Supporting Information

Experimental

Synthesis. Compound **1** was prepared by dissolving hpz, $KClO_4$ and $HClO_4$ with a molar ratio of 1:1:2 in distilled water. Colorless block-like crystals were harvested after several days at room temperature with slow evaporation of the solution. Yield: 77% based on $KClO_4$. Elemental analysis calcd (%) for $C_5H_{14}N_2KCl_3O_{12}$ (439.63): C, 13.66; H, 3.21, N, 6.37; found: C, 13.63; H, 3.20; N, 6.35.

Materials and measurements. All chemicals were commercially obtained and used without further purification. Thermal gravimetric analysis (TGA) was carried out on a METTLER TOLEDO STARe System. DSC measurements were performed on a TA Instruments SDT-Q10 from 250 K to 390 K with scanning rates of 5, 10, 15 and 20 K min^{-1} under nitrogen. Powder X-ray diffraction (PXRD) patterns were measured on a Rigaku SmartLab X-ray diffraction instrument. Dielectric constant measurements were performed on a TongHui 2828 impedance analyzer in the frequency range from 1 kHz to 1 MHz under an applied field of 1.0 V in the temperature range 273−400 K with the rate of 10 K min^{-1}.

X-ray Diffraction Experiments. Variable-temperature single-crystal diffraction data of **1** were collected on a Rigaku Saturn 724^+ diffractometer by using graphite-monochromated Mo Kα (λ = 0.71075 Å) radiation. Data processing was performed using the Crystalclear software package. The structures were solved by direct methods and refined by full-matrix least-square refinements on F^2 by means of the SHELXL-2014 software package. All non-hydrogen atoms were refined anisotropically using all reflections with $I > 2\sigma(I)$. H atoms bonded to N and C atoms were positioned geometrically and refined using a "riding" model with $U_{iso} = 1.2U_{eq}$ (C and N). Details of crystallographic data and structure refinements are listed in Table S1. CCDC 1564728-1564731 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

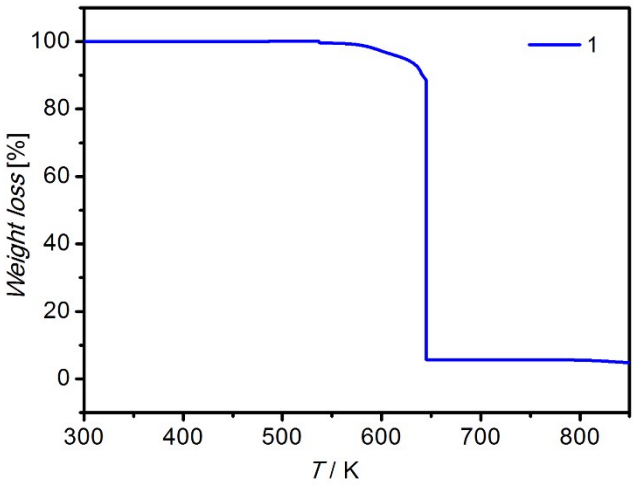

Figure S1. TGA curve of **1**.

