4(11)	107.7(18)
N5–C2–C1	126.0(17)	127.5(2)		
N8–C2–C1	126.7(17)	124.3(2)		
N10–C3–N9	112.0(17)	121.4(2)		
O1–N4–N3	122.9(4)	123.7(19)	121.1(9)	
N7–N8–O2	122.8(4)	122.9(18)		
C3–N11–N12		119.0(2)		
N4–C2–C1		124.6(2)		
N1–C1–C1^{i}				124.2(2)
N4–C1–C1^{i}				128.1(2)
N6^{ii}–N6–C3				108.0(12)
C3^{ii}–C2–C3				104.4(3)
N5–C2–C3^{ii}				127.8 (13)
O1–N4–C1		126.6(2)	130.0(10)	
N4–C1–C1^{iii}			124.1(14)	
N1–C1–C1^{iii}			127.5(13)	

Symmetry transformations used to generate equivalent atoms:

i -x+2, -y+1, -z+1   ii -x+1, y, -z+3/2   iii -x, 1-y, 1-z

Table S4. Selected hydrogen bond angles [°] of 2-5

Atoms A···H–D*	**d(A···H) [Å]**		**Atoms A···H–D***	**d(A···H) [Å]**	
2			**3**		
O1···H2–O2	1.508	-x+1, y-1/2, -z+3/2	O2···H1–O1	1.548	x+1, y, z
N1···H2–O2	2.293	-x+1, y-1/2, -z+3/2	N7···H1–O1	2.628	x+1, y, z
N2···H2–O2	2.524	-x+1, y-1/2, -z+3/2	N8···H1–O1	2.365	x+1, y, z
N3···H11–N12	2.124	x+1, -y+3/2, z-1/2	N2···H9A–N9	2.218	3-x/2, y+1/2, 1-z/2
N3···H12A–N12	2.637	x+1, -y+3/2, z-1/2	O2···H9B–N9	2.505	x+1/2, -y+3/2, z+1/2
N10···H11–N11	2.455	-x+3, -y+2, -z+1	N1···H9B–N9	2.532	x+1/2, -y+3/2, z+1/2
N6···H12B–N12	2.598	-x+1, y-1/2, -z+3/2	N6···H10A–N10	2.206	
			O2···H11–N11	2.320	x+1/2, -y+3/2, z+1/2
			N7···H12A–N12	2.523	-x+1, -y+1, -z+1
			N1···H12B–N12	2.465	x+1/2, -y+1/2, z+1/2
4			**5**		
N2···H5A–N5	2.053	x, y, z-1	N3···H1–O1	2.621	-x+3/2, y-1/2, -z+1
N3···H5A–N5	2.657	-x+1, -y, -z	N5···H1–O1	2.614	-x+1, -y+1, -z+1
O1···H5B–N5	1.875	x+1, y, z	N3···H5A–N5	2.359	x-1/2, y+1/2, z
O1···H5C–N5			N3···H5B–N5	2.359	3-x/2, y+1/2, 3-z/2
N3···H5C–N5					

Table S5. Selected bond lengths [Å] of **6·2H_2O-7**

Atoms 1–2	**d (1–2) [Å]**	**d (1–2) [Å]**	**Atoms 1–2**	**d (1–2) [Å]**	**d (1–2) [Å]**
	6·2H_2O	**7**		**6·2H_2O**	**7**
O1–N3	1.347(7)		N6–C5	1.344(8)	
O2–N7	1.331(7)		N7–N8	1.333(8)	1.327(6)
N1–C2	1.343(8)		N7–C6	1.348(8)	
N1–N4	1.377(9)		N8–N9	1.327(8)	
N2–C2	1.342(8)		N9–N10	1.342(7)	1.322(7)
N2–C3	1.371(9)		N10–C6	1.337(8)	
N3–C5	1.329(8)		C1–C2	1.472(10)	
N3–N4	1.337(7)	1.366(7)	C3–C4	1.346(9)	
N4–N5	1.324(8)		C5–C5^i	1.439(12)	
N5–N6	1.337(8)	1.365(7)	C6–C6^i	1.438(12)	
O1–N1		1.338(6)	N13–N14		1.333(7)
O2–N8		1.331(6)	N13–C9		1.364(7)
N1–N2		1.325(6)	N14–N15		1.315(7)
N1–C4		1.346(7)	N15–N16		1.340(7)
N2–N3		1.298(7)	N16–C9		1.333(8)
N4–C4		1.311(7)	C9–C10		1.409(8)
N9–C10		1.366(7)	N19–C3		1.345(8)
N10–N11		1.323(8)	N20–C1		1.332(8)
N11–N12		1.343(7)	N20–C2		1.375(8)
N12–C10		1.339(8)	C2–C3		1.325(8)

