Supporting Information

Alkali and Alkaline Earth Metal Salts of Tetrazolone: Structurally Interesting and Excellently Thermostable

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1. Experimental section

General: All chemicals were used as obtained from commercial suppliers. Melting and decomposition points were determined by differential scanning calorimetry (DSC) with a Pekin Elmer (PE) STA-6000 apparatus at a heating rate of 10 °C min^{-1} apparatus. Calorimetric measurements were performed with a Parr-6200 bomb calorimeter. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker instrument. The chemical shifts quoted in ppm relative to tetramethylsilane (^{1}H, ^{13}C). Infrared spectra were measured using a Nicolet Nexus 470 FT-IR spectrometer as KBr pellets. Mass spectra were measured at an Agilent 500-MS. Elemental analysis was performed on an Elementar Vario El III analyzer. Impact sensitivities were tested by fall hammer apparatus applying standard staircase method using a 2 kg drop weight and the results were reported in terms of height for 50% probability of explosion (h50%). Collection of XRD data was performed on a Rigaku Saturn 724+ CCD diffractometer equipped with graphite monochromatized MoKα radiation. The structure was solved with SHELXS-97[1] refined with SHELXL-97[2]. The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were located and freely refined.

CCDC-1018902 (**1**), CCDC-1018900 (**2**), CCDC-1018911 (**3**), CCDC-1018907 (**4**), CCDC-1018908 (**5**), CCDC-1018915 (**6**), CCDC-1018917 (**7**), CCDC-1018916 (**8**), CCDC-1018912 (**9**) contain the supplementary crystallographic data, which can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Caution! *All of these investigated compounds are potentially explosive energetic materials, thus this necessitates additional meticulous safety precautions (ear plugs, face shield and Kevlar gloves etc).*

Tetrazolone (TO)

Tetrazolone was obtained in three improved steps from commercially available benzyl isocyanate (Scheme 2). The reaction with trimethylsilane azide under the reflux of anhydrous toluene results in formyl benzylamine azide. Then the obtained oily liquid was cyclized under special conditions (trimethyl chlorosilane and triethylamine) to form 1-benzyl tetrazolone. Final catalytic hydrogenolysis with Pd/C catalyst gave the target product.

Lithium 5-oxotetrazolate hydrate (1)

Tetrazolone (86 mg, 1 mmol) was suspended in water (2 mL). The mixture was heated to reflux (70~80°C) to obtain a clear solution. The lithium hydrate (42 mg, 1 mmol) was added and the solution was cooled down to room temperature causing the white precipitation of the salt in good yield (94%). DSC (10 °C min^{-1}): 280.1 ºC (dec); IR(KBr, cm^{-1}): 3391.39, 3308.11, 3136.41, 3045.42, 2820.18, 2696.64, 2542.46, 2512.72, 2227.61, 2127.57, 1668.61, 1637.25, 1430.98, 1343.58, 1281.10, 1171.34, 1094.44, 1065.13, 1014.26, 791.93, 757.20, 686.42, 641.46, 548.03, 468.63, 446.75; ^{13}CNMR(400 MHz, DMSO-d_6): 166.5; MS(ESI^-): 84.95(CHN_4O^-); EA: Calcd C 10.92%, H2.75 %, N 50.93%; found C11.07 %, H 2.58%, N50.07 %.

Sodium 5-oxotetrazolate hydrate (2)

Tetrazolone (86 mg, 1 mmol) was suspended in water (2 mL). The mixture was heated to obtain a clear solution. Sodium carbonate (53 mg, 0.5 mmol) was added and the solution was cooled down to room temperature. The colorless crystal was obtained by filtration and dried under vacuum (92.3%). DSC (10 °C min^{-1}): 255.2 ºC (dec); IR (KBr, cm^{-1}): 3566.67, 3368.33, 3244.31, 3103.67, 3008.42, 2827.40, 2529.97, 2485.87, 2319.42, 1648.56, 1439.50, 1324.46, 1275.89, 1171.15, 1102.84, 1060.24, 1006.55, 944.77, 824.29, 799.81, 765.43, 692.10, 646.78, 569.70, 510.93, 455.69; ^{13}CNMR(400 MHz, DMSO-d_6): 166.9; MS(ESI^-): 84.95(CHN_4O^-); EA: Calcd C 9.53%, H2.40 %, N 44.45%; found C9.87 %, H 2.48%, N42.37 %.