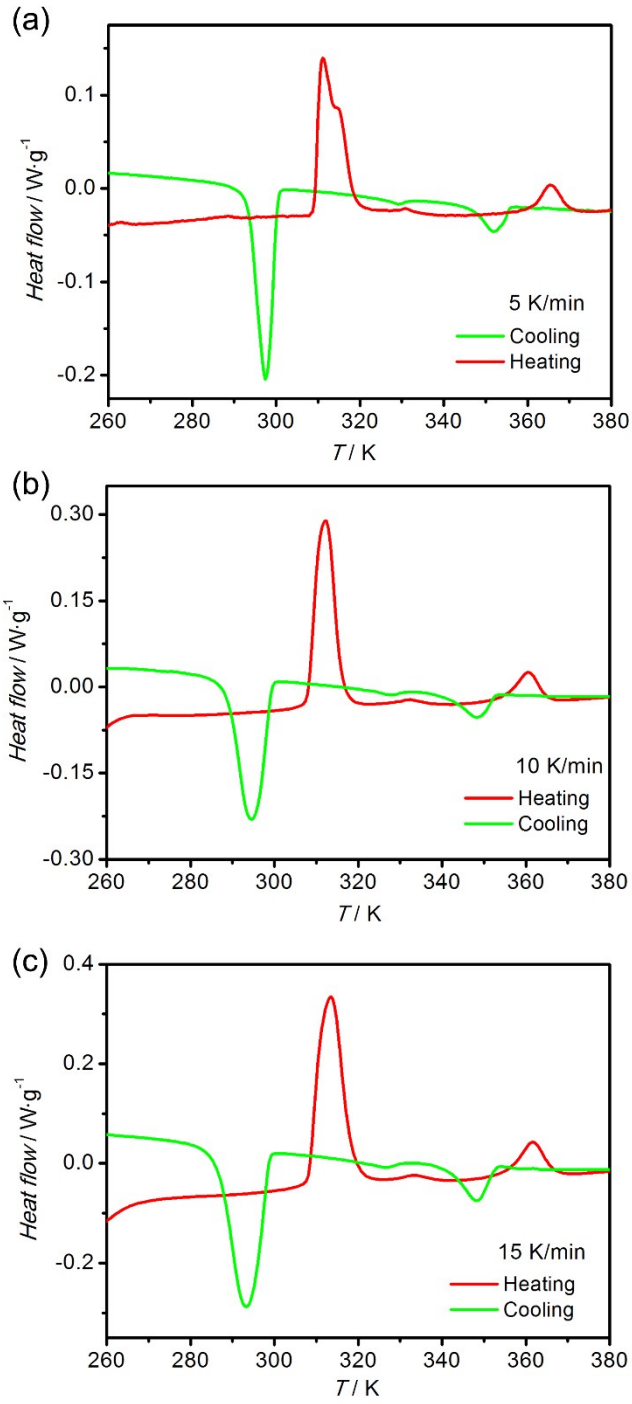

Figure S2. DSC curve of **1** measured at sweeping rates of (a) 5 K/min, (b) 10 K/min and (c) 15 K/min in a heating-cooling cycle.

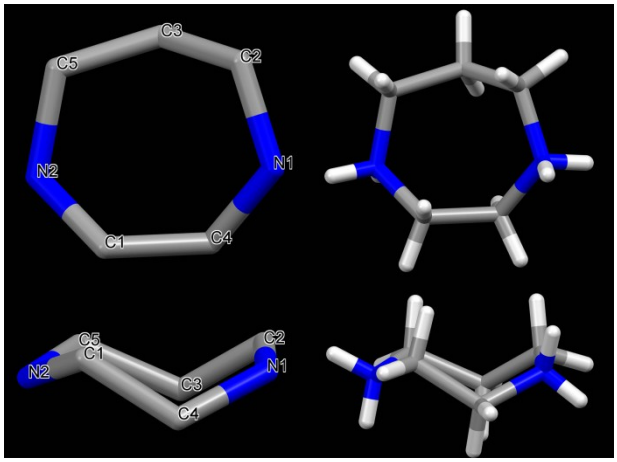

Figure S3. Conformations of the confined H_2hpz cation in the cage at 203 K.

