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Supporting Information

Alkali Metal Salts of 3,6-Dinitramino- 1,2,4,5-tetrazine：Promising Nitrogen-Rich Energetic Materials

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Table S1 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **1**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq.)
O1	7339(2)	-1468(2)	7370.0(18)	28.7(5)
O2	5456.8(19)	93(2)	7022(2)	32.1(5)
N1	6653(2)	-399(3)	6729(2)	22.4(5)
N2	7242(2)	325(3)	5536(2)	19.6(5)
N3	9429.0(19)	1586(2)	5164.9(19)	16.9(5)
N4	10798(2)	1436(2)	4870.8(19)	17.7(5)
C1	8695(2)	140(3)	5292(2)	16.2(5)

Table S2 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **1**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	30(1)	32.4(10)	23.8(9)	5.9(7)	0.4(7)	2.4(8)
O2	21.2(10)	37.8(11)	37.3(11)	0.5(8)	12.1(8)	3.9(8)
N1	20.9(11)	24.2(11)	22.1(9)	-2.4(8)	3.1(8)	-1.5(9)
N2	14.8(10)	18.4(10)	25.5(10)	4.1(8)	4.2(7)	2.0(8)
N3	14.0(9)	17.2(10)	19.5(9)	0.9(7)	1.7(7)	-1.2(7)
N4	15.5(9)	17.5(10)	20.0(9)	-0.6(7)	1.9(7)	0.2(8)
C1	16.8(11)	15.5(11)	16.5(10)	0.1(8)	-1.0(8)	0.6(9)

Table S3 Bond Lengths for **1**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	N1	1.222(3)	N3	N4	1.323(3)
O2	N1	1.221(3)	N3	C1	1.337(3)
N1	N2	1.382(3)	N4	C1[1]	1.337(3)
N2	C1	1.393(3)	C1	N4[1]	1.337(3)

[1]2-X,-Y,1-Z

Table S4 Bond Angles for **1**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	N1	N2	118.59(19)	N3	N4	C1[1]	117.02(19)
O2	N1	O1	126.3(2)	N3	C1	N2	115.60(19)
O2	N1	N2	115.1(2)	N3	C1	N4[1]	126.5(2)
N1	N2	C1	119.07(18)	N4[1]	C1	N2	117.7(2)
N4	N3	C1	116.43(19)				

[1]2-X,-Y,1-Z

Table S5 Torsion Angles for **1**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	N1	N2	C1	-15.4(3)	N4	N3	C1	N2	-177.10(18)
O2	N1	N2	C1	165.9(2)	N4	N3	C1	N4[1]	-1.1(3)
N1	N2	C1	N3	-122.3(2)	C1	N3	N4	C1[1]	1.0(3)
N1	N2	C1	N4[1]	61.3(3)					

[1]2-X,-Y,1-Z

Table S6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **1**.

Atom	*x*	*y*	*z*	U(eq)
H2	6902	1316	5424	23

Table S7 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **2**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq.)
O1	6013.9(13)	6996.9(5)	496.6(7)	16.4(2)
O2	3836.0(13)	5990.6(5)	1062.3(7)	16.6(2)
O3	957.0(13)	4117.7(5)	413.0(7)	15.42(19)
O4	2230.5(12)	4904.9(5)	3134.6(7)	14.42(19)
N1	801.9(15)	8192.4(6)	2205.9(8)	11.9(2)
N2	772.7(14)	6588.0(6)	2159.1(7)	11.2(2)
N3	3310.5(14)	7514.5(6)	1288.5(7)	11.4(2)
N4	4362.9(14)	6806.5(6)	953.1(8)	10.60(19)
C1	1593.2(16)	7378.1(7)	1884.0(8)	9.6(2)
Li1	854(3)	5282.2(13)	1338.2(17)	17.6(4)

Table S8 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **2**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	12.8(4)	18.0(4)	21.2(4)	1.9(3)	10.1(3)	0.5(3)
O2	16.7(4)	9.0(4)	26.2(4)	0.6(3)	9.6(3)	0.8(3)
O3	16.5(4)	11.9(4)	19.3(4)	-0.9(3)	7.1(3)	1.9(3)
O4	13.4(4)	9.3(4)	20.7(4)	-0.5(3)	3.5(3)	0.5(3)
N1	14.3(4)	10.0(4)	12.1(4)	-0.2(3)	4.6(3)	0.0(3)
N2	12.4(4)	10.3(4)	12.2(4)	0.6(3)	5.4(3)	-0.1(3)
N3	12.2(4)	10.1(4)	12.7(4)	0.1(3)	4.5(3)	0.7(3)
N4	9.4(4)	12.3(4)	10.2(4)	1.5(3)	2.2(3)	1.0(3)
C1	10.8(5)	9.8(5)	7.8(4)	0.2(3)	0.5(3)	0.3(3)
Li1	19.9(9)	14.6(8)	19.5(9)	-2.1(7)	6.7(7)	1.3(7)

Table S9 Bond Lengths for **2**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	N4	1.2550(12)	N2	$N2^2$	1.3352(16)
O2	N4	1.2601(11)	N2	C1	1.3318(13)
O2	Li1	2.182(2)	N2	Li1	2.151(2)
O3	$Li1^1$	2.287(2)	N3	N4	1.3230(12)
O3	Li1	2.028(2)	N3	C1	1.3719(13)
O4	Li1	2.150(2)	Li1	$O3^1$	2.287(2)
O4	$Li1^2$	2.164(2)	Li1	$O4^2$	2.164(2)
N1	$N1^2$	1.2913(17)	Li1	$Li1^2$	3.035(4)
N1	C1	1.3729(13)	Li1	$Li1^1$	3.165(4)

^{1}-X,1-Y,-Z; ^{2}-X,+Y,1/2-Z

Table S10 Bond Angles for **2**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N4	O2	Li1	135.29(8)	O3	Li1	N2	174.27(11)
Li1	O3	Li1[1]	94.18(8)	O3	Li1	Li1[1]	46.10(5)
Li1	O4	Li1[2]	89.41(8)	O3[1]	Li1	Li1[1]	39.71(5)
N1[2]	N1	C1	118.78(6)	O3[1]	Li1	Li1[2]	125.38(10)
N2[2]	N2	Li1	109.37(6)	O3	Li1	Li1[2]	120.50(6)
C1	N2	N2[2]	118.60(6)	O4[2]	Li1	O2	164.75(10)
C1	N2	Li1	129.98(9)	O4	Li1	O2	94.00(8)
N4	N3	C1	119.29(8)	O4	Li1	O3[1]	169.38(10)
O1	N4	O2	119.84(8)	O4[2]	Li1	O3[1]	92.01(8)
O1	N4	N3	114.76(8)	O4	Li1	O4[2]	82.92(8)
O2	N4	N3	125.41(9)	O4	Li1	N2	81.40(7)
N2	C1	N1	122.44(9)	O4	Li1	Li1[1]	149.47(12)
N2	C1	N3	127.24(9)	O4[2]	Li1	Li1[2]	45.12(6)
N3	C1	N1	110.31(8)	O4[2]	Li1	Li1[1]	92.93(9)
O2	Li1	O3[1]	88.45(8)	O4	Li1	Li1[2]	45.47(6)
O2	Li1	Li1[1]	97.11(9)	N2	Li1	O2	73.76(7)
O2	Li1	Li1[2]	124.13(10)	N2	Li1	O3[1]	89.40(7)
O3	Li1	O2	102.93(9)	N2	Li1	O4[2]	91.00(8)
O3	Li1	O3[1]	85.82(8)	N2	Li1	Li1[1]	129.04(11)
O3	Li1	O4[2]	92.31(8)	N2	Li1	Li1[2]	64.97(6)
O3	Li1	O4	103.65(9)	Li1[2]	Li1	Li1[1]	138.03(13)

[1]-X,1-Y,-Z; [2]-X,+Y,1/2-Z

Table S11 Torsion Angles for **2**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N1[1]	N1	C1	N2	-0.22(17)	C1	N3	N4	O1	-174.78(8)
N1[1]	N1	C1	N3	-178.89(11)	C1	N3	N4	O2	5.02(15)
N2[1]	N2	C1	N1	-4.62(17)	Li1	O2	N4	O1	-161.26(10)
N2[1]	N2	C1	N3	173.82(10)	Li1	O2	N4	N3	18.95(17)
N4	N3	C1	N1	176.86(8)	Li1	N2	C1	N1	157.26(10)
N4	N3	C1	N2	-1.73(15)	Li1	N2	C1	N3	-24.31(17)

[1]-X,+Y,1/2-Z

Table S12 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **2**.

Atom	*x*	*y*	*z*	U(eq.)
H3A	2082	3854	258	19
H3B	234	3706	675	19
H4A	2663	4372	3063	17
H4B	3343	5232	3370	17

Table S13 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **3**. $U_{eq.}$ is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq.)
O3	2543(3)	4477.5(13)	7176(4)	21.0(4)
O4	1595(3)	5706.7(13)	8615(4)	18.8(4)
O1	0	4165.2(19)	0	18.1(5)
Na1	2714.3(13)	3313.7(6)	4132.0(18)	16.4(3)
O2	5912(3)	2924.5(14)	8199(3)	19.2(4)
N1	2360(3)	5444.2(15)	7484(4)	13.5(4)
N2	2905(3)	6258.0(15)	6752(4)	14.6(4)
N3	4476(3)	7040.6(17)	5406(4)	16.8(4)
N4	4433(3)	5124.8(16)	5373(4)	15.8(4)
C1	3946(3)	6071.6(17)	5801(5)	13.0(5)

Table S14 Anisotropic Displacement Parameters (Å^2×10^3) for **3**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O3	33.3(10)	10.5(8)	30.5(10)	0.2(8)	25.5(8)	1.2(8)
O4	25.3(9)	17.8(9)	25.6(9)	1.2(7)	22.0(8)	1.5(7)
O1	19.0(12)	17.5(12)	21.8(12)	0	14.9(10)	0
Na1	19.3(5)	12.5(5)	20.3(5)	0.3(4)	13.9(4)	-0.6(3)
O2	25.1(9)	14.1(8)	18.6(8)	1.9(7)	13.8(8)	3.9(7)
N1	13.5(10)	13.9(10)	13.1(9)	0.3(8)	8.4(8)	0.5(8)
N2	17.6(10)	11.7(10)	20.3(10)	1.8(8)	14.6(9)	1.0(8)
N3	21.8(10)	12.0(11)	23.7(10)	-0.1(8)	17.8(9)	0.0(8)
N4	17.1(10)	13.7(10)	22.3(11)	0.8(8)	15.3(9)	0.9(8)
C1	12.6(10)	10.4(10)	14(1)	0.6(9)	7.5(9)	0.7(9)

