Electronic Supplementary Material (ESI) for RSC Advances.

Crystal structure transformation and step-by-step thermal decomposition behavior of dihydroxylammonium 5,5'-bistetrazole-1,1'-diolate

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Contents

Table S1 Lattice parameters of TKX-50 refined from X-ray diffraction data.

T(℃)	a(Å)	b(Å)	c(Å)	β(°)	Volume(Å^3)
30	5.43027	11.73754	6.55503	95.09271	416.15511
40	5.42885	11.74634	6.5577	95.06889	416.54324
50	5.42869	11.75677	6.56126	95.04905	417.13995
60	5.42759	11.76182	6.56179	95.02958	417.28096
70	5.42738	11.77116	6.56496	95.01165	417.80908
80	5.42663	11.77906	6.56757	94.99583	418.20815
90	5.42596	11.78494	6.56861	94.97622	418.44396
100	5.42564	11.79563	6.57218	94.95797	419.03818
110	5.42568	11.80018	6.57278	94.94274	419.25088
120	5.42551	11.81087	6.57651	94.92525	419.86641
125	5.42507	11.81067	6.57552	94.91674	419.76767
130	5.42571	11.81806	6.57833	94.90666	420.26602
135	5.42536	11.82135	6.57987	94.90386	420.45582
140	5.42508	11.82318	6.57946	94.89723	420.4773
145	5.42539	11.82684	6.58021	94.88794	420.68501
150	5.42487	11.83144	6.5818	94.87426	420.91862
155	5.42487	11.83533	6.58303	94.8667	421.14075
160	5.42513	11.83608	6.58242	94.85825	421.15357
165	5.42524	11.8418	6.5848	94.85186	421.5218
170	5.42566	11.84819	6.58673	94.84437	421.911
175	5.42567	11.85086	6.5879	94.83339	422.0888

Fourier Transform Infrared Spectroscopy characterization of the main intermediate product

Fourier Transform Infrared Spectroscopy characterization was utilized to analysis the main intermediate product. The data was collected by Nicolet 6700. The resolution ratio of instrument was 4 cm^{-1} and the scan range from 400 cm^{-1} to 4000 cm^{-1}. The raw TKX-50 and materials after initial decomposition by in-situ XRD at different temperatures were tested. We found that the absorption bands of tetrazole (729, 998, 1165, 1234cm^{-1}) were kept same, and cation moiety was converted to NH_4^+ (1403, 2851, 3056, 3184 cm^{-1}) at last with the increase temperature. Therefore, the intermediate product was presumed to be ABTOX. The obtained IR spectrograms are shown in Fig.S1.

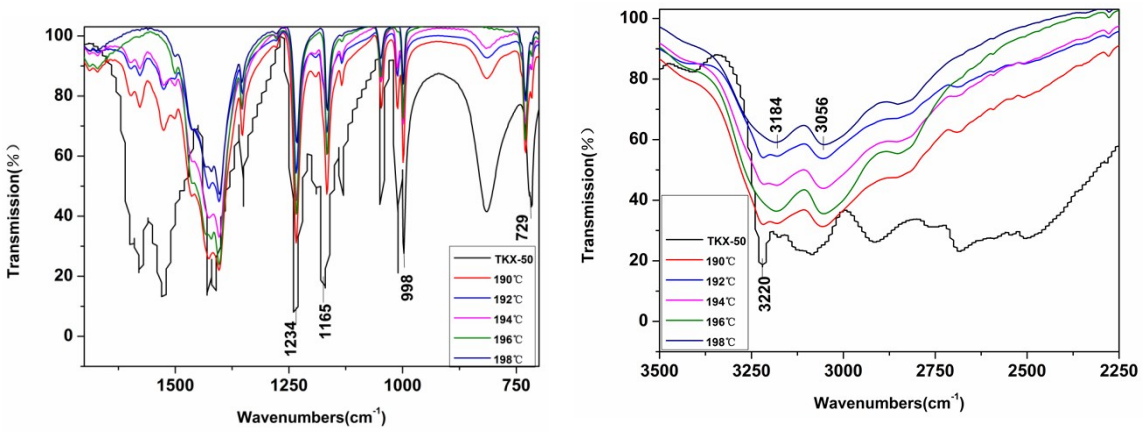

Fig. S1 The IR spectrograms of materials after initial decomposition by in-situ XRD at different temperatures