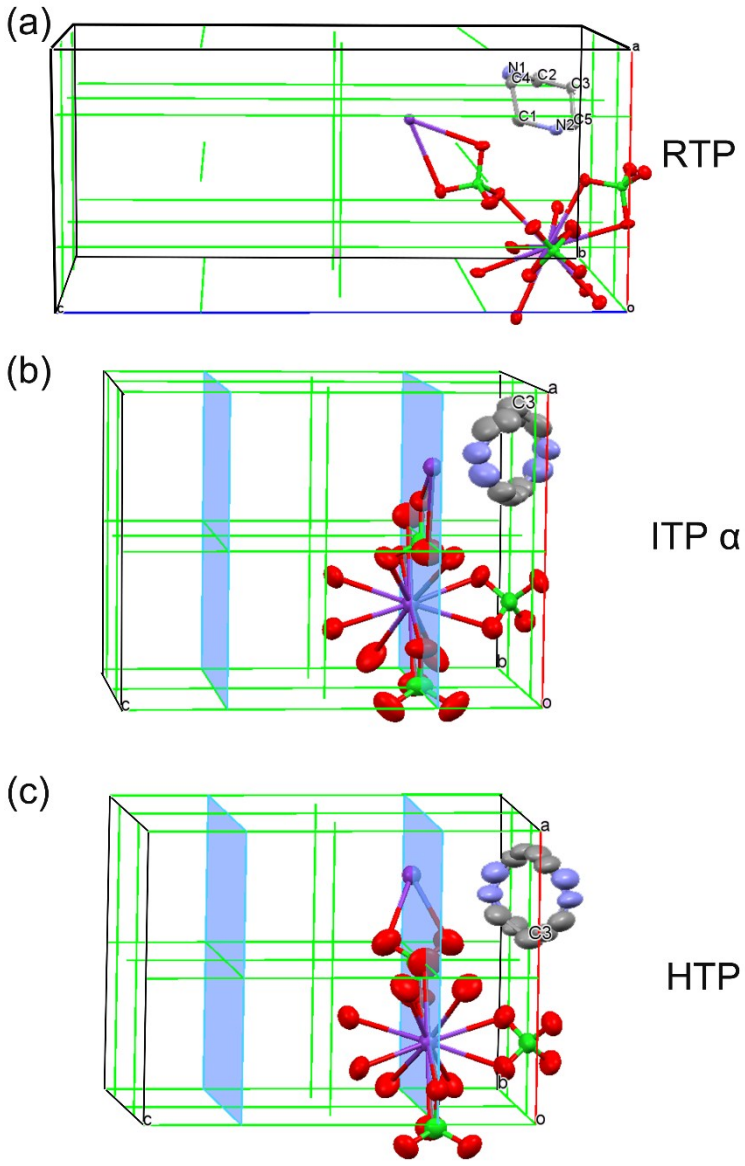

Figure S4. Crystallographic symmetries of **1** shown in the (a) RTP, (b) ITP α and (c)

HTP. The green lines and the blue planes indicate crystallographic twofold rotation axes and mirror planes, respectively.

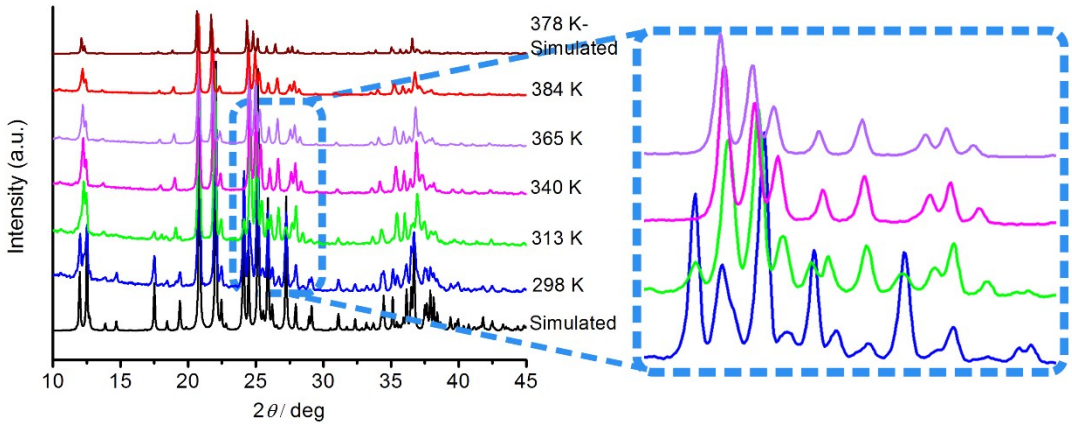

Figure S5. Variable-temperature PXRD patterns of **1** measured upon heating, together with simulated patterns from single-crystal X-ray diffraction data.