Potassium 5-oxotetrazolate (3)

Tetrazolone (86 mg, 1 mmol) was suspended in water (2 mL). The mixture was heated to obtain a clear solution. Potassium carbonate (69 mg, 0.5 mmol) was added and the solution was cooled down to room temperature. The white powder was collected by filtration and dried under vacuum (96.7%). DSC (10 °C min^{-1}): 245.8 ºC (dec); IR (KBr, cm^{-1}): 3566.10, 3457.92, 3381.97, 3247.63, 3115.96, 2985.67, 2819.74, 2689.87, 2527.90, 1731.48, 1671.85, 1615.03, 1460.42, 1339.42, 1311.30, 1268.53, 1156.24, 1132.24, 1086.64, 1059.50, 993.87, 970.76, 889.80, 780.95,

768.41, 738.90, 689.11, 537.82, 495.87; ^{13}CNMR(400 MHz, DMSO-d_6): 161.4; MS(ESI$^-$): 84.95(CHN_4O^-); EA: Calcd C 9.67%, H 0.81 %, N 45.13%; found C9.89 %, H 0.93%, N43.82 %.

Rubidium 5-oxotetrazolate (4)

Tetrazolone (86 mg, 1 mmol) was suspended in water (2 mL). The mixture was heated to obtain a clear solution. Rubidium carbonate (115 mg, 0.5 mmol) was added and the solution was cooled down to room temperature. The filtration and dried under vacuum leave the colorless crystals (88.8%). DSC (10 °C min^{-1}): 184.9 ºC (dec); IR (KBr, cm^{-1}): 3395.36, 3117.48, 2980.15, 2783.07, 2689.80, 2509.82, 2291.85, 1970.87, 1662.36, 1468.82, 1308.28, 1263.69, 1148.47, 1091.22, 1053.07, 978.47, 847.67, 769.27, 684.28, 512.36; ^{13}CNMR(400 MHz, DMSO-d_6): 163.4; MS(ESI$^-$): 84.95(CHN_4O^-); EA: Calcd C 7.04%, H 0.59 %, N 32.86%; found C 7.13 %, H 0.64%, N 30.45 %.

Cesium 5-oxotetrazolate (5)

Tetrazolone (86 mg, 1 mmol) was suspended in water (2 mL). The mixture was heated to obtain a clear solution. Caesium hydroxide (150 mg, 1 mmol) was added and the solution was cooled down to room temperature. The filtration and dried under vacuum crystalline colorless solid (88.5%). DSC (10 °C min^{-1}): 229.5 ºC (dec); IR (KBr, cm^{-1}): 3434.85, 3106.69, 2973.49, 2769.54, 2684.95, 2486.73, 1653.43, 1469.27, 1455.55, 1372.00, 1306.86, 1275.39, 1145.08, 1091.52, 1055.24, 973.08, 867.51, 771.59, 683.67, 509.59; ^{13}CNMR(400 MHz, DMSO-d_6): 166.1; MS(ESI$^-$): 84.95(CHN_4O^-); EA: Calcd C 5.51%, H 0.46 %, N 25.71%; found C 5.75 %, H 0.54%, N 23.46 %.

Magnesium 5-oxotetrazolate tetrahydrate (6)

Tetrazolone (172 mg, 2 mmol) was suspended in water (5 mL). The mixture was heated to reflux in order to dissolve the acid. After obtaining a clear solution magnesium oxide (40 mg, 1 mmol) was added. The solution was reflux for 1h and followed by filtration of the hot solution. The filtrate was then cooled down to room temperature and the solid was precipitated in a good yield (92.7%). DSC (10 °C min^{-1}): 271.5 ºC (dec); IR (KBr, cm^{-1}): 3799.24, 3708.6, 3625.67, 3563.96, 3558.17, 3550.46, 3542.74, 3521.53, 3508.03, 3500.31, 3479.1, 2792.54, 2690.32, 2316.19, 1681.69, 1639.27, 1405.91, 1324.91, 1294.06, 1168.7, 1099.27, 1035.63, 755.99, 698.13, 592.06, 530.35, 405.00; ^{13}CNMR(400 MHz, DMSO-d_6): 163.1; MS(ESI$^-$): 84.95(CHN_4O^-); EA: Calcd C 9.02%, H 3.78 %, N 42.05%; found C 9.16 %, H 3.85%, N 41.02 %.