Symmetry transformations used to generate equivalent atoms:

i -x, -y, 2-z   ii 2-x, -y, 1-z

Table S6. Selected bond angles [°] of $6\cdot 2H_2O$-7

Atoms 1–2–3	∢ (1–2–3) [°]	∢ (1–2–3) [°]	Atoms 1–2–3	∢ (1–2–3) [°]	∢ (1–2–3) [°]
	$6\cdot 2H_2O$	**7**		**$6\cdot 2H_2O$**	**7**
C2–N1–C4	121.8(5)		N8–N9–N10	111.1(5)	
C2–N2–C3	109.7(6)		N2–C2–N1	106.6(6)	
C5–N3–N4	109.5(5)		N2–C2–C1	126.8(6)	
C5–N3–O1	110.5(5)		N1–C2–C1	126.6(6)	
N4–N3–O1	128.2(5)		C4–C3–N2	107.6(6)	
N5–N4–N3	121.3(5)		C3–C4–N1	106.6(6)	
N4–N5–N6	105.2(5)		N3–C5–C5^{i}	126.5(7)	
N5–N6–C5	110.7(5)		N6–C5–C5^{i}	126.6(7)	
O2–N7–N8	106.6(5)		N10–C6–C6^{ii}	128.5(7)	
N9–N8–N7	105.3(5)		N7–C6–C6^{ii}	124.2(7)	
O1–N1–C4		128.4(4)	O4–N13–N14		123.0(4)
N3–N2–N1		107.0(5)	N15–N14–N13		106.1(5)
N2–N3–N4		109.6(4)	N14–N15–N16		110.8(5)
N7–N6–N5		128.4(4)	C9–N16–N15		107.2(5)
N6–N7–N8		107.0(5)	N12–C10–C9		128.8(5)
N7–N8–O2		109.6(4)	C8–N17–C7		110.0(5)
N8–C5–C4		125.5(5)	C6–C7–N17		106.7(5)
O3–N9–C10		127.1(5)	N19–C1–N20		107.2(5)
N9–N10–N11		106.1(5)	C3–C2–N20		107.1(5)
N10–N11–N12		110.9(5)	C2–C3–N19		107.6(5)

Symmetry transformations used to generate equivalent atoms:

i -x, -y, 2-z **ii 2-x, -y, 1-z**

Table S7. Selected hydrogen bond angles [°] of 6·2H$_2$O-7

Atoms A···H–D*	**d(A···H) [Å]**		**Atoms A···H–D***	**d(A···H) [Å]**	
6·2H$_2$O			**7**		
O1···H1WA–O1W	1.793		N3···H1WB–O1W	2.591	
N3···H1WB–O1W	2.591		O1···H1WA–O1W	1.793	
N4···H1WB–O1W	2.208		N4···H1WB–O1W	2.208	
O1W···H2A–O2	2.208	x+1, y, z	O1W···H2A–O2	2.208	x+1, y, z
N10···H2A–O2	2.318	-x, -y, -z+1	N10···H2A–O2	2.318	-x, -y, -z+1
O2···H1–N1	1.860	x-1, y, z	O2···H1–N1	1.860	x-1, y, z
N7···H1–N1	2.592	x-1, y, z	N7···H1–N1	2.592	x-1, y, z
O1···H2–N2	2.622	x, y+1, z	O1···H2–N2	2.622	x, y+1, z
N6···H2–N2	2.026	-x+1, -y+1, -z+2	N6···H2–N2	2.026	-x+1, -y+1, -z+2