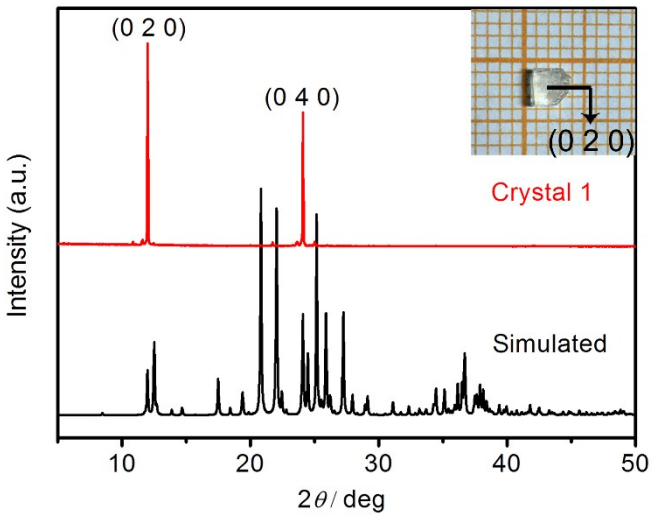

Figure S6. Crystal orientation of **1**.

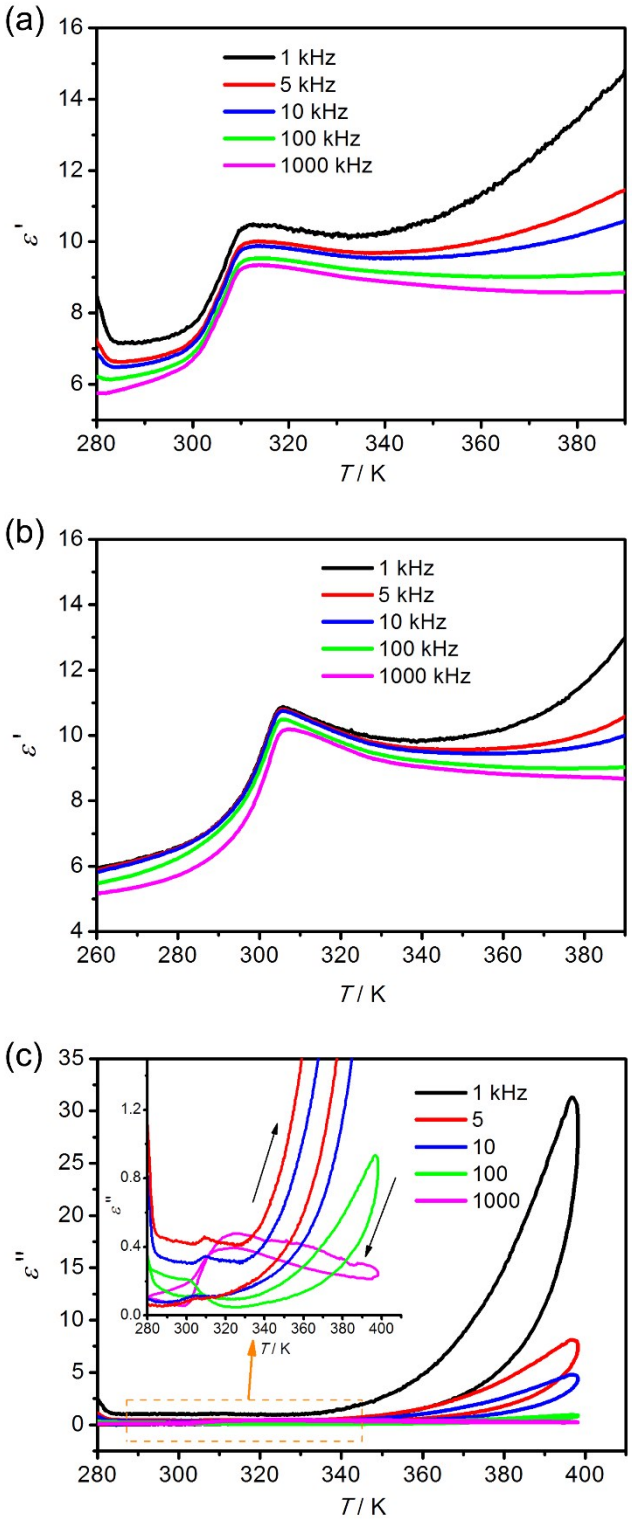

Figure S7. (a) Heating and (b) cooling modes of the real part and (c) imaginary part of dielectric constant of polycrystalline sample **1** measured at selected frequencies 1–1000 kHz in a heating/cooling cycle.

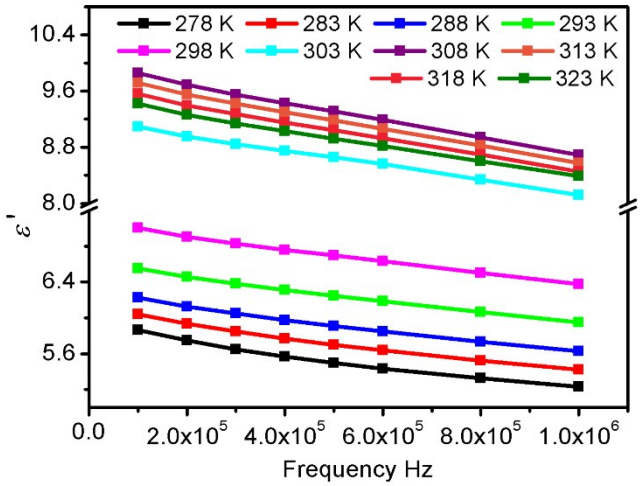

Figure S8. Frequency dependence of ε' of polycrystalline sample **1** from 273 K to 323 K.

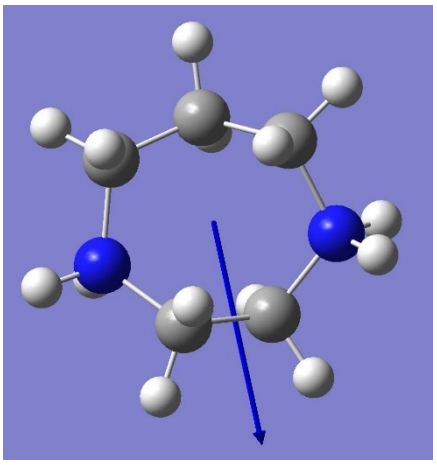

Figure S9. Dipole moment of the free H_2hpz cation.

Table S1. Crystal data and structure refinements for **1**.

	1 (203 K)	**1** (328 K)	**1** (378 K)
Formula	$C_5H_{14}N_2KCl_3O_{12}$	$C_5H_{14}N_2KCl_3O_{12}$	$C_5H_{14}N_2KCl_3O_{12}$
M_w	439.63	439.63	439.63