Characterization of ABTOX

The molecular structure of ABTOX was shown in Fig. S2, and the anion moiety in the crystal structure of ABTOX was disorder. The detailed crystallographic data and structure refinements are shown in Table S2. About the reason of the different structure with reported, a more advanced space group was used for structural analysis in our study. That is to say, if I222 space group can be used to solve the structure, I-4 can also solve the crystal structure. Conversely, if I-4 can solve the crystal structure, the I222 space group can not necessarily solve the structure. Compared the unit cell parameters with the reported, no particular difference is found and the same crystal structure can be considered.

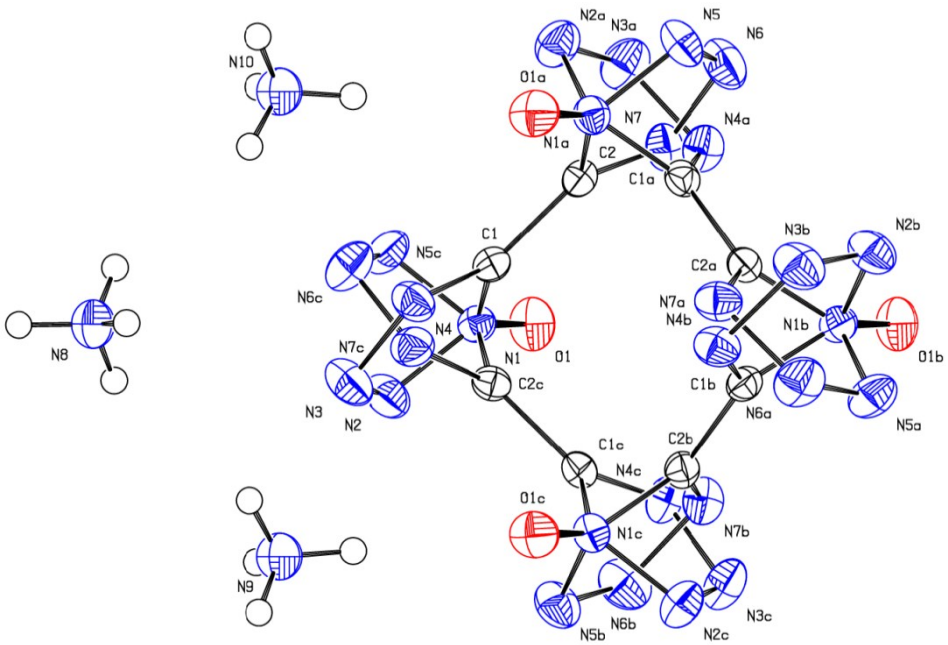

Fig. S2 Molecular structure of ABTOX.

Table S2 Crystal data and structure refinement details for ABTOX at 296K.

Empirical formula	$C_2 H_8 N_{10} O_2$
Formula weight	204.18
Temperature	296 K
Wavelength(Å)	0.71073
Crystal system	Tetragonal
Space group	I -4
Z	4
Unit cell dimensions	
a (Å)	7.5982(12)
b (Å)	7.5982(12)
c (Å)	c = 13.294(3)
α (°)	90
β (°)	90
γ(°)	90
Volume ($Å^3$)	767.5(3)
D_{calc} (Mg/m^3)	1.767
Absorption coefficient (mm^{-1})	0.151
F(000)	424
Crystal size (mm)	0.15 x 0.12 x 0.08
Θ	3.065° to 30.682°
Index ranges	-9<=h<=10, -10<=k<=10, -18<=l<=19
Reflections collected	3930
Completeness to theta (%)	100
Goodness-of-fit on F^2	1.078
Final R indices [I>2sigma(I)]	R1 = 0.0389, wR2 = 0.0967
CCDC	1567754