Table S15 Bond Lengths for **3**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O3	Na1	2.4311(18)	Na1	N4	2.556(2)
O3	N1	1.246(3)	O2	Na1[2]	2.4285(18)
O4	N1	1.275(2)	N1	N2	1.316(3)
O1	Na1[1]	2.3641(17)	N2	Na1[4]	2.605(2)
O1	Na1	2.3641(17)	N2	C1	1.382(3)
Na1	Na1[2]	3.4769(19)	N3	Na1[4]	2.654(2)
Na1	O2	2.350(2)	N3	N3[2]	1.298(4)
Na1	O2[2]	2.4286(18)	N3	C1	1.371(3)
Na1	N2[3]	2.605(2)	N4	N4[2]	1.337(4)
Na1	N3[3]	2.654(2)	N4	C1	1.337(3)

[1]-X,+Y,-Z; [2]1-X,+Y,1-Z; [3]1/2-X,-1/2+Y,1-Z; [4]1/2-X,1/2+Y,1-Z

Table S16 Bond Angles for **3**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	O3	Na1	140.19(14)	O2[2]	Na1	N4	85.70(7)
Na1	O1	Na1[1]	126.62(11)	N2[3]	Na1	Na1[2]	96.64(5)
O3	Na1	Na1[2]	112.89(6)	N2[3]	Na1	N3[3]	50.26(6)
O3	Na1	N2[3]	129.66(7)	N3[3]	Na1	Na1[2]	139.06(5)
O3	Na1	N3[3]	82.85(7)	N4	Na1	Na1[2]	63.19(5)
O3	Na1	N4	63.86(6)	N4	Na1	N2[3]	159.82(7)
O1	Na1	O3	91.78(7)	N4	Na1	N3[3]	146.66(7)
O1	Na1	Na1[2]	121.96(5)	Na1	O2	Na1[2]	93.36(6)
O1	Na1	O2[2]	90.96(5)	O3	N1	O4	119.51(18)
O1	Na1	N2[3]	106.40(8)	O3	N1	N2	125.83(18)
O1	Na1	N3[3]	93.51(7)	O4	N1	N2	114.66(18)
O1	Na1	N4	86.16(7)	N1	N2	Na1[4]	138.96(14)
O2	Na1	O3	86.26(7)	N1	N2	C1	119.70(18)
O2[2]	Na1	O3	149.16(7)	C1	N2	Na1[4]	100.84(13)
O2	Na1	O1	162.09(7)	N3[2]	N3	Na1[4]	141.79(7)
O2	Na1	Na1[2]	44.21(5)	N3[2]	N3	C1	118.17(12)
O2[2]	Na1	Na1[2]	42.43(5)	C1	N3	Na1[4]	98.96(13)
O2	Na1	O2[2]	81.88(7)	N4[2]	N4	Na1	109.51(8)
O2	Na1	N2[3]	88.32(7)	C1	N4	Na1	129.25(15)
O2[2]	Na1	N2[3]	78.50(6)	C1	N4	N4[2]	117.95(12)
O2	Na1	N3[3]	103.88(7)	N3	C1	N2	108.47(18)
O2[2]	Na1	N3[3]	127.62(7)	N4	C1	N2	127.69(19)
O2	Na1	N4	77.00(7)	N4	C1	N3	123.83(19)

[1]-X,+Y,-Z; [2]1-X,+Y,1-Z; [3]1/2-X,-1/2+Y,1-Z; [4]1/2-X,1/2+Y,1-Z

Table S17 Torsion Angles for **3**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O3	N1	N2	Na1[1]	163.22(18)	Na1[1]	N3	C1	N4	170.10(19)
O3	N1	N2	C1	-6.8(3)	Na1	N4	C1	N2	27.3(3)
O4	N1	N2	Na1[1]	-17.2(3)	Na1	N4	C1	N3	-154.44(17)
O4	N1	N2	C1	172.8(2)	N1	N2	C1	N3	-175.0(2)
Na1	O3	N1	O4	152.68(17)	N1	N2	C1	N4	3.4(3)
Na1	O3	N1	N2	-27.7(4)	N3[2]	N3	C1	N2	177.9(2)
Na1[1]	N2	C1	N3	11.67(19)	N3[2]	N3	C1	N4	-0.6(4)
Na1[1]	N2	C1	N4	-169.9(2)	N4[2]	N4	C1	N2	-175.5(2)
Na1[1]	N3	C1	N2	-11.39(19)	N4[2]	N4	C1	N3	2.8(4)

[1]1/2-X,1/2+Y,1-Z; [2]1-X,+Y,1-Z

Table S18 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **3**.

Atom	*x*	*y*	*z*	U(eq)
H1	423	4624	-504	22
H2A	6444	3296	9671	23
H2B	6229	2278	8633	23

Table S19 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **4**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq.)
K1	4848.9(2)	7500	7500	22.90(19)
K2	2937.3(3)	7500	7500	37.2(2)
O1	3868.9(6)	6374.8(18)	5070(3)	23.9(3)
O2	4494.2(5)	5352.2(18)	2306(3)	22.5(3)
O3	2500	5000	4064(5)	32.1(5)
N4	4003.4(6)	5477(2)	2979(3)	17.7(3)
N3	3596.8(6)	4732(2)	1662(4)	19.2(4)
N2	3209.3(6)	3060(2)	-1510(4)	21.1(4)
N1	4179.2(7)	3064(2)	-1435(4)	23.9(4)
C1	3701.0(7)	3608(2)	-491(4)	16.8(4)

Table S20 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **4**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
K1	14.5(3)	26.3(3)	27.8(4)	-4.0(3)	0	0
K2	15.2(3)	46.3(5)	50.2(5)	-17.4(4)	0	0
O1	24.3(7)	25.6(7)	21.8(7)	-8.6(6)	4.5(6)	-1.1(6)
O2	13.1(6)	24.6(7)	29.9(8)	-6.2(6)	1.7(5)	0.0(5)
O3	19.5(10)	44.0(13)	33.0(12)	0	0	7.9(9)
N4	17.0(7)	16.2(7)	20.0(8)	-0.4(6)	1.3(6)	0.2(6)
N3	14.1(7)	21.0(8)	22.4(8)	-4.4(7)	2.4(6)	-2.0(6)
N2	14.6(7)	26.5(8)	22.3(8)	-4.3(7)	-1.0(6)	0.0(6)
N1	16.2(7)	28.2(8)	27.3(9)	-11.0(8)	0.0(7)	-0.9(7)
C1	15.7(8)	16.8(8)	17.8(9)	2.7(7)	0.2(7)	-0.2(7)

Table S21 Bond Lengths for **4.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
K1	O1	2.8089(16)	K2	N3[5]	3.3741(18)
K1	O1[1]	2.8090(15)	K2	N3[2]	3.3741(18)
K1	O2	3.1145(15)	K2	N2[9]	2.8832(18)
K1	O2[1]	3.1145(15)	K2	N2[10]	2.8832(18)
K1	O2[2]	2.9732(16)	O1	N4	1.263(2)
K1	O2[3]	2.8006(15)	O2	K1[11]	2.9732(16)
K1	O2[4]	2.8006(15)	O2	K1[4]	2.8005(15)
K1	O2[5]	2.9732(16)	O2	N4	1.248(2)
K1	N4[1]	3.3843(17)	O3	K2[6]	2.7909(14)
K1	N4	3.3842(17)	N4	N3	1.317(2)
K1	N1[4]	3.0503(19)	N3	K2[11]	3.3741(18)
K1	N1[3]	3.0503(18)	N3	C1	1.380(2)
K2	K2[6]	4.5505(10)	N2	K2[12]	2.8833(18)
K2	K2[5]	4.7044(9)	N2	N2[13]	1.294(3)
K2	K2[7]	4.5505(10)	N2	C1	1.370(2)
K2	O1[1]	2.7082(15)	N1	K1[4]	3.0502(18)
K2	O1	2.7083(15)	N1	N1[13]	1.351(3)
K2	O3[8]	2.7909(14)	N1	C1	1.327(2)
K2	O3	2.7909(14)			

[1]+X,3/2-Y,3/2-Z; [2]+X,3/2-Y,1/2-Z; [3]1-X,1/2+Y,1/2+Z; [4]1-X,1-Y,1-Z; [5]+X,+Y,1+Z; [6]1/2-X,1-Y,+Z; [7]1/2-X,2-Y,+Z; [8]1/2-X,1/2+Y,3/2-Z; [9]1/2-X,1/2+Y,1/2-Z; [10]1/2-X,1-Y,1+Z; [11]+X,+Y,-1+Z; [12]1/2-X,1-Y,-1+Z; [13]+X,1/2-Y,-1/2-Z

Table S22 Bond Angles for **4.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	K1	O1[1]	62.49(6)	O1[1]	K2	O1	65.09(6)
O1	K1	O2	42.61(4)	O1	K2	O3[8]	143.90(4)
O1	K1	O2[2]	82.70(4)	O1[1]	K2	O3[8]	80.76(4)
O1[1]	K1	O2[2]	68.11(4)	O1[1]	K2	O3	143.90(4)
O1[1]	K1	O2[1]	42.61(4)	O1	K2	O3	80.76(4)
O1	K1	O2[1]	104.99(4)	O1[1]	K2	N3[3]	67.75(5)
O1[1]	K1	O2	104.99(4)	O1[1]	K2	N3[2]	64.60(4)
O1	K1	O2[3]	68.11(4)	O1	K2	N3[3]	64.60(4)
O1[1]	K1	O2[3]	82.70(4)	O1	K2	N3[2]	67.75(5)
O1[1]	K1	N4	83.49(4)	O1	K2	N2[9]	146.90(5)
O1[1]	K1	N4[1]	21.01(4)	O1[1]	K2	N2[9]	143.63(5)
O1	K1	N4[1]	83.49(4)	O1[1]	K2	N2[10]	146.90(5)
O1	K1	N4	21.01(4)	O1	K2	N2[10]	143.64(5)
O1	K1	N1[4]	150.09(5)	O3[8]	K2	K1	112.579(18)
O1[1]	K1	N1[5]	150.09(5)	O3	K2	K1	112.578(18)
O1[1]	K1	N1[4]	117.93(4)	O3[8]	K2	K2[2]	54.61(4)
O1	K1	N1[5]	117.93(4)	O3	K2	K2[6]	35.39(4)
O2[4]	K1	O1[1]	137.83(4)	O3	K2	K2[7]	116.97(3)
O2[5]	K1	O1[1]	103.99(4)	O3[8]	K2	K2[7]	35.39(4)
O2[4]	K1	O1	103.99(4)	O3	K2	K2[2]	125.39(4)
O2[5]	K1	O1	137.83(4)	O3[8]	K2	K2[6]	116.97(3)
O2[4]	K1	O2[3]	131.84(5)	O3[8]	K2	O3	134.84(4)
O2[3]	K1	O2	69.08(5)	O3	K2	N3[3]	108.76(5)
O2[5]	K1	O2[1]	74.54(5)	O3	K2	N3[2]	92.65(4)
O2[5]	K1	O2[4]	109.83(6)	O3[8]	K2	N3[2]	108.76(5)
O2[2]	K1	O2	101.18(4)	O3[8]	K2	N3[3]	92.65(4)
O2[4]	K1	O2[2]	70.67(5)	O3[8]	K2	N2[10]	66.88(4)
O2	K1	O2[1]	147.59(5)	O3	K2	N2[10]	69.17(4)
O2[4]	K1	O2[1]	125.98(5)	O3	K2	N2[9]	66.88(4)
O2[3]	K1	O2[2]	146.00(6)	O3[8]	K2	N2[9]	69.17(4)
O2[2]	K1	O2[1]	69.08(5)	N3[3]	K2	K1	61.38(3)
O2[5]	K1	O2[3]	70.67(5)	N3[2]	K2	K1	61.38(3)
O2[5]	K1	O2	125.98(5)	N3[3]	K2	K2[2]	125.47(3)
O2[3]	K1	O2[1]	101.18(4)	N3[3]	K2	K2[7]	69.18(3)
O2[5]	K1	O2[2]	131.84(5)	N3[2]	K2	K2[7]	143.77(3)
O2[4]	K1	O2	74.54(5)	N3[3]	K2	K2[6]	143.77(3)
O2[5]	K1	N4	136.36(4)	N3[2]	K2	K2[2]	54.53(3)
O2	K1	N4	21.63(4)	N3[2]	K2	K2[6]	69.18(3)