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	*Pbca*	*Pbcm*	*Pbcm*
a [Å]	9.603(3)	10.682(10)	10.739(11)
b [Å]	14.769(5)	9.876(10)	9.967(11)
c [Å]	20.786(7)	14.264(14)	14.350(15)
α [°]	90	90	90
β [°]	90	90	90
γ [°]	90	90	90
V [Å^3]	2948.0(17)	1505(3)	1536(3)
Z	8	4	4
ρ_{calcd} [g cm^{-3}]	1.981	1.941	1.901
μ [mm^{-1}]	0.971	0.951	0.932
Reflections collected / unique	20108 / 3317	10356 / 1793	10597 / 1556
R_{int}	0.0709	0.0743	0.0664
R_1[a], wR_2[b] ($I > 2\sigma(I)$)	0.0509, 0.1175	0.0896, 0.2411	0.1210, 0.3235
R_1[a], wR_2[b] (all data)	0.0617, 0.1321	0.1254, 0.2758	0.1264, 0.3286
GOF	1.149	1.193	1.247
$\Delta\rho$[c] [e·Å^{-3}]	0.746 / –0.543	0.497 / –0.700	0.627 / −0.713

[a] $R_1 = \Sigma||F_o|-|F_c||/|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. [c] Maximum and minimum residual electron density.