Table S3 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for ABTOX. U (eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	7735(3)	7735(3)	3433(1)	29(1)
N(1)	7752(3)	7754(3)	4428(1)	20(1)
N(2)	7761(6)	6216(5)	4916(5)	29(1)
N(3)	7826(6)	6583(6)	5878(4)	32(1)
N(4)	7868(9)	8351(9)	6030(6)	24(1)
C(1)	7791(5)	9070(5)	5111(4)	18(1)
N(8)	5000	5000	7244(2)	28(1)
N(9)	10000	5000	7500	28(1)
N(10)	5000	10000	7500	28(1)
N(5)	7755(5)	13789(5)	5086(5)	29(1)
N(6)	7824(6)	13417(6)	4128(4)	33(1)
N(7)	7854(9)	11661(10)	3973(7)	25(1)

C(2)	7794(6)	10935(5)	4889(4)	18(1)

Table S4 Bond lengths (Å), angles (deg) for ABTOX.

O(1)-N(1)	1.322(2)	N(8)-H(8A)	0.82(2)
N(1)-N(2)	1.337(5)	N(8)-H(8B)	0.86(2)
N(1)-C(1)	1.351(5)	N(9)-H(9)	0.88(2)
N(1)-N(5)#1	1.338(5)	N(10)-H(10)	0.87(2)
N(1)-C(2)#1	1.350(5)	N(5)-N(1)#3	1.338(5)
N(2)-N(3)	1.310(8)	N(5)-N(2)#4	1.858(5)
N(2)-N(5)#1	1.660(5)	N(5)-N(2)#3	1.659(5)
N(2)-N(5)#2	1.858(5)	N(5)-C(1)#3	1.584(6)
N(2)-C(2)#1	1.577(6)	N(5)-N(6)	1.305(8)
N(3)-N(4)	1.359(8)	N(6)-N(3)#3	1.335(5)
N(3)-N(6)#1	1.335(5)	N(6)-N(4)#3	1.076(10)
N(3)-N(7)#1	1.060(10)	N(6)-C(1)#3	1.662(6)
N(3)-C(2)#1	1.664(6)	N(6)-N(7)	1.350(8)
N(4)-C(1)	1.339(10)	N(7)-N(3)#3	1.060(10)
N(4)-N(6)#1	1.076(10)	N(7)-N(4)#3	0.520(5)
N(4)-N(7)#1	0.520(5)	N(7)-C(1)#3	1.584(9)
N(4)-C(2)#1	1.580(9)	N(7)-C(2)	1.337(10)
C(1)-N(5)#1	1.584(6)	C(2)-N(1)#3	1.350(5)
C(1)-N(6)#1	1.662(6)	C(2)-N(2)#3	1.577(6)
C(1)-N(7)#1	1.584(9)	C(2)-N(3)#3	1.664(6)
C(1)-C(2)	1.448(5)	C(2)-N(4)#3	1.580(9)
C(1)-C(2)#1	1.370(5)	C(2)-C(1)#3	1.370(5)