Calcium 5-oxotetrazolate pentahydrate (7)

Tetrazolone (172 mg, 2 mmol) was suspended in water (5 mL). The mixture was heated to reflux in order to a clear solution. Calcium hydroxide (74 mg, 1 mmol) was added. The solution was reflux for 1h and followed by filtration

of the hot solution. The filtrate was then cooled down to room temperature and the colorless crystalline was obtained (82.4%). DSC (10 °C min^{-1}): 328.2 ºC (dec); IR (KBr, cm^{-1}): 3585.17, 3563.96, 3239.96, 1639.27, 1612.27, 1373.13, 1265.13, 1058.77, 800.35, 746.35, 682.71, 499.49; ^{13}CNMR(400 MHz, DMSO-d_6): 165.0; MS(ESI^-): 84.95(CHN_4O^-); EA: Calcd C 8.00%, H 4.03 %, N 37.32%; found C 8.09 %, H 4.10%, N 37.25 %.

Strontium 5-oxotetrazolate pentahydrate (8)

Tetrazolone (172 mg, 2 mmol) was suspended in water (5 mL). The mixture was heated to reflux in order to a clear solution. Strontium carbonate (147 mg, 1 mmol) was added. The solution was reflux for 2h and followed by filtration of the hot solution. The filtrate was then cooled down to room temperature and the colorless crystalline was obtained (79.3%). DSC (10 °C min^{-1}): 225.0 ºC (dec); IR (KBr, cm^{-1}): 3853.24, 3670.03, 3500.31, 3417.39, 2966.11, 2782.89, 2320.04, 1697.12, 1608.41, 1421.34, 1330.70, 1272.84, 1261.27, 1153.27, 1097.34, 1054.92, 997.06, 788.78, 769.49, 694.28, 622.92, 538.06; ^{13}CNMR(400 MHz, DMSO-d_6): 165.6; MS(ESI^-): 84.95(CHN_4O^-); EA: Calcd C 6.91%, H 3.48 %, N 32.22%; found C 7.15 %, H 3.51%, N 31.02 %.

Barium 5-oxotetrazolate dehydrate (9)

Tetrazolone (172 mg, 2 mmol) was suspended in water (5 mL). The mixture was heated to reflux in order to a clear solution. Barium carbonate (197 mg, 1 mmol) was added. The solution was reflux for 2h and followed by filtration of the hot solution. The filtrate was then cooled down to room temperature and the colorless crystalline was obtained (82.2%). DSC (10 °C min^{-1}): 227.8 ºC (dec); IR (KBr, cm^{-1}): 3851.31, 3392.32, 2364.40, 1812.84, 1605.84, 1477.27, 1459.91, 1338.41, 1259.34, 1126.27, 1064.56, 1012.49, 983.56, 931.49, 784.92, 773.35, 700.06, 638.35, 512.99, 441.64; ^{13}CNMR(400 MHz, DMSO-d_6): 164.5; MS(ESI^-): 84.95(CHN_4O^-). EA: Calcd C 6.99%, H1.76 %, N 32.63%; found C 7.24 %, H1.88%, N29.74 %.