Table S2. Selected bond lengths [Å] and angles [°] for **1**.

1 (203 K)			
K(1)–O(3)	2.749(3)	O(3)–K(1)–O(10)	72.75(8)
K(1)–O(10)	2.847(3)	O(3)–K(1)–O(12)#1	177.00(8)
K(1)–O(12)#1	2.866(3)	O(10)–K(1)–O(12)#1	109.02(7)
K(1)–O(1)#2	2.898(3)	O(10)–K(1)–O(1)#2	137.15(7)
K(1)–O(11)#1	2.917(3)	O(12)#1–K(1)–O(11)#1	48.14(6)
K(1)–O(2)#2	2.966(3)	O(3)–K(1)–O(2)#2	110.96(8)
K(1)–O(5)	2.966(3)	O(12)#1–K(1)–O(7)#3	113.07(7)
Cl(1)–O(2)	1.440(2)	O(2)–Cl(1)–O(1)	109.27(15)
Cl(2)–O(8)	1.449(2)	O(7)–Cl(2)–O(8)	109.30(16)
Cl(3)–O(9)	1.445(2)	O(10)–Cl(3)–O(9)	108.46(15)
C(1)–N(2)	1.459(4)	N(1)–C(2)–C(3)	115.5(3)
C(3)–C(5)	1.513(5)	C(2)–C(3)–C(5)	115.3(3)

Symmetry code: #1 x–1/2, –y+1/2, –z; #2 x–1/2, y, –z+1/2; #3 –x+1/2, y+1/2, z.

1 (328 K)

K(1)–O(7)	2.941(7)	O(7)–K(1)–O(4)	113.49(9)
K(1)–O(4)	2.943(5)	O(7)–K(1)–O(2)#2	141.84(18)
K(1)–O(2)#2	2.965(6)	O(4)–K(1)–O(3)#1	114.60(14)
K(1)–O(5)	2.999(5)	O(5)–K(1)–O(7)	71.17(9)
K(1)–O(8)#3	3.038(6)	O(2)#2–K(1)–O(3)	107.70(16)
K(1)–O(6)	3.120(8)	O(3)#1–K(1)–O(5)	113.83(14)
K(1)–O(1)#2	3.151(8)	O(3)–K(1)–O(8)#3	134.68(15)
Cl(1)–O(2)	1.445(6)	O(3)–K(1)–O(6)	66.82(17)
Cl(2)–O(5)	1.429(5)	O(1)–Cl(1)–O(3)	110.7(3)
Cl(3)–O(8)#1	1.422(5)	O(5)–Cl(2)–O(4)	107.6(3)
C(1)–N(1)	1.32(2)	O(7)–Cl(3)–O(8)	110.8(3)
C(1)–C(4)	1.309(15)	C(5)–C(3)–C(2)	119.0(14)

Symmetry code: #1 x, y, –z+1/2; #2 –x+1, y+1/2, z; #3 –x, y+1/2, –z+1/2.

1 (378 K)

K(1)–O(5)	2.968(7)	O(7)–K(1)–O(4)	108.48(13)
K(1)–O(7)	3.156(10)	O(7)–K(1)–O(2)#2	129.9(3)
K(1)–O(2)#1	3.159(13)	O(4)–K(1)–O(3)#2	105.0(2)
K(1)–O(8)#3	2.999(7)	O(5)–K(1)–O(7)	68.26(14)
K(1)–O(6)	2.986(9)	O(2)#1–K(1)–O(3)	105.7(2)
K(1)–O(1)#1	2.957(11)	O(3)#2–K(1)–O(5)	108.3(2)
Cl(1)–O(2)	1.414(11)	O(3)–K(1)–O(8)#3	172.1(2)
Cl(2)–O(5)	1.433(6)	O(3)–K(1)–O(6)	79.6(2)
Cl(3)–O(8)#2	1.439(6)	O(1)–Cl(1)–O(3)	111.0(4)
C(1)–N(1)	1.39(3)	O(5)–Cl(2)–O(4)	107.8(4)
C(1)–C(4)	1.293(19)	O(7)–Cl(3)–O(8)	110.9(4)
		C(5)–C(3)–C(2)	118.6(18)