O2^{2}	K1	N4	91.18(4)	N3^{3}	K2	N3^{2}	122.76(6)
O2^{2}	K1	N4^{1}	67.75(4)	N2^{10}	K2	K1	167.03(3)
O2^{1}	K1	N4	126.00(4)	N2^{9}	K2	K1	167.03(3)
O2^{4}	K1	N4^{1}	136.36(4)	N2^{10}	K2	K2^{6}	71.25(4)
O2	K1	N4^{1}	126.00(4)	N2^{9}	K2	K2^{2}	80.70(3)
O2^{1}	K1	N4^{1}	21.63(4)	N2^{10}	K2	K2^{7}	53.39(4)
O2^{5}	K1	N4^{1}	88.86(4)	N2^{9}	K2	K2^{6}	53.39(4)
O2^{3}	K1	N4	67.75(4)	N2^{9}	K2	K2^{7}	71.25(4)
O2^{3}	K1	N4^{1}	91.18(4)	N2^{10}	K2	K2^{2}	99.30(3)
O2^{4}	K1	N4	88.86(4)	N2^{10}	K2	N3^{2}	131.54(5)
O2^{3}	K1	N1^{4}	140.88(5)	N2^{9}	K2	N3^{2}	105.69(4)
O2^{2}	K1	N1^{5}	140.88(5)	N2^{9}	K2	N3^{3}	131.54(5)
O2^{5}	K1	N1^{5}	53.84(5)	N2^{10}	K2	N3^{3}	105.69(4)
O2^{5}	K1	N1^{4}	72.08(5)	N2^{10}	K2	N2^{9}	25.94(7)
O2^{4}	K1	N1^{4}	53.84(5)	K2	O1	K1	116.21(5)
O2^{4}	K1	N1^{5}	72.08(5)	N4	O1	K1	106.10(10)
O2^{2}	K1	N1^{4}	71.39(5)	N4	O1	K2	137.64(11)
O2^{3}	K1	N1^{5}	71.39(5)	K1^{11}	O2	K1	101.18(4)
N4	K1	N4^{1}	104.50(6)	K1^{4}	O2	K1^{11}	109.33(5)
N1^{5}	K1	O2	79.86(4)	K1^{4}	O2	K1	105.47(5)
N1^{4}	K1	O2^{1}	79.86(4)	N4	O2	K1	91.44(11)
N1^{4}	K1	O2	127.72(4)	N4	O2	K1^{4}	127.71(12)
N1^{5}	K1	O2^{1}	127.73(4)	N4	O2	K1^{11}	115.35(12)
N1^{5}	K1	N4^{1}	142.02(4)	K2	O3	K2^{6}	109.22(8)
N1^{4}	K1	N4^{1}	99.67(4)	O1	N4	K1	52.89(9)
N1^{5}	K1	N4	99.67(4)	O1	N4	N3	115.36(15)
N1^{4}	K1	N4	142.02(4)	O2	N4	K1	66.93(10)
N1^{4}	K1	N1^{5}	77.32(7)	O2	N4	O1	119.68(16)
K1	K2	K2^{2}	90.0	O2	N4	N3	124.96(16)
K2^{6}	K2	K1	118.098(16)	N3	N4	K1	167.64(12)
K2^{7}	K2	K1	118.098(16)	N4	N3	K2^{11}	109.63(11)
K2^{7}	K2	K2^{2}	90.0	N4	N3	C1	120.15(16)
K2^{6}	K2	K2^{2}	90.0	C1	N3	K2^{11}	95.37(11)
K2^{6}	K2	K2^{7}	123.80(3)	N2^{12}	N2	K2^{13}	77.03(3)
O1^{1}	K2	K1	32.54(3)	N2^{12}	N2	C1	118.36(11)
O1	K2	K1	32.54(3)	C1	N2	K2^{13}	164.59(13)
O1	K2	K2^{7}	133.73(3)	N1^{12}	N1	K1^{4}	110.54(10)
O1^{1}	K2	K2^{6}	133.73(3)	C1	N1	K1^{4}	122.37(13)
O1	K2	K2^{2}	114.96(3)	C1	N1	N1^{12}	117.96(11)
O1	K2	K2^{6}	95.90(3)	N2	C1	N3	107.70(16)

O1[1]	K2	K2[7]	95.90(3)	N1	C1	N3	128.61(17)
O1[1]	K2	K2[2]	65.03(3)	N1	C1	N2	123.65(17)

[1]+X,3/2-Y,3/2-Z; [2]+X,+Y,1+Z; [3]+X,3/2-Y,1/2-Z; [4]1-X,1-Y,1-Z; [5]1-X,1/2+Y,1/2+Z; [6]1/2-X,1-Y,+Z; [7]1/2-X,2-Y,+Z; [8]1/2-X,1/2+Y,3/2-Z; [9]1/2-X,1-Y,1+Z; [10]1/2-X,1/2+Y,1/2-Z; [11]+X,+Y,-1+Z; [12]+X,1/2-Y,-1/2-Z; [13]1/2-X,1-Y,-1+Z

Table S23 Torsion Angles for **4.**

A	B	C	D	Angle/°	A	B	C	D	Angle/°
K1	O1	N4	O2	-4.5(2)	K2	O1	N4	N3	-7.3(3)
K1	O1	N4	N3	175.50(13)	K2[1]	N3	C1	N2	-62.27(14)
K1[1]	O2	N4	K1	-103.10(8)	K2[1]	N3	C1	N1	119.8(2)
K1[2]	O2	N4	K1	110.90(12)	K2[3]	N2	C1	N3	-0.3(6)
K1[1]	O2	N4	O1	-99.22(17)	K2[3]	N2	C1	N1	177.7(4)
K1	O2	N4	O1	3.88(17)	O1	N4	N3	K2[1]	76.92(16)
K1[2]	O2	N4	O1	114.78(16)	O1	N4	N3	C1	-174.29(16)
K1[2]	O2	N4	N3	-65.2(2)	O2	N4	N3	K2[1]	-103.10(18)
K1[1]	O2	N4	N3	80.81(19)	O2	N4	N3	C1	5.7(3)
K1	O2	N4	N3	-176.09(17)	N4	N3	C1	N2	-178.68(17)
K1	N4	N3	K2[1]	93.9(6)	N4	N3	C1	N1	3.4(3)
K1	N4	N3	C1	-157.3(5)	N2[4]	N2	C1	N3	-177.5(2)
K1[2]	N1	C1	N3	35.4(3)	N2[4]	N2	C1	N1	0.5(3)
K1[2]	N1	C1	N2	-142.14(15)	N1[4]	N1	C1	N3	179.2(2)
K2	O1	N4	K1	177.2(2)	N1[4]	N1	C1	N2	1.6(4)
K2	O1	N4	O2	172.71(13)					

[1]+X,+Y,-1+Z; [2]1-X,1-Y,1-Z; [3]1/2-X,1-Y,-1+Z; [4]+X,1/2-Y,-1/2-Z

Table S24 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **4.**

Atom	*x*	*y*	*z*	U(eq)
H3	2236	5324	3068	39

Table S25 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **5**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq.)
Rb1	0	466.7(5)	2500	14.8(2)
Rb2	0	4568.0(5)	2500	18.9(2)
O1	1946(4)	2435(3)	3076(5)	19.6(9)
O2	3569(4)	3821(3)	4135(4)	16.4(8)
N1	3331(5)	2782(4)	3752(5)	13.7(8)
N4	8033(5)	3583(3)	4887(5)	17.7(9)
N3	6512(5)	3420(4)	4432(5)	18.7(10)
N2	4450(5)	1972(3)	4014(5)	16.0(9)
C1	5998(6)	2334(4)	4548(6)	13.1(10)

Table S26 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **5**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rb1	21.0(4)	9.4(4)	13.3(4)	0	5.5(3)	0
Rb2	20.6(4)	12.8(4)	23.1(4)	0	7.5(3)	0
O1	10.9(19)	21(2)	24(2)	0.7(14)	3.0(18)	-7.2(13)
O2	20.7(19)	12.4(15)	18.8(18)	-2.3(14)	10.2(15)	-0.3(14)
N1	20(2)	18.3(19)	4.6(19)	0.4(16)	5.9(17)	-2.0(18)
N4	20(2)	13.4(19)	20(2)	4.3(17)	6.9(19)	-0.3(17)
N3	17(2)	18(2)	21(2)	2.6(18)	7.0(19)	-0.4(18)
N2	22(2)	11.3(19)	14(2)	-0.1(16)	6.0(18)	4.7(17)
C1	11(2)	16(2)	13(3)	-0.1(19)	5(2)	0.7(18)