2. Packing schemes

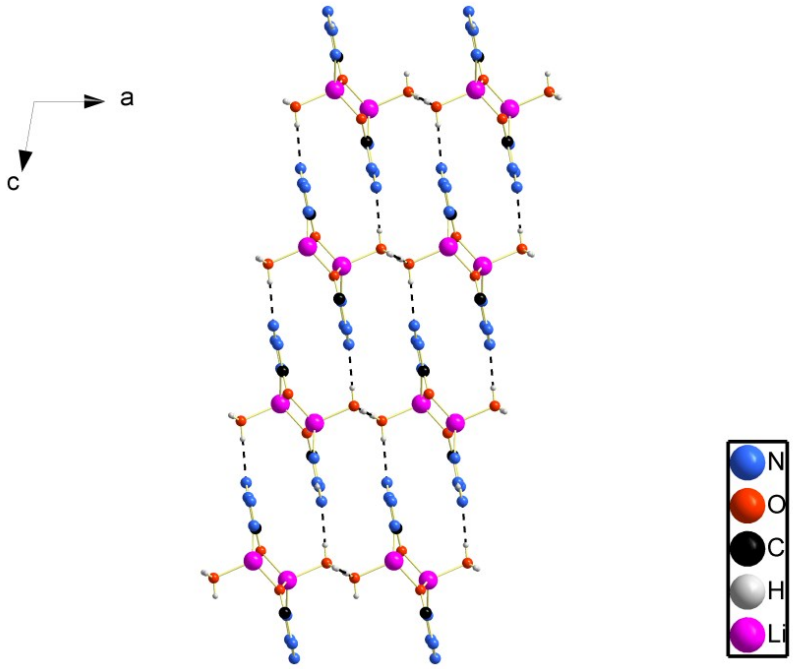

Figure S1 Packing scheme of compound **1** view along b axis

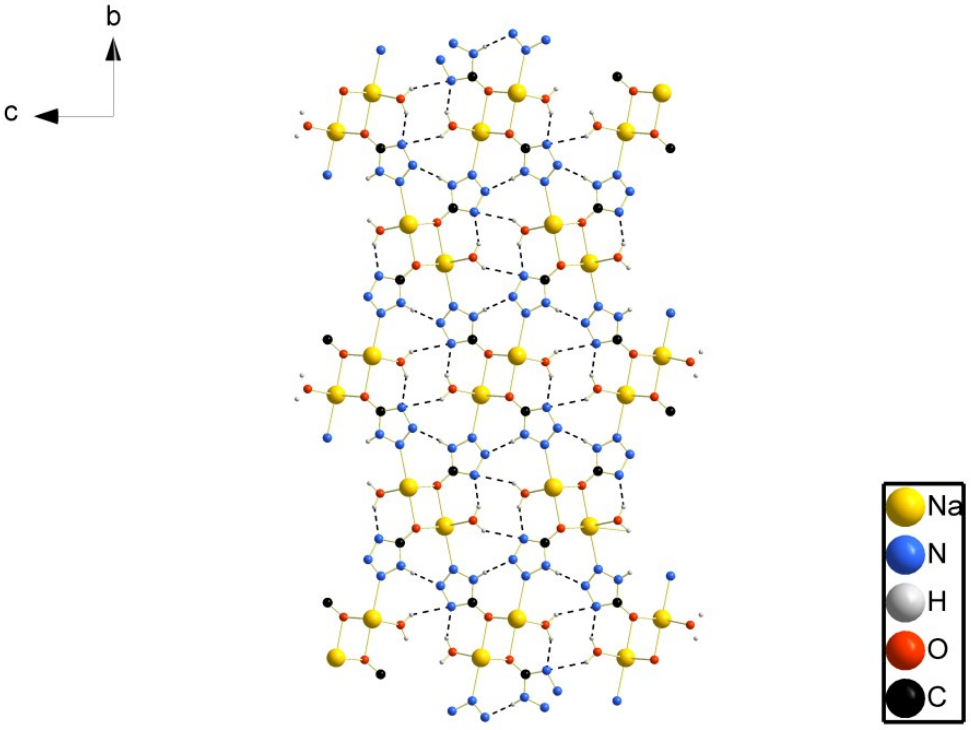

Figure S2 Packing scheme of compound **2** view along a axis

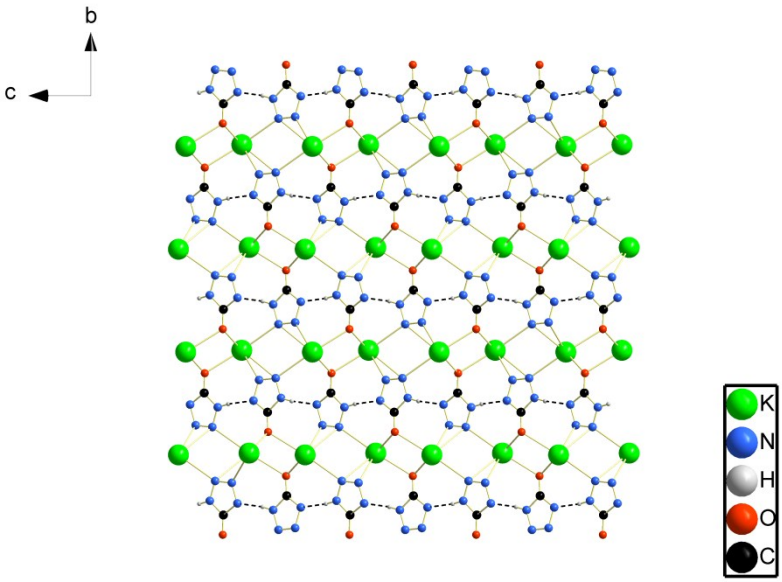

Figure S3 Packing scheme of compound **3** view along a axis

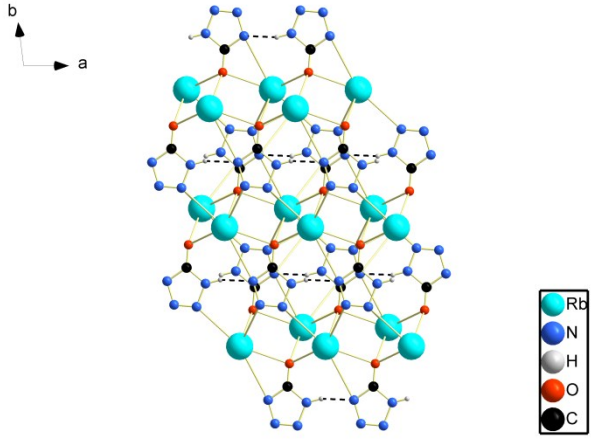

Figure S4 Packing scheme of compound **4** view along c axis

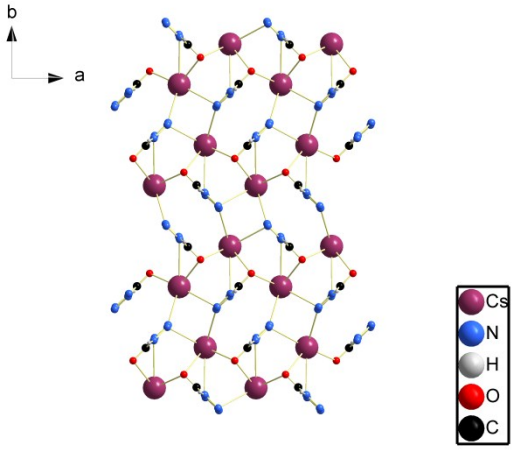

Figure S5 Packing scheme of compound **5** view along c axis

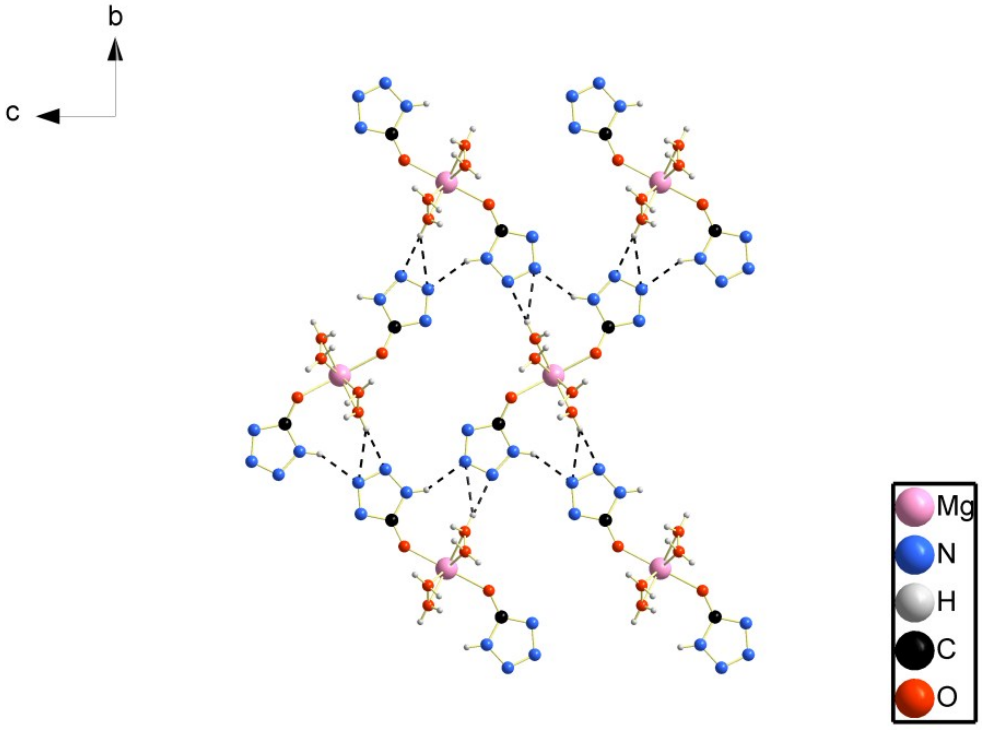

Figure S6 Packing scheme of compound **6** view along a axis

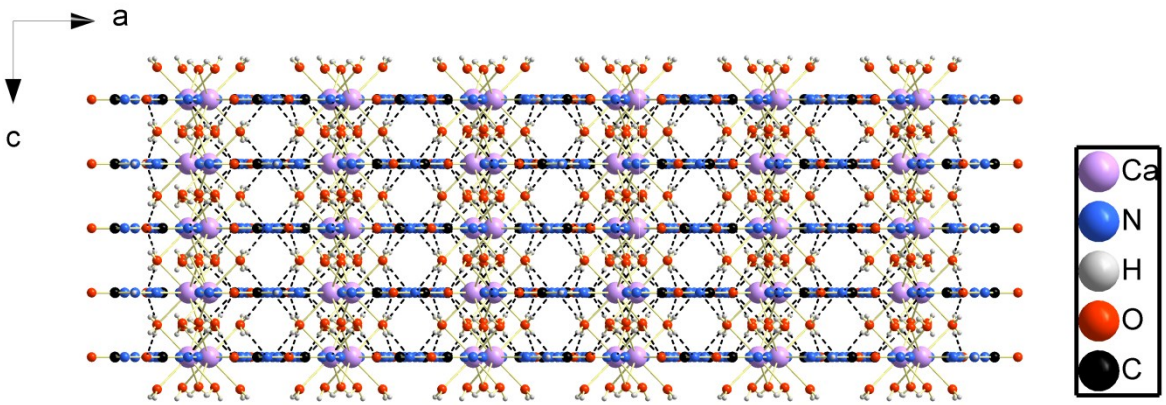

Figure S7 Packing scheme of compound **7** view along b axis

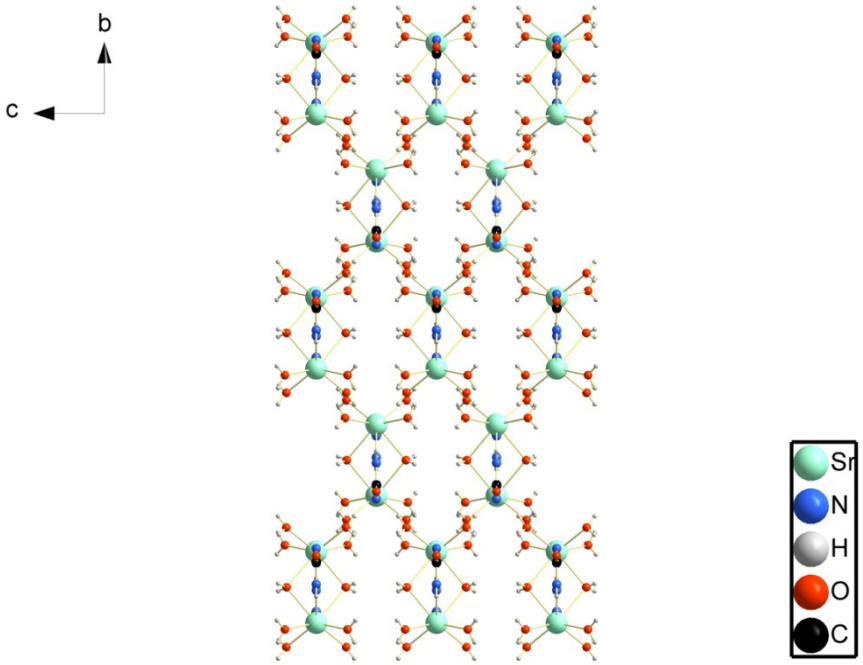

Figure S8 Packing scheme of compound **8** view along a axis