O(1)-N(1)-N(2)	118.4(3)	C(2)-C(1)-N(6)#1	133.0(4)
O(1)-N(1)-C(1)	132.9(3)	C(2)-C(1)-N(7)#1	136.7(5)
O(1)-N(1)-N(5)#1	118.4(3)	C(2)#1-C(1)-N(7)#1	53.2(4)
O(1)-N(1)-C(2)#1	132.9(3)	C(2)#1-C(1)-C(2)	133.8(5)
N(2)-N(1)-C(1)	108.7(4)	H(8A)-N(8)-H(8B)	111(5)
N(2)-N(1)-N(5)#1	76.7(3)	N(1)#3-N(5)-N(2)#4	158.0(4)
N(2)-N(1)-C(2)#1	71.9(3)	N(1)#3-N(5)-N(2)#3	51.6(3)
N(5)#1-N(1)-C(1)	72.2(3)	N(1)#3-N(5)-C(1)#3	54.3(2)
N(5)#1-N(1)-C(2)#1	108.7(4)	N(2)#3-N(5)-N(2)#4	134.9(4)
C(2)#1-N(1)-C(1)	60.9(3)	C(1)#3-N(5)-N(2)#3	84.6(3)
N(1)-N(2)-N(5)#2	157.9(4)	C(1)#3-N(5)-N(2)#4	137.0(3)
N(1)-N(2)-N(5)#1	51.7(3)	N(6)-N(5)-N(1)#3	106.4(4)
N(1)-N(2)-C(2)#1	54.4(3)	N(6)-N(5)-N(2)#3	82.8(4)
N(3)-N(2)-N(1)	106.7(4)	N(6)-N(5)-N(2)#4	95.5(3)
N(3)-N(2)-N(5)#1	83.0(4)	N(6)-N(5)-C(1)#3	69.5(4)
N(3)-N(2)-N(5)#2	95.3(3)	N(3)#3-N(6)-C(1)#3	90.8(4)
N(3)-N(2)-C(2)#1	69.7(4)	N(3)#3-N(6)-N(7)	46.5(4)

N(5)#1-N(2)-N(5)#2	134.3(4)	N(4)#3-N(6)-N(3)#3	67.6(4)
C(2)#1-N(2)-N(5)#2	137.4(3)	N(4)#3-N(6)-C(1)#3	53.5(5)
C(2)#1-N(2)-N(5)#1	84.8(3)	N(4)#3-N(6)-N(5)	113.7(6)
N(2)-N(3)-N(4)	110.9(6)	N(4)#3-N(6)-N(7)	21.1(4)
N(2)-N(3)-N(6)#1	96.8(5)	N(5)-N(6)-N(3)#3	97.5(5)
N(2)-N(3)-C(2)#1	62.7(3)	N(5)-N(6)-C(1)#3	63.2(3)
N(4)-N(3)-C(2)#1	62.0(4)	N(5)-N(6)-N(7)	111.3(6)
N(6)#1-N(3)-N(4)	47.1(4)	N(7)-N(6)-C(1)#3	62.4(4)
N(6)#1-N(3)-C(2)#1	90.4(4)	N(3)#3-N(7)-C(1)#3	106.9(7)
N(7)#1-N(3)-N(2)	113.0(6)	N(3)#3-N(7)-N(6)	66.0(5)
N(7)#1-N(3)-N(4)	20.4(5)	N(3)#3-N(7)-C(2)	87.1(6)
N(7)#1-N(3)-N(6)#1	67.5(4)	N(4)#3-N(7)-N(3)#3	114(2)
N(7)#1-N(3)-C(2)#1	53.3(5)	N(4)#3-N(7)-C(1)#3	53.2(16)
N(3)-N(4)-C(2)#1	68.5(4)	N(4)#3-N(7)-N(6)	48.2(17)
C(1)-N(4)-N(3)	105.5(6)	N(4)#3-N(7)-C(2)	108.4(19)
C(1)-N(4)-C(2)#1	55.2(4)	N(6)-N(7)-C(1)#3	68.5(4)
N(6)#1-N(4)-N(3)	65.3(5)	C(2)-N(7)-C(1)#3	55.1(4)
N(6)#1-N(4)-C(1)	86.2(6)	C(2)-N(7)-N(6)	105.6(7)
N(6)#1-N(4)-C(2)#1	105.8(7)	N(1)#3-C(2)-N(2)#3	53.7(3)
N(7)#1-N(4)-N(3)	45.3(17)	N(1)#3-C(2)-N(3)#3	89.0(3)
N(7)#1-N(4)-C(1)	109(2)	N(1)#3-C(2)-N(4)#3	95.8(4)
N(7)#1-N(4)-N(6)#1	111(2)	N(1)#3-C(2)-C(1)#3	59.6(3)
N(7)#1-N(4)-C(2)#1	53.4(17)	N(1)#3-C(2)-C(1)	125.9(4)
N(1)-C(1)-N(5)#1	53.5(3)	N(2)#3-C(2)-N(3)#3	47.6(3)
N(1)-C(1)-N(6)#1	88.6(3)	N(2)#3-C(2)-N(4)#3	88.3(5)
N(1)-C(1)-N(7)#1	95.2(4)	N(4)#3-C(2)-N(3)#3	49.4(3)
N(1)-C(1)-C(2)#1	59.5(3)	C(1)-C(2)-N(2)#3	125.5(4)
N(1)-C(1)-C(2)	126.0(4)	C(1)#3-C(2)-N(2)#3	95.4(3)
N(4)-C(1)-N(1)	108.2(4)	C(1)-C(2)-N(3)#3	132.7(4)
N(4)-C(1)-N(5)#1	85.8(5)	C(1)#3-C(2)-N(3)#3	89.6(4)
N(4)-C(1)-N(6)#1	40.2(4)	C(1)#3-C(2)-N(4)#3	53.4(4)
N(4)-C(1)-N(7)#1	18.1(4)	C(1)-C(2)-N(4)#3	136.2(5)
N(4)-C(1)-C(2)#1	71.3(4)	C(1)#3-C(2)-C(1)	133.8(5)
N(4)-C(1)-C(2)	125.8(5)	N(7)-C(2)-N(1)#3	108.0(5)
N(5)#1-C(1)-N(6)#1	47.3(3)	N(7)-C(2)-N(2)#3	85.2(5)
N(5)#1-C(1)-N(7)#1	87.6(5)	N(7)-C(2)-N(3)#3	39.5(4)
N(7)#1-C(1)-N(6)#1	49.1(4)	N(7)-C(2)-N(4)#3	18.2(3)
C(2)-C(1)-N(5)#1	125.8(4)	N(7)-C(2)-C(1)	126.1(5)
C(2)#1-C(1)-N(5)#1	95.1(4)	N(7)-C(2)-C(1)#3	71.6(4)
C(2)#1-C(1)-N(6)#1	89.2(4)		