Table S27 Bond Lengths for **5.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Rb1	$Rb2^1$	4.6687(9)	Rb2	$N4^{10}$	3.218(4)
Rb1	$Rb2^2$	4.6687(9)	Rb2	$N2^{11}$	3.207(4)
Rb1	$O1^3$	2.806(3)	Rb2	$N2^{12}$	3.207(4)
Rb1	O1	2.806(3)	O1	N1	1.256(6)
Rb1	$O2^4$	2.979(3)	O2	$Rb1^{13}$	2.979(3)
Rb1	$O2^5$	2.987(4)	O2	$Rb1^5$	2.987(4)
Rb1	$O2^2$	2.979(3)	O2	N1	1.241(5)
Rb1	$O2^6$	2.987(4)	N1	N2	1.338(6)
Rb1	$N4^2$	3.574(4)	N4	$Rb1^{13}$	3.574(4)
Rb1	$N4^4$	3.574(4)	N4	$Rb2^{14}$	3.463(4)

Rb1	N3[2]	2.967(4)	N4	Rb2[9]	3.218(4)
Rb1	N3[4]	2.967(4)	N4	N3	1.311(6)
Rb2	O1[3]	2.961(3)	N4	C1[15]	1.353(6)
Rb2	O1	2.961(3)	N3	Rb1[13]	2.967(4)
Rb2	O2	3.174(4)	N3	C1	1.350(6)
Rb2	O2[3]	3.174(4)	N2	Rb2[5]	3.512(4)
Rb2	N1	3.500(4)	N2	Rb2[1]	3.207(4)
Rb2	N1[3]	3.500(4)	N2	C1	1.382(7)
Rb2	N4[7]	3.463(4)	C1	Rb2[1]	3.635(5)
Rb2	N4[8]	3.463(4)	C1	N4[15]	1.353(6)
Rb2	N4[9]	3.218(4)			

[1]1/2+X,-1/2+Y,+Z; [2]-1/2+X,-1/2+Y,+Z; [3]-X,+Y,1/2-Z; [4]1/2-X,-1/2+Y,1/2-Z; [5]1/2-X,1/2-Y,1-Z; [6]-1/2+X,1/2-Y,-1/2+Z; [7]-1+X,+Y,+Z; [8]1-X,+Y,1/2-Z; [9]1-X,1-Y,1-Z; [10]-1+X,1-Y,-1/2+Z; [11]1/2-X,1/2+Y,1/2-Z; [12]-1/2+X,1/2+Y,+Z; [13]1/2+X,1/2+Y,+Z; [14]1+X,+Y,+Z; [15]3/2-X,1/2-Y,1-Z

Table S28 Bond Angles for **5.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Rb2[1]	Rb1	Rb2[2]	154.43(2)	O1	Rb2	N2[12]	127.92(11)
O1	Rb1	Rb2[1]	136.84(8)	O2[3]	Rb2	O2	148.61(11)
O1[3]	Rb1	Rb2[1]	68.13(8)	O2	Rb2	N1[3]	128.18(9)
O1	Rb1	Rb2[2]	68.13(8)	O2[3]	Rb2	N1	128.18(9)
O1[3]	Rb1	Rb2[2]	136.84(8)	O2[3]	Rb2	N1[3]	20.70(9)
O1	Rb1	O1[3]	72.51(15)	O2	Rb2	N1	20.70(9)
O1	Rb1	O2[4]	89.22(11)	O2	Rb2	N4[10]	67.94(10)
O1	Rb1	O2[1]	141.09(11)	O2	Rb2	N4[7]	106.80(9)
O1[3]	Rb1	O2[5]	89.22(11)	O2[3]	Rb2	N4[8]	106.80(9)
O1	Rb1	O2[6]	104.24(10)	O2	Rb2	N4[9]	137.14(10)
O1[3]	Rb1	O2[1]	104.24(10)	O2[3]	Rb2	N4[9]	67.94(10)
O1[3]	Rb1	O2[6]	141.09(11)	O2[3]	Rb2	N4[7]	62.23(9)
O1	Rb1	O2[5]	64.63(11)	O2[3]	Rb2	N4[10]	137.14(10)
O1[3]	Rb1	O2[4]	64.63(11)	O2	Rb2	N4[8]	62.22(9)
O1	Rb1	N4[6]	154.46(11)	O2[3]	Rb2	N2[12]	108.79(10)
O1[3]	Rb1	N4[6]	94.31(10)	O2	Rb2	N2[12]	98.29(10)
O1[3]	Rb1	N4[1]	154.46(11)	O2[3]	Rb2	N2[11]	98.29(10)
O1	Rb1	N4[1]	94.31(10)	O2	Rb2	N2[11]	108.79(10)
O1[3]	Rb1	N3[1]	151.53(13)	N1[3]	Rb2	N1	108.19(14)
O1[3]	Rb1	N3[6]	113.57(12)	N4[7]	Rb2	N1[3]	55.32(10)
O1	Rb1	N3[1]	113.57(12)	N4[8]	Rb2	N1	55.32(10)
O1	Rb1	N3[6]	151.53(13)	N4[7]	Rb2	N1	100.68(10)
O2[6]	Rb1	Rb2[1]	117.35(7)	N4[10]	Rb2	N1[3]	144.88(10)

O2^{4}	Rb1	Rb2^{2}	97.45(7)	N4^{9}	Rb2	N1^{3}	87.52(10)
O2^{5}	Rb1	Rb2^{2}	89.52(7)	N4^{8}	Rb2	N1^{3}	100.68(10)
O2^{1}	Rb1	Rb2^{2}	117.35(7)	N4^{9}	Rb2	N1	144.88(10)
O2^{5}	Rb1	Rb2^{1}	97.45(7)	N4^{10}	Rb2	N1	87.53(10)
O2^{6}	Rb1	Rb2^{2}	42.22(7)	N4^{10}	Rb2	N4^{8}	113.86(13)
O2^{1}	Rb1	Rb2^{1}	42.22(7)	N4^{10}	Rb2	N4^{7}	91.58(10)
O2^{4}	Rb1	Rb2^{1}	89.52(7)	N4^{9}	Rb2	N4^{8}	91.58(10)
O2^{6}	Rb1	O2^{4}	76.67(10)	N4^{8}	Rb2	N4^{7}	141.83(14)
O2^{1}	Rb1	O2^{5}	76.67(10)	N4^{9}	Rb2	N4^{7}	113.86(13)
O2^{1}	Rb1	O2^{4}	125.35(11)	N4^{10}	Rb2	N4^{9}	97.32(15)
O2^{6}	Rb1	O2^{1}	101.16(12)	N2^{11}	Rb2	N1^{3}	113.31(10)
O2^{6}	Rb1	O2^{5}	125.35(11)	N2^{12}	Rb2	N1	113.31(10)
O2^{5}	Rb1	O2^{4}	148.19(12)	N2^{12}	Rb2	N1^{3}	127.96(10)
O2^{5}	Rb1	N4^{6}	138.66(10)	N2^{11}	Rb2	N1	127.96(10)
O2^{1}	Rb1	N4^{1}	72.05(9)	N2^{12}	Rb2	N4^{8}	79.44(10)
O2^{4}	Rb1	N4^{1}	138.66(10)	N2^{12}	Rb2	N4^{9}	40.85(11)
O2^{1}	Rb1	N4^{6}	62.52(10)	N2^{12}	Rb2	N4^{7}	138.32(10)
O2^{6}	Rb1	N4^{1}	62.52(10)	N2^{11}	Rb2	N4^{9}	67.53(10)
O2^{5}	Rb1	N4^{1}	65.25(9)	N2^{11}	Rb2	N4^{7}	79.44(10)
O2^{4}	Rb1	N4^{6}	65.25(9)	N2^{11}	Rb2	N4^{8}	138.32(10)
O2^{6}	Rb1	N4^{6}	72.05(9)	N2^{11}	Rb2	N4^{10}	40.85(11)
N4^{6}	Rb1	Rb2^{1}	47.42(7)	N2^{12}	Rb2	N4^{10}	67.53(10)
N4^{6}	Rb1	Rb2^{2}	114.10(7)	N2^{11}	Rb2	N2^{12}	60.96(15)
N4^{1}	Rb1	Rb2^{2}	47.42(7)	Rb1	O1	Rb2	109.66(13)
N4^{1}	Rb1	Rb2^{1}	114.10(7)	N1	O1	Rb1	143.6(3)
N4^{6}	Rb1	N4^{1}	105.40(13)	N1	O1	Rb2	104.9(3)
N3^{1}	Rb1	Rb2^{2}	65.04(8)	Rb1^{13}	O2	Rb1^{5}	103.33(10)
N3^{1}	Rb1	Rb2^{1}	94.07(8)	Rb1^{13}	O2	Rb2	98.67(10)
N3^{6}	Rb1	Rb2^{1}	65.04(8)	Rb1^{5}	O2	Rb2	114.02(11)
N3^{6}	Rb1	Rb2^{2}	94.07(8)	N1	O2	Rb1^{5}	121.4(3)
N3^{6}	Rb1	O2^{6}	52.63(10)	N1	O2	Rb1^{13}	122.3(3)
N3^{1}	Rb1	O2^{6}	66.42(11)	N1	O2	Rb2	94.6(3)
N3^{6}	Rb1	O2^{1}	66.42(11)	O1	N1	Rb2	54.8(2)
N3^{1}	Rb1	O2^{5}	70.60(11)	O1	N1	N2	115.7(4)
N3^{6}	Rb1	O2^{5}	140.07(11)	O2	N1	Rb2	64.7(2)
N3^{1}	Rb1	O2^{4}	140.07(11)	O2	N1	O1	119.3(4)
N3^{1}	Rb1	O2^{1}	52.63(10)	O2	N1	N2	125.0(4)
N3^{6}	Rb1	O2^{4}	70.60(11)	N2	N1	Rb2	169.4(3)
N3^{1}	Rb1	N4^{6}	88.58(11)	Rb2^{10}	N4	Rb1^{13}	98.96(11)
N3^{1}	Rb1	N4^{1}	20.55(10)	Rb2^{14}	N4	Rb1^{13}	83.12(9)