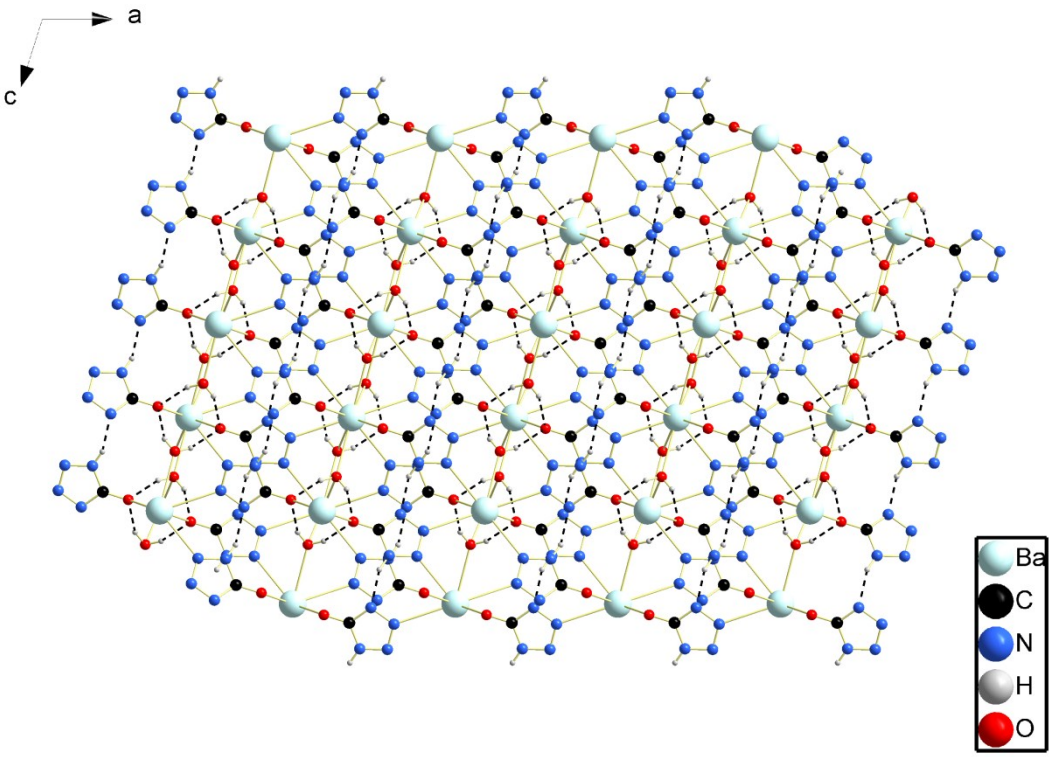

Figure S9 Packing scheme of compound **9** view along b axis

3. Crystallographic data

Table 1 Crystallographic data and structure refinement details for compounds **1-9**

Compound	**1·H_2O**	**2·H_2O**	**3**	**4**	**5**	**6·4H_2O**	**7·5H_2O·TO(H_2O)**	**8·5H_2O**	**9·2H_2O**
Formula	$CH_3LiN_4O_2$	$CH_3N_4NaO_2$	$CHKN_4O$	CHN_4ORb	$CHCsN_4O$	$C_2H_{10}MgN_8O_6$	$C_5H_{28}Ca_2N_{20}O_{16}$	$C_2H_{12}N_8O_7Sr$	$C_2H_6BaN_8O_4$
Formula weight	110.01	126.06	124.16	170.53	217.97	266.49	704.6	347.82	343.49
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic
Space group	*P2(1)/c*	*P2(1)/n*	*P2(1)/n*	*P-1*	*Pbam*	*Cmca*	*Cccm*	*Pnnm*	*C2/c*
a [Å]	6.6019(4)	3.5385(2)	4.1001(4)	4.9480(3)	6.9541(5)	6.6379(5)	14.9853(10)	11.2966(9)	15.4882(13)
