Electronic Supplementary Information

Insensitive Energetic Compounds: Alkaline Earth Metal Salts of 5,5′-dinitramino-3,3′-methylene-1H-1,2,4-bistriazolate

Yanna Wang[a,b], Xiaoming Yang[a], Jie Hu[b], Haibo Li[a], Zhimin Li[*a], Tonglai Zhang[*a]

[a] *State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing, China;* [b] *College of Chemistry and Chemical Engineering, Xingtai University, Xing tai, China*

*Corresponding author: Tonglai Zhang and Zhimin Li
Email:
Tonglai Zhang: ztlbit@bit.edu.cn
Zhimin Li: lizm@bit.edu.cn

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1. Crystal data and structure refinement details of compounds 1-3

Table S1 X-ray crystallographic data for compounds 1-3

Compound	**1**	**2**	**3**
Formula	$C_5H_{18}MgN_{10}O_{11}$	$C_{10}H_{44}Ca_2N_{20}O_{26}$	$C_{10}H_{34}N_{20}O_{21}Sr_2$
M (g·mol^{-1})	418.60	940.81	945.81
Cryst. Syst.	monoclinic	monoclinic	orthorhombic
Space Group	*P*21/c	*P*21/n	*P*bca
a (Å)	10.8475	20.6915	17.068(3)
b (Å)	8.7335	8.2319	17.764(4)
c (Å)	17.6426	21.7079	21.772(4)
β (deg.)	91.275	91.831	90
V (Å^3)	1671.0(6)	3695.6(13)	6601(2)
Z	4	4	8
ρ (g·cm^{-3})	1.664	1.691	1.903
F(000)	872	1968	3824
Index ranges	-13≤*h*≤14	-26≤*h*≤25	-19≤*h*≤22
	-11≤*k*≤10	-10≤*k*≤10	-23≤*k*≤18
	-21≤*l*≤22	-28≤*l*≤28	-28≤*l*≤18
Reflections collected	3801	8280	7535
Independent reflections	3550	6822	6087
Rint.	0.0387	0.0465	0.0619
R1 I>2σ(I))[a]	0.0490	0.1230	0.0760
R1 (all data)	0.0533	0.1412	0.0972
wR2 (I>2σ(I))[a]	0.1096	0.2810	0.1284
wR2 (all data)	0.1126	0.2933	0.1368
CCDC number	1888530	2014336	2014337

2. X-ray crystallography

Table S2 Selected bond lengths (Å) and bond angles (°) of compound **1**

Selected bond lengths (Å)					
Mg1- O10	2.0802(16)	Mg1- O5	2.0874(15)	Mg1- O8	2.0351(17)
Mg1- O7	2.0603(16)	Mg1- O6	2.0605(17)	Mg1- O9	2.0548(18)
Selected bond angles (°)					
O7- Mg1- O9	95.09(7)	O5- Mg1- O6	90.32(7)	O6- Mg1- O7	85.41(7)
O7- Mg1- O10	169.86(7)	O5- Mg1- O7	93.78(7)	O6- Mg1- O8	98.70(7)
O8- Mg1- O9	87.35(7)	O5- Mg1- O8	170.51(8)	O6- Mg1- O9	173.93(7)

O8- Mg1- O10	87.91(7)	O5- Mg1- O9	83.61(7)	O6- Mg1- O10	85.13(7)
O9- Mg1- O10	94.70(7)	O5- Mg1- O10	89.93(7)	O7- Mg1- O8	89.91(7)

Table S3 Selected bond lengths (Å) and bond angles (°) of compound **2**

Selected bond lengths (Å)					
Ca1-O14	2.604(4)	Ca1-O20	2.434(6)	Ca2-O11	2.467(6)
Ca1-O16	2.553(5)	Ca1-O21	2.472(5)	Ca2 -O12	2.475(4)
Ca1-O17	2.389(5)	Ca1-O22	2.362(5)	Ca2-O13	2.440(6)
Ca1-O18	2.458(5)	Ca2-O9	2.377(5)	Ca2-O14	2.567(5)
Ca1-O19	2.493(4)	Ca2-O10	2.458(5)	Ca2-O15	2.397(5)
Selected bond angles (°)					
Ca1-O14-Ca2	110.74(17)	O11-Ca2-O15	143.14(17)	O14-Ca1-O21	75.72(15)
Ca1-O16-Ca2	110.88(17)	O11-Ca2-O16	139.19(18)	O16-Ca1-O17	81.37(16)
O9-Ca2-O10	82.83(16)	O14-Ca2-O15	79.84(16)	O16-Ca1-O20	121.27(15)
O9-Ca2-O15	97.60(16)	O15-Ca2-O16	72.70(15)	O18-Ca1-O21	117.14(16)
O9-Ca2-O14	143.41(15)	O14-Ca1-O19	129.54(15)	O20-Ca1-O21	68.63(17)