N3[6]	Rb1	N4[1]	88.58(11)	Rb2[10]	N4	Rb2[14]	88.42(10)
N3[6]	Rb1	N4[6]	20.55(10)	N3	N4	Rb1[13]	52.6(2)
N3[6]	Rb1	N3[1]	75.06(17)	N3	N4	Rb2[14]	125.0(3)
O1	Rb2	O1[3]	68.17(14)	N3	N4	Rb2[10]	125.1(3)
O1[3]	Rb2	O2	107.91(9)	N3	N4	C1[15]	118.8(4)
O1	Rb2	O2[3]	107.91(9)	C1[15]	N4	Rb1[13]	164.0(3)
O1[3]	Rb2	O2[3]	40.93(9)	C1[15]	N4	Rb2[10]	96.8(3)
O1	Rb2	O2	40.93(9)	C1[15]	N4	Rb2[14]	94.6(3)
O1[3]	Rb2	N1	88.08(10)	N4	N3	Rb1[13]	106.8(3)
O1	Rb2	N1	20.29(9)	N4	N3	C1	117.6(4)
O1	Rb2	N1[3]	88.08(10)	C1	N3	Rb1[13]	132.8(3)
O1[3]	Rb2	N1[3]	20.29(9)	Rb2[2]	N2	Rb2[5]	87.74(9)
O1[3]	Rb2	N4[7]	55.23(11)	N1	N2	Rb2[5]	111.5(3)
O1[3]	Rb2	N4[8]	91.64(10)	N1	N2	Rb2[2]	138.5(3)
O1	Rb2	N4[9]	144.93(11)	N1	N2	C1	118.0(4)
O1	Rb2	N4[8]	55.23(11)	C1	N2	Rb2[5]	92.0(3)
O1	Rb2	N4[10]	106.00(11)	C1	N2	Rb2[2]	96.6(3)
O1	Rb2	N4[7]	91.64(10)	N4[15]	C1	Rb2[2]	61.5(3)
O1[3]	Rb2	N4[9]	106.00(11)	N4[15]	C1	N2	110.1(4)
O1[3]	Rb2	N4[10]	144.93(11)	N3	C1	Rb2[2]	143.0(4)
O1[3]	Rb2	N2[11]	127.92(11)	N3	C1	N4[15]	123.6(5)
O1	Rb2	N2[11]	144.38(11)	N3	C1	N2	126.1(4)
O1[3]	Rb2	N2[12]	144.38(11)	N2	C1	Rb2[2]	61.2(2)

[1]-1/2+X,-1/2+Y,+Z; [2]1/2+X,-1/2+Y,+Z; [3]-X,+Y,1/2-Z; [4]-1/2+X,1/2-Y,-1/2+Z; [5]1/2-X,1/2-Y,1-Z; [6]1/2-X,-1/2+Y,1/2-Z; [7]-1+X,+Y,+Z; [8]1-X,+Y,1/2-Z; [9]-1+X,1-Y,-1/2+Z; [10]1-X,1-Y,1-Z; [11]-1/2+X,1/2+Y,+Z; [12]1/2-X,1/2+Y,1/2-Z; [13]1/2+X,1/2+Y,+Z; [14]1+X,+Y,+Z; [15]3/2-X,1/2-Y,1-Z

Table S29 Torsion Angles for **5.**

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Rb1	O1	N1	Rb2	-161.5(6)	Rb2[5]	N4	N3	C1	119.4(4)
Rb1	O1	N1	O2	-155.5(4)	Rb2[6]	N4	N3	C1	-123.8(4)
Rb1	O1	N1	N2	24.1(8)	Rb2[1]	N2	C1	Rb2[3]	87.95(12)
Rb1[1]	O2	N1	Rb2	121.9(3)	Rb2[1]	N2	C1	N4[4]	49.3(4)
Rb1[2]	O2	N1	Rb2	-103.3(3)	Rb2[3]	N2	C1	N4[4]	-38.7(4)
Rb1[1]	O2	N1	O1	116.4(4)	Rb2[3]	N2	C1	N3	136.7(5)
Rb1[2]	O2	N1	O1	-108.7(4)	Rb2[1]	N2	C1	N3	-135.4(5)
Rb1[2]	O2	N1	N2	71.8(5)	O1	N1	N2	Rb2[1]	-84.5(4)
Rb1[1]	O2	N1	N2	-63.0(5)	O1	N1	N2	Rb2[3]	28.0(7)
Rb1[2]	N4	N3	C1	163.5(6)	O1	N1	N2	C1	170.9(4)
Rb1[2]	N3	C1	Rb2[3]	72.7(7)	O2	N1	N2	Rb2[3]	-152.5(4)

Rb1[2]	N3	C1	N4[4]	158.7(4)	O2	N1	N2	Rb2[1]	95.0(4)
Rb1[2]	N3	C1	N2	-16.1(8)	O2	N1	N2	C1	-9.6(7)
Rb2	O1	N1	O2	6.0(5)	N1	N2	C1	Rb2[3]	-156.3(5)
Rb2	O1	N1	N2	-174.5(3)	N1	N2	C1	N4[4]	165.0(4)
Rb2	O2	N1	O1	-5.4(4)	N1	N2	C1	N3	-19.7(8)
Rb2	O2	N1	N2	175.1(4)	N4	N3	C1	Rb2[3]	-85.7(7)
Rb2	N1	N2	Rb2[1]	-109.9(16)	N4	N3	C1	N4[4]	0.4(8)
Rb2	N1	N2	Rb2[3]	3(2)	N4	N3	C1	N2	-174.4(5)
Rb2	N1	N2	C1	145.5(14)	C1[4]	N4	N3	Rb1[2]	-163.9(4)
Rb2[5]	N4	N3	Rb1[2]	-44.1(4)	C1[4]	N4	N3	C1	-0.3(8)
Rb2[6]	N4	N3	Rb1[2]	72.7(3)					

[1]1/2-X,1/2-Y,1-Z; [2]1/2+X,1/2+Y,+Z; [3]1/2+X,-1/2+Y,+Z; [4]3/2-X,1/2-Y,1-Z; [5]1+X,+Y,+Z; [6]1-X,1-Y,1-Z

Table S30 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **6**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq.)**
Cs1	12075.4(5)	958.6(4)	6969.3(4)	13.90(19)
O1	7303(8)	4635(7)	3679(6)	20.3(9)
O2	3808(9)	7467(7)	1655(7)	20.0(8)
N1	5070(9)	5414(8)	2600(7)	13.7(9)
N2	4247(9)	3940(7)	2549(7)	14.5(9)
N3	1538(9)	2877(8)	1397(8)	17.2(9)
N4	-482(9)	3208(8)	206(7)	14.7(9)
C1	1993(10)	4652(9)	1196(8)	13.1(10)

Table S31 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **6**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	$\mathbf{U_{11}}$	$\mathbf{U_{22}}$	$\mathbf{U_{33}}$	$\mathbf{U_{23}}$	$\mathbf{U_{13}}$	$\mathbf{U_{12}}$
Cs1	16.7(3)	10.1(3)	13.9(3)	-4.55(18)	-0.88(16)	-5.60(17)
O1	16.2(19)	26(2)	19(2)	-12.4(18)	-3.6(16)	-6.1(16)
O2	24(2)	10.7(19)	24(2)	-6.2(17)	-7.3(17)	-7.0(15)
N1	18(2)	17(2)	13(2)	-10.3(18)	3.6(17)	-10.4(17)
N2	18(2)	8.7(19)	16(2)	-5.5(17)	-0.8(17)	-4.8(16)
N3	19(2)	11(2)	18(2)	-5.1(18)	-0.7(19)	-5.6(18)
N4	16(2)	14(2)	18(2)	-6.4(18)	-1.5(18)	-9.8(17)
C1	12(2)	16(2)	16(2)	-10(2)	2.3(19)	-6.0(19)

Table S32 Bond Lengths for **6.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cs1	O1	3.048(4)	Cs1	N4[6]	3.181(5)
Cs1	O1[1]	3.180(4)	Cs1	N4[7]	3.509(5)
Cs1	O2[1]	3.230(4)	O1	N1	1.259(6)
Cs1	O2[2]	3.113(5)	O2	N1	1.245(6)
Cs1	O2[3]	3.275(5)	N1	N2	1.323(6)
Cs1	N1[1]	3.650(5)	N2	C1	1.386(7)
Cs1	N2[4]	3.405(5)	N3	N4	1.311(7)
Cs1	N2[5]	3.298(5)	N3	C1	1.350(7)
Cs1	N3[5]	3.405(5)	N4	C1[8]	1.358(7)
Cs1	N3[4]	3.671(5)			

[1]2-X,1-Y,1-Z; [2]1+X,-1+Y,1+Z; [3]1-X,1-Y,1-Z; [4]1+X,+Y,+Z; [5]2-X,-Y,1-Z; [6]1-X,-Y,1-Z; [7]1+X,+Y,1+Z; [8]-X,1-Y,-Z

Table S33 Bond Angles for **6.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Cs1	O1[1]	77.41(12)	N4[6]	Cs1	O2[2]	69.06(12)
O1[1]	Cs1	O2[2]	89.33(10)	N4[7]	Cs1	N1[1]	61.55(10)
O1	Cs1	O2[1]	116.51(11)	N4[6]	Cs1	N1[1]	140.56(11)
O1[1]	Cs1	O2[1]	39.39(11)	N4[6]	Cs1	N2[5]	149.63(12)
O1	Cs1	O2[3]	144.08(12)	N4[6]	Cs1	N2[4]	60.92(12)
O1	Cs1	O2[2]	60.36(11)	N4[7]	Cs1	N3[5]	137.47(12)
O1	Cs1	N1[1]	97.00(12)	N4[6]	Cs1	N3[4]	84.32(12)
O1[1]	Cs1	N1[1]	19.73(11)	N4[6]	Cs1	N3[5]	117.09(12)
O1	Cs1	N2[4]	128.09(12)	N4[6]	Cs1	N4[7]	89.60(12)
O1	Cs1	N2[5]	70.00(12)	Cs1	O1	Cs1[1]	102.59(12)
O1[1]	Cs1	N2[5]	62.26(11)	N1	O1	Cs1[1]	101.7(3)
O1[1]	Cs1	N2[4]	139.88(11)	N1	O1	Cs1	154.7(4)
O1[1]	Cs1	N3[4]	103.55(11)	Cs1[8]	O2	Cs1[1]	101.91(12)
O1	Cs1	N3[5]	53.46(11)	Cs1[8]	O2	Cs1[2]	96.13(12)
O1	Cs1	N3[4]	153.80(11)	Cs1[1]	O2	Cs1[2]	112.00(13)
O1[1]	Cs1	N3[5]	92.17(11)	N1	O2	Cs1[1]	99.6(3)
O1[1]	Cs1	N4[6]	148.11(12)	N1	O2	Cs1[2]	113.9(3)
O1[1]	Cs1	N4[7]	58.94(11)	N1	O2	Cs1[8]	132.7(3)
O1	Cs1	N4[6]	108.93(12)	O1	N1	Cs1[1]	58.6(3)
O1	Cs1	N4[7]	87.87(11)	O1	N1	N2	116.1(5)
O2[3]	Cs1	O1[1]	107.35(11)	O2	N1	Cs1[1]	60.7(3)