Symmetry transformations used to generate equivalent atoms:

#1 -y+2,x,-z+1 #2 x,y-1,z #3 y,-x+2,-z+1

#4 x,y+1,z

Table S5 Anisotropic displacement parameters ($Å^2 \times 10^3$) for ABTOX. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(1)	35(1)	34(1)	17(1)	-1(1)	-2(1)	-5(1)
N(1)	19(1)	21(1)	19(1)	0(1)	0(1)	1(1)
N(2)	37(2)	20(2)	30(3)	2(2)	1(2)	2(2)
N(3)	44(3)	23(2)	29(3)	6(2)	-1(2)	3(2)
N(4)	31(4)	22(3)	21(2)	4(3)	0(3)	4(2)
C(1)	15(2)	21(2)	20(3)	0(2)	-1(2)	1(1)
N(8)	29(2)	29(2)	26(1)	0	0	-4(1)
N(9)	31(1)	31(1)	23(2)	0	0	0
N(10)	31(1)	31(1)	21(2)	0	0	0
N(5)	39(2)	18(2)	30(2)	4(2)	-1(2)	-2(2)
N(6)	45(3)	25(2)	29(3)	7(2)	3(2)	-1(2)
N(7)	27(4)	26(4)	22(2)	4(3)	0(3)	-5(2)
C(2)	16(2)	20(2)	19(2)	-2(2)	2(2)	-1(1)

Table S6 Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for ABTOX.

	x	y	z	U(eq)
H(8A)	5600(70)	4390(70)	6870(30)	97(16)
H(8B)	5660(60)	5680(50)	7600(20)	69(13)
H(9)	10540(40)	5660(40)	7060(30)	42(9)
H(10)	5640(40)	10540(40)	7050(30)	44(10)