Table S4 Selected bond lengths (Å) and bond angles (°) of compound **3**

Selected bond lengths (Å)					
Sr1-O1	2.692(4)	Sr1-N2	2.837(4)	Sr2-O15	2.572(4)
Sr1-O9	2.603(5)	Sr1-O4	2.690(4)	Sr2-O16	2.555(5)
Sr1-O10	2.638(4)	Sr1-N9	2.773(4)	Sr2-O17	2.644(4)
Sr1-O11	2.688(4)	Sr2-O11	2.684(3)	Sr2-O18	2.553(5)
Sr1-O12	2.481(5)	Sr2-O13	2.650(4)	Sr2-O19	2.654(4)
Sr1-O13	2.648(4)	Sr2-O14	2.582(5)		
Selected bond angles (°)					
O1-Sr1-O9	81.19(13)	O4-Sr1-N9	47.23(12)	O1-Sr1-N2	46.30(11)
O9-Sr1-O10	154.35(14)	O9-Sr1-O11	126.53(13)	O9-Sr1-O12	77.84(17)
O11-Sr1-O13	70.46(10)	O10-Sr1-O11	68.74(11)	O10-Sr1-O12	127.69(14)
O11-Sr2-O13	70.48(10)	O11-Sr2-O14	83.73(13)	O11-Sr2-O16	134.66(14)
O11-Sr2-O17	145.78(11)	O13-Sr2-O14	133.49(14)	O13-Sr2-O15	89.33(11)
O13-Sr2-O17	142.55(11)	O13-Sr2-O18	77.86(13)	O13-Sr2-O19	136.41(14)
O14-Sr2-O15	76.40(14)	O14-Sr2-O16	141.57(16)	O14-Sr2-O17	75.20(14)

3. The distances of hydrogen bonds of compounds 1-3

Table S5 Hydrogen bond lengths / Å and angles / º of compound 1-3

$[Mg(H_2O)_6](DNAMT)\cdot H_2O$ (1)				
D-H···A	**d(D–H)**	**d(H···A)**	**d(D···A)**	**∠DHA**
N4-H4···O1	0.8500	2.1200	2.578(2)	113.00
N4-H4···O4	0.8500	2.1200	2.935(2)	159.00
N7-H7···O4	0.8500	2.0800	2.545(2)	114.00
N7-H7···O1	0.8500	2.0500	2.852(2)	156.00
O7-H7···O10	0.8400	2.2000	3.017(2)	165.00
O9-H9···O2	0.8400	1.9600	2.792(2)	169.00
O9-H9···O3	0.8400	1.9300	2.760(2)	167.00
O10-H10···O11	0.8400	1.9200	2.752(2)	169.00
O11-H11···O2	0.8400	1.9700	2.791(2)	166.00
$[Ca_2(H_2O)_{14}](DNAMT)_2\cdot 4H_2O$ (2)				
D-H···A	**d(D–H)**	**d(H···A)**	**d(D···A)**	**∠DHA**
N3-H3···O2	0.8800	2.0600	2.558(7)	115.00
N3-H3···O6	0.8800	2.0700	2.770(7)	136.00
N8-H8···O4	0.8800	2.0400	2.542(6)	115.00
N8-H8···O8	0.8800	2.1000	2.832(6)	141.00
N18-H18···O8	0.8800	2.0400	2.541(7)	116.00
N18-H18···O2	0.8800	2.1700	2.855(7)	134.00
N13-H13···O6	0.8800	2.0500	2.544(6)	115.00
O9-H9A···O23	0.8400	2.0600	2.893(6)	174.00
O10-H10B···O25	0.8400	1.9800	2.818(7)	176.00
O11-H11A···O3	0.8400	2.0100	2.810(6)	160.00
O11-H11B···O3	0.8400	2.3200	3.122(7)	159.00
O12-H12B···O1	0.8400	2.0600	2.890(6)	169.00
O18-H18B···O5	0.8400	1.9700	2.806(6)	174.00
O20-H20A···O5	0.8700	2.4200	3.207(7)	151.00
O22-H22A···O26	0.8400	2.2100	2.995(8)	156.00
$[Sr_2(DNAMT)(H_2O)_{11}](DNAMT)\cdot 2H_2O$ (3)				
D-H···A	**d(D–H)**	**d(H···A)**	**d(D···A)**	**∠DHA**
N4-H4···O2	0.8500	2.2100	2.600(5)	108.00
N7-H7···O3	0.8500	2.2200	2.580(6)	105.00
N7-H7···O7	0.8500	2.0700	2.900(6)	167.00
O9-H9B···O8	0.8400	2.0300	2.798(6)	152.00
O13- H13B···O20	0.8400	2.0500	2.858(5)	161.00
N14-H14···O6	0.8500	2.0400	2.539(6)	117.00