O2[3]	Cs1	O2[1]	78.09(12)	O2	N1	O1	119.3(5)
O2[1]	Cs1	O2[2]	112.00(13)	O2	N1	N2	124.6(5)
O2[3]	Cs1	O2[2]	83.87(12)	N2	N1	Cs1[1]	174.6(4)
O2[2]	Cs1	N1[1]	101.15(10)	Cs1[4]	N2	Cs1[9]	85.00(11)
O2[1]	Cs1	N1[1]	19.66(11)	N1	N2	Cs1[9]	114.2(3)
O2[3]	Cs1	N1[1]	92.78(11)	N1	N2	Cs1[4]	128.1(3)
O2[1]	Cs1	N2[4]	105.42(11)	N1	N2	C1	120.1(5)
O2[3]	Cs1	N2[4]	71.21(12)	C1	N2	Cs1[9]	96.9(3)
O2[1]	Cs1	N2[5]	74.37(12)	C1	N2	Cs1[4]	103.3(3)
O2[3]	Cs1	N2[5]	144.51(11)	Cs1[9]	N3	Cs1[6]	79.68(10)
O2[2]	Cs1	N2[5]	127.18(11)	Cs1[4]	N3	Cs1[9]	79.50(11)
O2[2]	Cs1	N2[4]	129.06(11)	Cs1[4]	N3	Cs1[6]	98.83(12)
O2[1]	Cs1	N3[4]	66.50(11)	N4	N3	Cs1[9]	126.9(3)
O2[3]	Cs1	N3[4]	61.35(12)	N4	N3	Cs1[6]	57.3(3)
O2[2]	Cs1	N3[4]	145.04(11)	N4	N3	Cs1[4]	132.2(3)
O2[2]	Cs1	N3[5]	111.49(11)	N4	N3	C1	119.2(4)
O2[1]	Cs1	N3[5]	111.03(11)	C1	N3	Cs1[4]	99.3(3)
O2[3]	Cs1	N3[5]	155.59(10)	C1	N3	Cs1[9]	86.2(3)
O2[1]	Cs1	N4[7]	67.54(11)	C1	N3	Cs1[6]	154.5(3)
O2[3]	Cs1	N4[6]	49.18(12)	Cs1[6]	N4	Cs1[10]	90.40(12)
O2[3]	Cs1	N4[7]	66.79(12)	N3	N4	Cs1[10]	108.3(3)
O2[2]	Cs1	N4[7]	45.26(11)	N3	N4	Cs1[6]	102.4(3)
N1[1]	Cs1	N3[5]	102.16(11)	N3	N4	C1[11]	117.4(5)
N2[4]	Cs1	N1[1]	123.14(11)	C1[11]	N4	Cs1[10]	101.5(3)
N2[5]	Cs1	N1[1]	67.01(11)	C1[11]	N4	Cs1[6]	131.5(3)
N2[4]	Cs1	N2[5]	95.00(11)	Cs1[9]	C1	Cs1[4]	72.20(11)
N2[5]	Cs1	N3[4]	87.08(12)	N2	C1	Cs1[4]	56.2(3)
N2[4]	Cs1	N3[4]	39.01(12)	N2	C1	Cs1[9]	62.1(3)
N2[5]	Cs1	N3[5]	36.68(11)	N3	C1	Cs1[4]	60.5(3)
N2[4]	Cs1	N3[5]	84.44(12)	N3	C1	Cs1[9]	73.2(3)
N2[4]	Cs1	N4[7]	137.98(12)	N3	C1	N2	109.9(5)
N2[5]	Cs1	N4[7]	120.27(11)	N3	C1	N4[11]	123.5(5)
N3[4]	Cs1	N1[1]	84.95(12)	N4[11]	C1	Cs1[9]	133.6(3)
N3[4]	Cs1	N3[5]	100.50(11)	N4[11]	C1	Cs1[4]	154.0(3)
N3[4]	Cs1	N4[7]	115.42(13)	N4[11]	C1	N2	126.5(5)
N4[6]	Cs1	O2[1]	127.24(11)				

[1]2-X,1-Y,1-Z; [2]1-X,1-Y,1-Z; [3]1+X,-1+Y,1+Z; [4]2-X,-Y,1-Z; [5]1+X,+Y,+Z; [6]1-X,-Y,1-Z; [7]1+X,+Y,1+Z; [8]-1+X,1+Y,-1+Z; [9]-1+X,+Y,+Z; [10]-1+X,+Y,-1+Z; [11]-X,1-Y,-Z

Table S34 Torsion Angles for **6.**

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Cs1	O1	N1	Cs1[1]	163.8(8)	Cs1[7]	N3	C1	Cs1[5]	134.8(9)
Cs1	O1	N1	O2	164.0(5)	Cs1[5]	N3	C1	Cs1[4]	-78.69(14)
Cs1[1]	O1	N1	O2	0.1(5)	Cs1[4]	N3	C1	Cs1[5]	78.69(14)
Cs1[1]	O1	N1	N2	179.6(4)	Cs1[7]	N3	C1	Cs1[4]	56.1(8)
Cs1	O1	N1	N2	-16.6(10)	Cs1[5]	N3	C1	N2	-27.7(4)
Cs1[2]	O2	N1	Cs1[1]	-119.4(3)	Cs1[7]	N3	C1	N2	107.1(8)
Cs1[3]	O2	N1	Cs1[1]	116.1(4)	Cs1[4]	N3	C1	N2	51.0(4)
Cs1[3]	O2	N1	O1	116.0(5)	Cs1[5]	N3	C1	N4[6]	149.7(4)
Cs1[2]	O2	N1	O1	-119.5(4)	Cs1[4]	N3	C1	N4[6]	-131.6(5)
Cs1[1]	O2	N1	O1	-0.1(5)	Cs1[7]	N3	C1	N4[6]	-75.4(10)
Cs1[1]	O2	N1	N2	-179.5(4)	O1	N1	N2	Cs1[5]	-29.2(6)
Cs1[3]	O2	N1	N2	-63.4(7)	O1	N1	N2	Cs1[4]	74.1(5)
Cs1[2]	O2	N1	N2	61.1(6)	O1	N1	N2	C1	-171.6(4)
Cs1[4]	N2	C1	Cs1[5]	-86.47(17)	O2	N1	N2	Cs1[5]	150.2(4)
Cs1[5]	N2	C1	Cs1[4]	86.47(17)	O2	N1	N2	Cs1[4]	-106.5(5)
Cs1[4]	N2	C1	N3	-57.3(4)	O2	N1	N2	C1	7.8(8)
Cs1[5]	N2	C1	N3	29.2(5)	N1	N2	C1	Cs1[4]	-123.1(5)
Cs1[5]	N2	C1	N4[6]	-148.2(5)	N1	N2	C1	Cs1[5]	150.4(6)
Cs1[4]	N2	C1	N4[6]	125.3(5)	N1	N2	C1	N3	179.6(5)
Cs1[7]	N3	N4	Cs1[8]	-94.6(2)	N1	N2	C1	N4[6]	2.2(8)
Cs1[5]	N3	N4	Cs1[8]	-24.3(5)	N4	N3	C1	Cs1[5]	-150.7(5)
Cs1[5]	N3	N4	Cs1[7]	70.3(4)	N4	N3	C1	Cs1[4]	130.6(5)
Cs1[4]	N3	N4	Cs1[7]	-41.6(4)	N4	N3	C1	N2	-178.4(4)
Cs1[4]	N3	N4	Cs1[8]	-136.2(2)	N4	N3	C1	N4[6]	-0.9(8)
Cs1[5]	N3	N4	C1[6]	-138.4(4)	C1	N3	N4	Cs1[7]	-150.4(4)
Cs1[7]	N3	N4	C1[6]	151.3(5)	C1	N3	N4	Cs1[8]	114.9(4)
Cs1[4]	N3	N4	C1[6]	109.7(5)	C1	N3	N4	C1[6]	0.9(8)

[1]2-X,1-Y,1-Z; [2]1-X,1-Y,1-Z; [3]-1+X,1+Y,-1+Z; [4]-1+X,+Y,+Z; [5]2-X,-Y,1-Z; [6]-X,1-Y,-Z; [7]1-X,-Y,1-Z; [8]-1+X,+Y,-1+Z

Figure S1. Molecular structure of DNAT (**1**) and its labeling scheme.

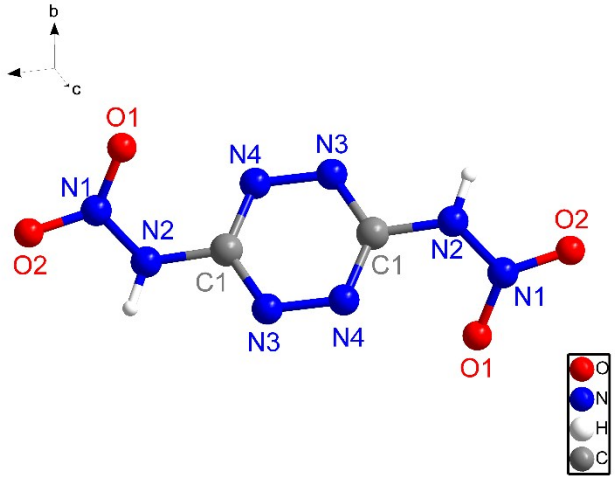

Figure S2. The packing diagram of compound **1** viewed along *c* axis.

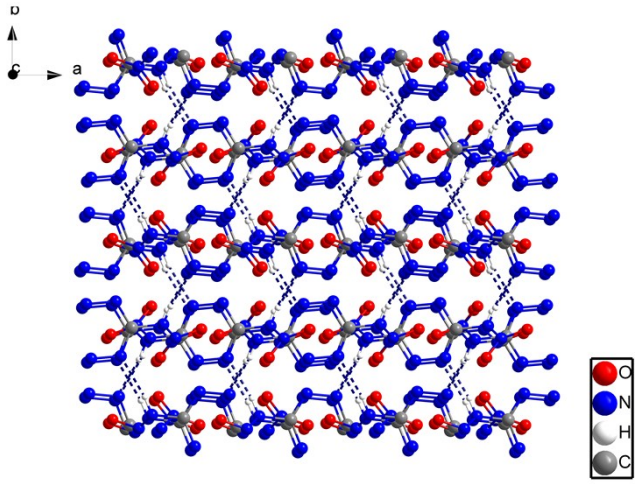

Figure S3. Molecular structure of $Li_2(H_2O)_4$(DNAT) (**2**) and its labeling scheme.