b [Å]	5.0870(3)	15.1510(12)	12.9476(11)	7.1191(6)	13.8119(12)	16.5198(14)	24.4542(15)	14.7871(13)	6.3340(5)
c [Å]	14.9308(9)	8.3696(6)	8.1433(8)	7.4189(7)	4.9030(4)	9.1359(7)	6.7717(3)	6.9961(5)	9.3181(8)
α [°]	90.00	90.00	90.00	67.2890(10)	90.00	90.00	90.00	90.00	90.00
β [°]	99.846(2)	94.465(2)	101.419(2)	71.8880(10)	90.00	90.00	90.00	90.00	107.545(2)
γ [°]	90.00	90.00	90.00	89.451(2)	90.00	90.00	90.00	90.00	90.00
Z	4	4	4	2	4	4	4	4	4
Volume [Å]^3	494.05(5)	447.35(5)	423.74(7)	227.30(3)	470.93(7)	1001.81(14)	2481.5(3)	1168.66(16)	871.60(13)
ρ [g·cm^{-3}]	1.479	1.872	1.946	2.492	3.074	1.767	1.886	1.977	2.618
μ [mm^{-1}]	0.129	0.244	1.107	10.755	7.732	0.218	0.575	4.660	4.573
F(000)	224	256	248	160	392	552	1464	696	648
*θ*min-max [°]	2.77 , 25.02	2.69 , 24.97	3.00 , 25.00	3.16, 25.01	2.95, 25.01	2.47, 25.01	2.84 , 25.02	2.27, 25.01	2.76 , 25.02