N14-H14···O2	0.8500	2.2100	3.003(6)	156.00
O15-H15B···O10	0.8400	2.5400	3.058(5)	121.00
O16-H16A···O3	0.8400	2.6000	3.239(6)	134.00
O16-H16A···O4	0.8400	2.1400	2.969(6)	169.00
N17-H17···O7	0.8500	2.0000	2.561(6)	123.00
N17-H17···O3	0.8500	2.2500	3.013(6)	149.00
O17-H17A···O1	0.8400	2.2600	3.050(5)	157.00
O19-H19B···O1	0.8400	2.0700	2.861(5)	157.00
O19-H19B···O2	0.8400	2.5800	3.319(5)	147.00
O20-20B···O5	0.8400	2.0000	2.832(5)	169.00

4. The first exothermic decomposition peak temperature with four heating rates

Table S6 The first exothermic decomposition peak temperatures tested at different heating rates of compounds 1-3

compound	The first exothermic decomposition peak temperatures (K)			
	5K·min^{-1}	10K·min^{-1}	15K·min^{-1}	20K·min^{-1}
1	537.65	542.95	547.05	549.25
2	554.85	556.55	561.75	56.955
3	578.55	586.15	590.85	595.65

5. Non-isothermal kinetics analysis

The peak temperatures of first decomposition processes were used to calculated kinetics parameters (apparent activation energies (*E*a) and the pre-exponential factor (A)), by Kissinger's method [1] (Eq. (1)) and Ozawa's method [2] (Eq. (2)).

$$ln\frac{\beta}{T_P^2} = ln\frac{AR}{E_a} - \frac{E_a}{RT_P} \quad (1)$$

$$\lg\beta + 0.4567\frac{E_a}{RT_P} = C \quad (2)$$

Where, T_p is the peak temperature (K), R is the gas constant 8.314 (J·mol^{-1}·K^{-1}), β is the linear heating rate (^{o}C·min^{-1}), C is a constant, E_a is the average of E_k and E_o (kJ·mol^{-1}). The results are listed in Table S7.

Table S7 Non-isothermal reaction kinetics parameters of compounds 1 - 3

compound	Kissinger's method	Ozawa's method	*E*a/kJ·mol^{-1}

	E_K/kJ·mol^{-1}	lg A_K	R_K	E_O/kJ·mol^{-1}	R_O	
1	66.90	11.2	-0.99	67.89	-0.99	67.39
2	65.09	10.1	-0.91	66.44	-0.92	65.76
3	64.10	8.46	-0.99	64.01	-0.99	64.06

6. The calculation of thermodynamics parameters

The thermodynamics parameters (T_{p0}, T_b, $\Delta S^{\neq}$, $\Delta H^{\neq}$, $\Delta G^{\neq}$) were obtained by the Zhang's calculation equations [3] and the results list in Table S8. The equations for these calculations are as follows:

$$T_{Pi} = T_{P0} + a\beta + b\beta^2 + c\beta^3 \quad (3)$$

$$T_b = (E_k - \sqrt{E_k^2 - 4E_k R T_{P0}})/2\mathrm{R} \quad (4)$$

$$A = (k_B T_{P0}/h) exp(1 + \Delta S^{\neq}/R) \quad (5)$$

$$\Delta H^{\neq} = E_k - RT_{P0} \quad (6)$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T_{P0}\Delta S^{\neq} \quad (7)$$

where a, b, and c are coefficients, k_B is the Boltzmann constant (1.381×10^{-23} J·K^{-1}) and h is the Planck constant (6.626×10^{-34} J·s). T_b is the critical temperature of thermal explosion, T_{p0} is the peak temperature corresponding to $\beta\rightarrow0$, $\Delta S^{\neq}$ is activation entropy, $\Delta H^{\neq}$ is activation enthalpy and $\Delta G^{\neq}$ is free energy of activation.

Table S8 Calculation of critical temperatures of thermal explosion, $\Delta S^{\neq}$, $\Delta H^{\neq}$ and $\Delta G^{\neq}$

compound	T_{p0}/K	T_b/K	$\Delta S^{\neq}$/J·K^{-1}·mol^{-1}	$\Delta H^{\neq}$/kJ·mol^{-1}	$\Delta G^{\neq}$/kJ·mol^{-1}
1	531.85	572.59	-35.31	62.48	81.26
2	560.15	607.25	-56.80	60.43	92.25
3	565.05	613.94	-88.27	59.40	109.28

7. References

1 H. E. Kissinger, Anal. Chem., 1957, 29, 1702–1706.

2 T. Ozawa, Bull. Chem. Soc. Jpn., 1965, 38, 1881–1886.

3 T. Zhang, R. Hu, X. Yi and F. Li, Thermochim. Acta, 1994, 244, 171-176.