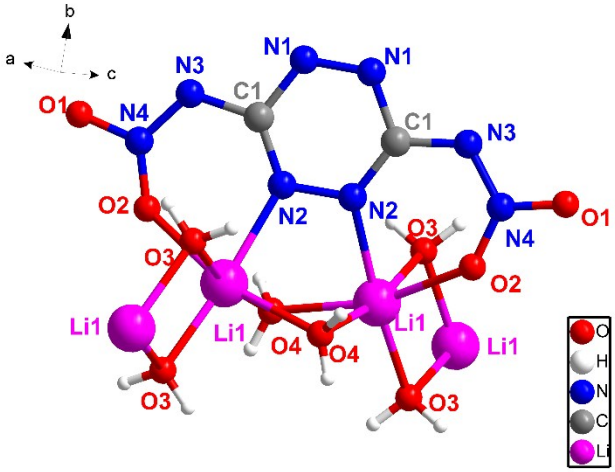

Figure S4. The packing diagram of compound **2** viewed along *a* axis.

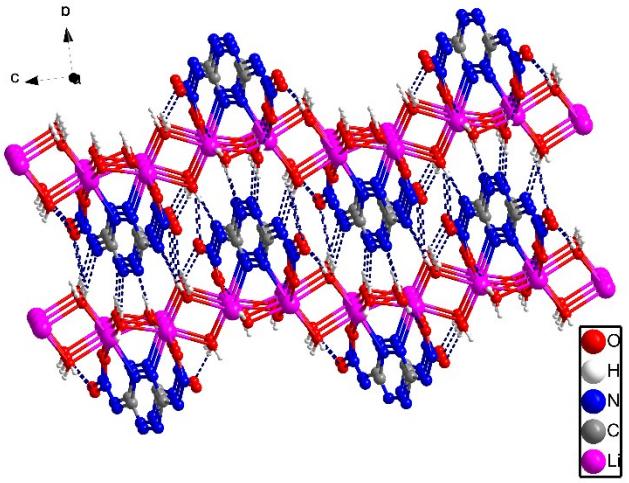

Figure S5. Molecular structure of $Na_2(H_2O)_3$(DNAT) (**3**) and its labeling scheme.

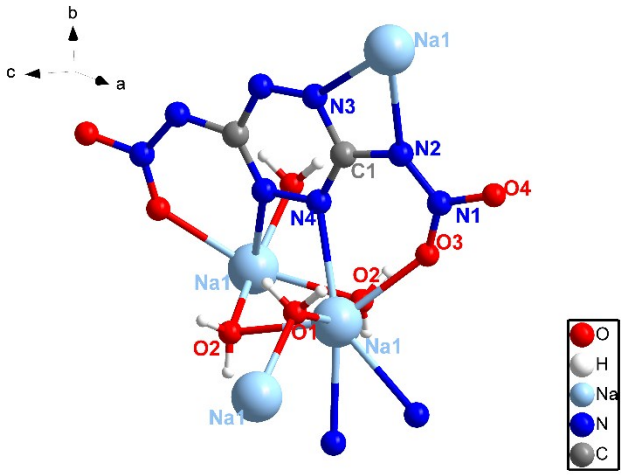

Figure S6. The packing diagram of compound **3** viewed along *b* axis.

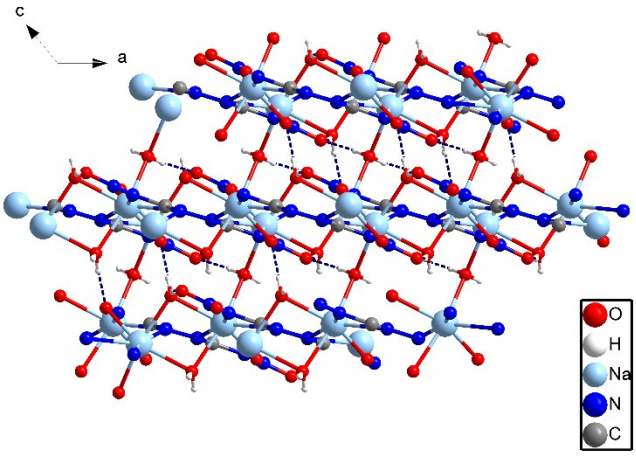

Figure S7. Molecular structure of $K_2(H_2O)$(DNAT) (**4**) and its labeling scheme.

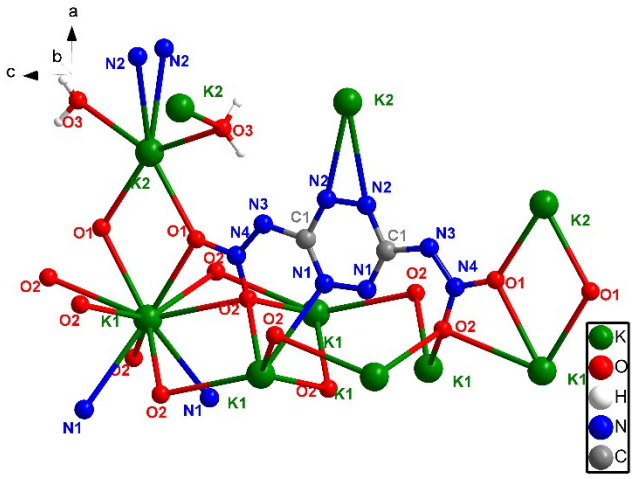

Figure S8. The packing diagram of compound **4** viewed along *c* axis.

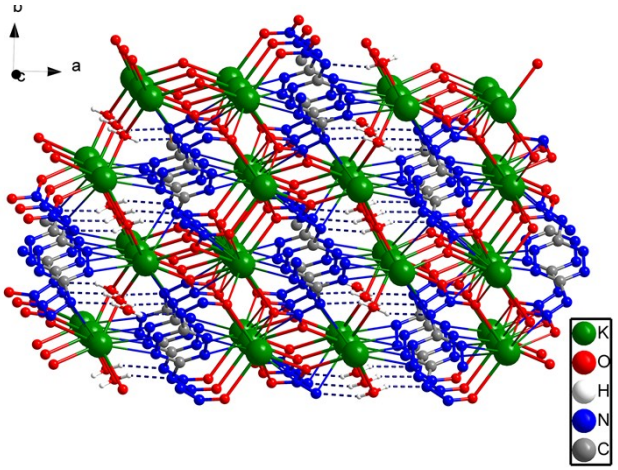

Figure S9. Molecular structure of Rb_2(DNAT) (**5**) and its labeling scheme.

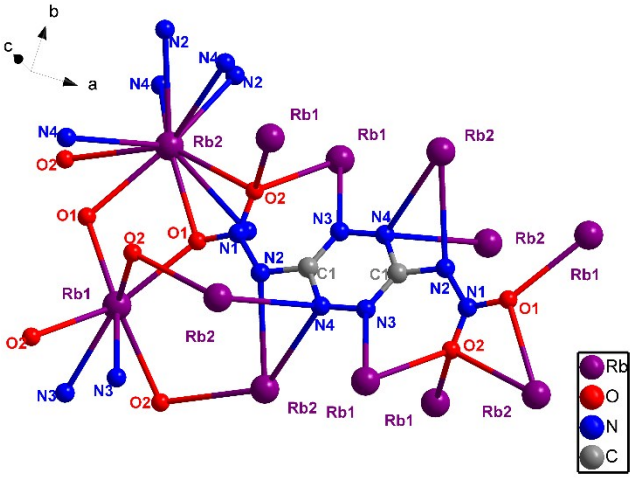

Figure S10. The packing diagram of compound **5** viewed along *a* axis.

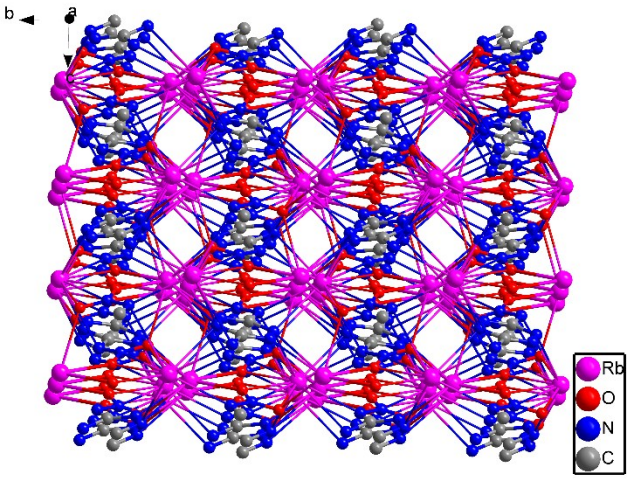

Figure S11. Molecular structure of $Cs_2(DNAT)$ (**6**) and its labeling scheme.

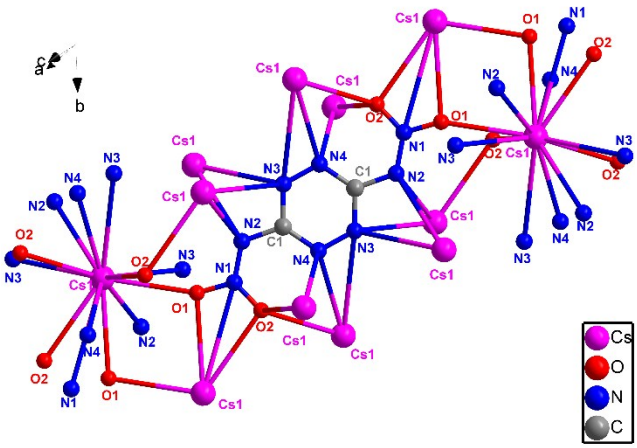

Figure S12. The packing diagram of compound **6** viewed along *a* axis.

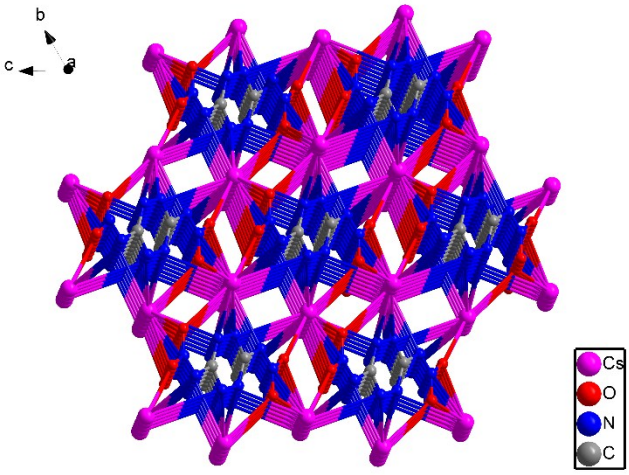

Figure S13. DSC curve of DNAT (**1**).