Dataset (h, k, l)	-7:7,-6:5, -17:15	-4:4, -18:13, -9:9	-4:4, -15:11, -9:9	-5:5, -8:7, -8:8	-8:8, -16:11, -5:5	-6:7, -14:19, -10:7	-13:17, -27:29, -8:8	-13:13, -12:17, -8:8	-18:17, -7:7, 0:10
Reflect. coll.	2272	2125	2015	1157	2125	1997	1171	5475	769
Independ. refl.	863	782	739	787	471	486	1171	1125	769
R_{int}	0.0393	0.0564	0.0365	0.0945	0.0636	0.0808	0.0000	0.0717	0.0000
No. parameters	74	74	64	64	55	64	148	103	70
R_1/wR_2 (all data)	0.0614/0.1339	0.0471/0.1289	0.0449/0.0753	0.1312/0.3099	0.0552/0.1213	0.0550/0.1401	0.1415/0.3075	0.0369/0.0747	0.0422/0.0931
R_1/wR_2 ($I>2\sigma(I)$)	0.0510/0.1296	0.0426/0.1241	0.0307/0.0708	0.1203/0.2972	0.0499/0.1190	0.0501/0.1354	0.1290/0.2995	0.0310/0.0722	0.0394/0.0925
S	1.163	1.092	1.079	1.368	1.155	1.109	1.091	1.014	1.151
CCDC number	1018902	1018900	1018911	1018907	1018908	1018915	1018917	1018916	1018912