Symmetry code: #1 –x+1, y–1/2, z; #2 x, y, –z+3/2; #3 –x, y–1/2, –z+3/2.

Table S3. Selected hydrogen bonds (Å, °) for **1** at 203 K.

D–H···A	D–H	H···A	D···A	D–H···A
N(1)–H(1C)···O(4)#7	0.89	2.22	2.979(4)	143.6
N(1)–H(1C)···O(7)#7	0.89	2.55	3.227(4)	133.5
N(1)–H(1D)···O(1)#7	0.89	2.44	2.952(4)	116.6
N(1)–H(1D)···O(4)#8	0.89	2.47	3.279(4)	151.8
N(1)–H(1D)···O(6)#8	0.89	2.47	3.065(4)	124.7
N(2)–H(2C)···O(8)#3	0.89	2.28	3.058(4)	145.3
N(2)–H(2C)···O(10)	0.89	2.39	3.061(4)	132.2
N(2)–H(2D)···O(9)#6	0.89	2.07	2.933(4)	163.8

Symmetry code: #3 –x+1/2 ,y+1/2, z; #6 x+1/2, –y+1/2, –z; #7 –x+3/2, y+1/2, z; #8 –x+1, y+1/2, –z+1/2.

Table S4. Fractional coordinates (10^4) and equivalent temperature factors ($Å^2 \cdot 10^3$) for O atoms in **1**. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	X	Y	Z	U_{eq}
1 (203 K)				
O(1)	6066(2)	2037(2)	2474(1)	29(1)
O(2)	4233(3)	2304(2)	3202(1)	31(1)
O(3)	4035(3)	2772(2)	2119(1)	30(1)
O(4)	3961(3)	1216(2)	2380(1)	33(1)
O(5)	3110(3)	450(2)	951(1)	44(1)
O(6)	1367(3)	225(2)	1729(1)	36(1)
O(7)	3403(3)	-669(2)	1743(1)	37(1)
O(8)	1736(2)	-870(2)	923(1)	30(1)
O(9)	2932(2)	2370(2)	-210(1)	34(1)
O(10)	4674(2)	2348(2)	579(1)	27(1)
O(11)	5089(2)	1679(2)	-439(1)	28(1)
O(12)	4954(3)	3267(2)	-332(1)	28(1)
1 (328 K)				
O(1)	4653(7)	3061(6)	2500	94(2)
O(2)	6140(5)	4774(6)	2500	64(2)
O(3)	4239(4)	5074(5)	1693(3)	79(1)
O(4)	3296(4)	8209(6)	663(3)	88(2)
O(5)	1759(4)	6577(6)	515(3)	84(2)
O(6)	1388(6)	4232(8)	2500	99(2)
O(7)	-13(7)	5980(6)	2500	88(2)
O(8)	-501(5)	3979(6)	3295(4)	112(2)
1 (378 K)				
O(1)	5008(11)	5953(8)	7500	114(3)
O(2)	6397(10)	4221(13)	7500	127(4)
O(3)	4528(7)	3978(8)	8289(6)	115(2)
O(4)	3243(6)	1589(7)	9485(4)	90(2)
O(5)	1705(6)	3211(8)	9345(4)	103(2)
O(6)	1149(8)	4782(8)	7500	75(2)
O(7)	-337(9)	3084(8)	7500	93(2)
O(8)	-749(6)	5083(6)	8309(4)	87(2)