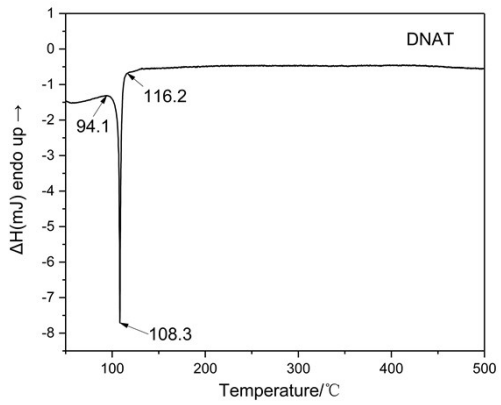

Figure S14. DSC curve of $Li_2(H_2O)_4$(DNAT) (**2**).

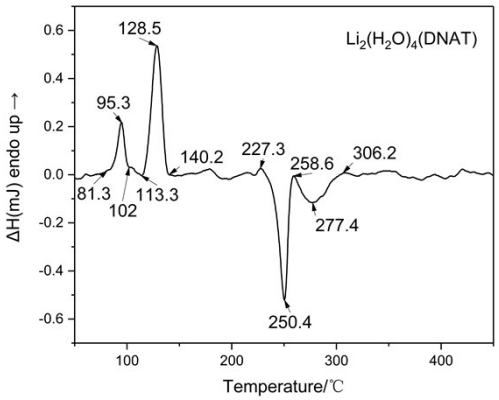

Figure S15. DSC curve of $Na_2(H_2O)_3$(DNAT) (**3**).

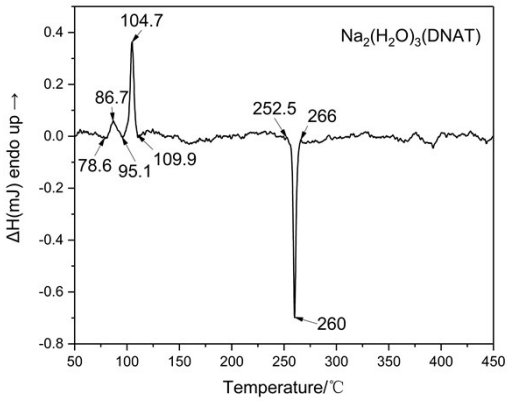

Figure S16. DSC curve of $K_2(H_2O)$(DNAT) (**4**).

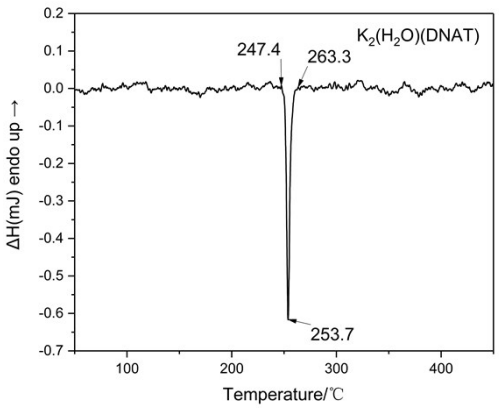

Figure S17. DSC curve of Rb_2(DNAT) (**5**).

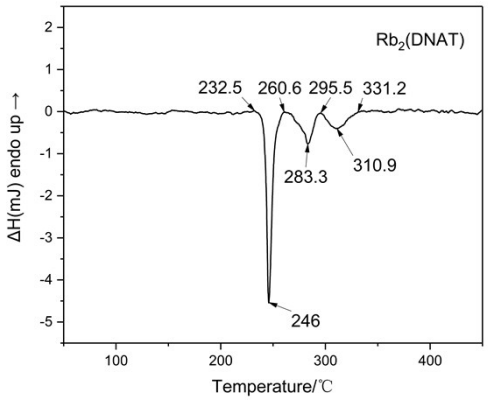

Figure S18. DSC curve of Cs_2(DNAT) (**6**).

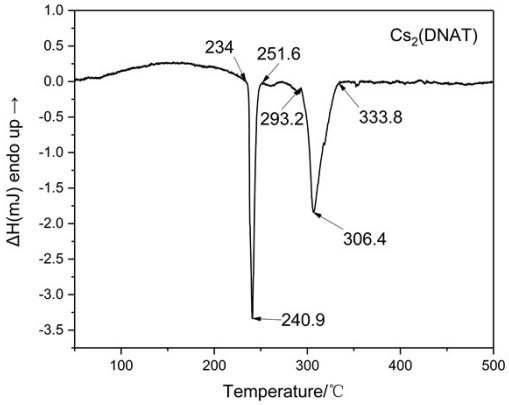

Figure S19. TG-DTG curve of DNAT (**1**).

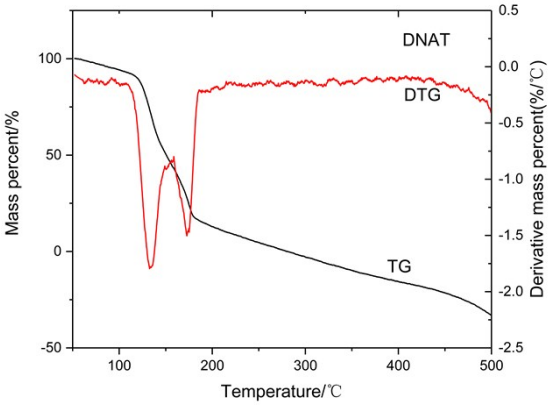

Figure S20. TG-DTG curve of $Li_2(H_2O)_4$(DNAT) (**2**).

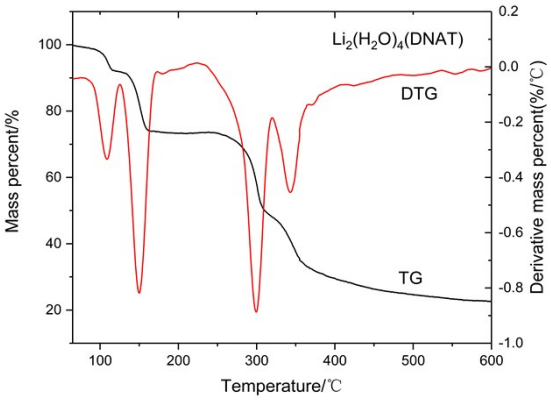

Figure S21. TG-DTG curve of $Na_2(H_2O)_3$(DNAT) (**3**).

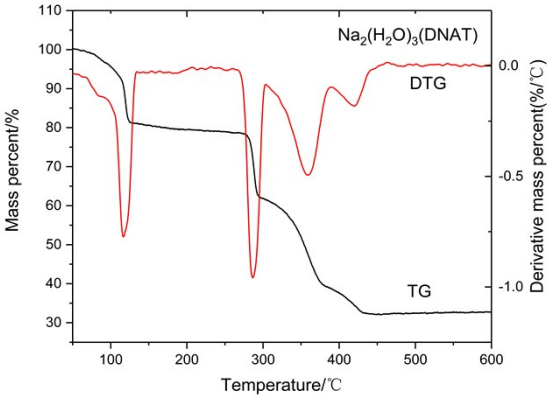

Figure S22. TG-DTG curve of $K_2(H_2O)$(DNAT) (**4**).

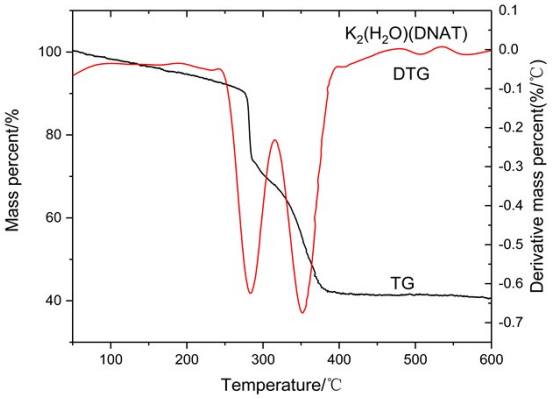

Figure S23. TG-DTG curve of Rb_2(DNAT) (**5**).

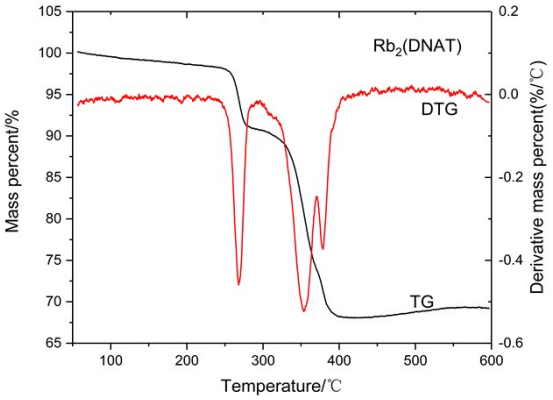

Figure S24. TG-DTG curve of Cs_2(DNAT) (**6**).

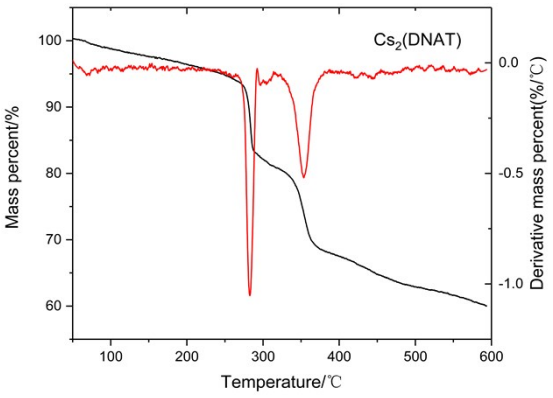

Table S35. The first exothermic decomposition peak temperatures tested at different heating rates of compounds **1** to **6**

compound	The first exothermic decomposition peak temperatures (°C)			
	5°C·min^{-1}	10°C·min^{-1}	15°C·min^{-1}	20°C·min^{-1}
1	106.5	108.3	110.0	110.9
2	245.1	250.4	252.6	254.2
3	253.2	260.0	266.2	266.6
4	243.5	253.7	261.4	264.4
5	232.2	246.0	253.0	253.5
6	230.2	240.9	251.9	260.3

Table S36. Results of 5 s bursting point tests

compound	1		2		3		4		T_{5s}/℃
	T/℃	τ/s	T/℃	τ/s	T/℃	τ/s	T/℃	τ/s	
1	133	6.2	136	5.3	145	2.9	147	2.4	136
2	303	6.2	306	5.5	308	4.7	310	4.2	307
3	296	6.8	298	5.6	300	4.5	302	4.1	299
4	317	7.0	320	6.1	325	4.7	328	3.6	323
5	269	8.2	279	6.4	290	4.1	295	2.5	282
6	303	5.8	305	5.5	308	4.6	311	3.9	306

Table S37. CCDC number of **1-6**.

	1	**2**	**3**	**4**	**5**	**6**
CCDC number	1567025	1832599	1832596	1832597	1832598	1858066