Heats of formation

Calculations were performed with the Gaussian 09 suite of programs.[2,3] The geometric optimization of the structures based on single-crystal structures, where available, and frequency analyses were carried out using the B3LYP functional with 6–31+G** basis set, and single energy points were calculated at the MP2/6–311+ +G** level. All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies. Based on a Born-Haber energy cycle (Scheme S1), the heat of formation of a salt can be simplified by the formula given in Equation (1):

$$\Delta H_f^*(\text{salt, 298K}) = \Delta H_f^*(\text{cation, 298K}) + \Delta H_f^*(\text{anion, 298K}) - \Delta H_L \qquad (1)$$

where ΔH_L is the lattice energy of the salts, which could be predicted by using the formula suggested by Jenkins et al. [3, 4] [Eq. (2)]

$$\Delta H_L = U_{pot} + [p\ (n_M/2 - 2) + q\ (n_X/2 - 2)]\ RT \qquad (2)$$

In this equation, n_M and n_X depend on the nature of the ions M_p^+ and X_q^-, respectively, and are equal to three for monoatomic ions, five for linear polyatomic ions, and six for nonlinear polyatomic ions. The equation for lattice potential energy U_{pot} [Eq. (3)] has the form:

$$\mathrm{U_{POT}}\ [\text{kJ mol}^{-1}] = \gamma\ (\rho_m/M_m)^{1/3} + \delta \qquad (3)$$

Where ρ_m [g cm^{-3}] is the density, M_m is the chemical formula mass of the ionic material, and values for g and the coefficients γ (kJ mol^{-1} cm) and δ (kJ mol^{-1}) are taken from the literature.[5]

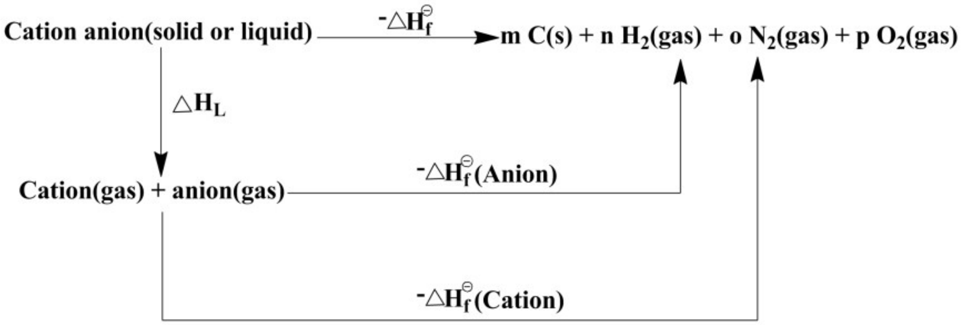
The heat of formation of a cocrystal can be simplified by the formula given in Equation (4):

$$\Delta H_f^*(\text{cocrystal, 298K}) = \Delta H_f^*(\text{molecule, 298K}) + \Delta H_f^*(\text{cation, 298K}) + \Delta H_f^*(\text{anion, 298K}) - \Delta H_L \qquad (4)$$

where ΔH_L is the lattice energy of the cocrystals, which could be predicted by using Equation (5) [4]:

$$\Delta H_L = (232.8/\sqrt[3]{V}) + 110 \qquad (5)$$

Where V is the molecular volume, calculated by multiwfn [6].



Scheme S1. Born-Haber cycle for the formation of Energetic salts.

If the compound contains a molecule of water, the heat of formation for the compound is calculated by addition of ΔH_f^*(s, 298 K) for H_2O, which is -311 kJ mol^{-1}.

Reference

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