4. Hydrogen bonds

Table S2a Hydrogen bonds for compound **1** [Å and °]

	Donor-H	Acceptor-H	Donor-Acceptor	Angle
N1--H1··N3	0.8600	2.1300	2.968(3)	166.00
O2--H2B··O2	0.8500	2.1100	2.945(3)	167.00
O2--H2C··N2	0.8500	2.0500	2.903(3)	179.00
O2--H2D··O2	0.8500	2.1000	2.945(3)	178.00

Table S2b Hydrogen bonds for compound **2** [Å and °]

	Donor-H	Acceptor-H	Donor-Acceptor	Angle
N1--H1··N3	0.8600	1.9800	2.840(3)	174.00
O2--H2A··N3	0.8500	2.3800	3.228(2)	174.00
O2--H2A··N4	0.8500	2.3600	3.117(2)	148.00
O2--H2B··N4	0.8500	2.1500	2.834(3)	137.00

Table **S2c** Hydrogen bonds for compound **3** [Å and °]

	Donor-H	Acceptor-H	Donor-Acceptor	Angle
N5--H4··N1	0.8600	1.9500	2.800(3)	173.00

Table **S2d** Hydrogen bonds for compound **4** [Å and °]

	Donor-H	Acceptor-H	Donor-Acceptor	Angle
N1--H1··N4	0.8600	1.9700	2.80(2)	161.00

Table S2f Hydrogen bonds for compound **6** [Å and °]

	Donor-H	Acceptor-H	Donor-Acceptor	Angle
N1--H1··N3	0.8600	2.0600	2.843(4)	151.00
O2--H2C··N2	0.8500	2.0600	2.912(4)	179.00
O2--H2C··N3	0.8500	2.4400	3.188(4)	148.00
O2--H2D··N4	0.8500	2.0700	2.918(4)	179.00

Table S2g Hydrogen bonds for compound **7** [Å and °]

	Donor-H	Acceptor-H	Donor-Acceptor	Angle
N1--H1··O1	0.8600	1.9200	2.769(14)	170.00
O4--H4··O2	0.67(12)	2.18(12)	2.848(10)	173.00
O5--H5C··O1	0.8500	1.9100	2.751(11)	170.00

O5--H5D··N5	0.8500	2.2100	3.047(11)	171.00
O6--H6B··O2	0.8500	2.0300	2.872(11)	173.00
O6--H6C··N4	0.8500	2.3100	3.151(12)	170.00
N8--H8··O3	0.8600	1.9300	2.72(3)	152.00
N8--H8··O7	0.8600	2.1700	2.97(3)	155.00
N8--H8··N11	0.8600	1.9800	2.84(4)	179.00
N8--H8··N11	0.8600	1.9800	2.84(4)	179.00
O7--H9··N3	1.0100	1.9600	2.84(3)	145.00

Table S2h Hydrogen bonds for compound **8** [Å and °]

	Donor-H	Acceptor-H	Donor-Acceptor	Angle
N1--H1··O1	0.8600	1.9400	2.793(4)	169.00
O3--H3··N8	0.8500	2.2800	3.130(3)	178.00
O4--H4C··N7	0.8500	2.1700	3.012(3)	171.00
O4--H4D··O1	0.8500	1.9500	2.795(3)	171.00
N5--H5··O2	0.8600	1.9400	2.793(4)	171.00
O5--H5C··O2	0.8500	1.9300	2.778(3)	173.00
O5--H5D··N4	0.8500	2.3200	3.167(3)	173.00

Table **S2i** Hydrogen bonds for compound **9** [Å and °]

	Donor-H	Acceptor-H	Donor-Acceptor	Angle
N4--H4··N1	0.8600	1.8700	2.682(10)	156.00

5. References

1. G. M. Sheldrick, *SHELXS-97, Program for the Solution of Crystal Structure*, University of Göttingen, Göttingen (Germany), 1997.
2. G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure Refinement from Diffraction Data*, University of Göttingen, Göttingen (Germany), 1997.