Supporting information

High-temperature reversible phase transitions and exceptional dielectric anomalies in cobalt (II) based ionic crystals: $[Me_3NCH_2X]_2[CoX_4]$ (X = Cl and Br)

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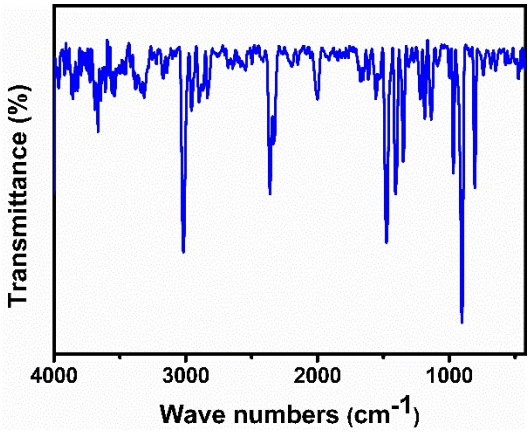

Fig. S1 Infrared (IR) spectra of solid compound **1** in KBr pellet was recorded on a Shimadzu model IR-60 spectrometer at room temperature.

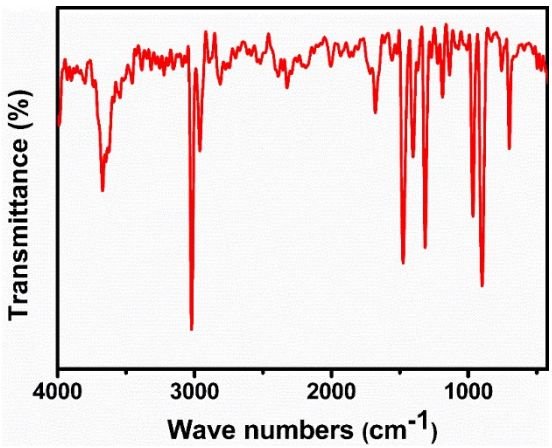

Fig. S2 Infrared (IR) spectra of solid compound **2** in KBr pellet was recorded on a Shimadzu model IR-60 spectrometer at room temperature.

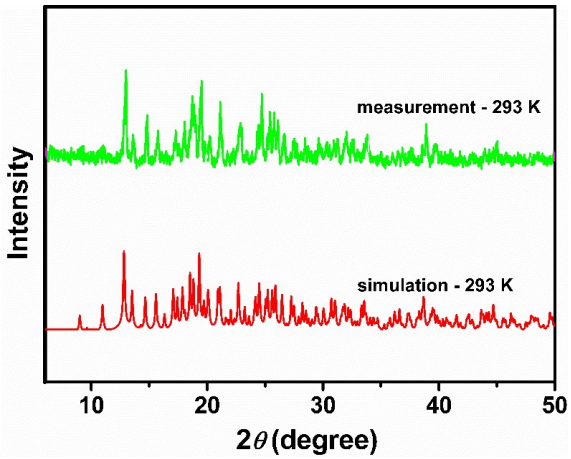

Fig. S3 PXRD patterns of **1** measured at 293 K matching very well with the simulated ones.

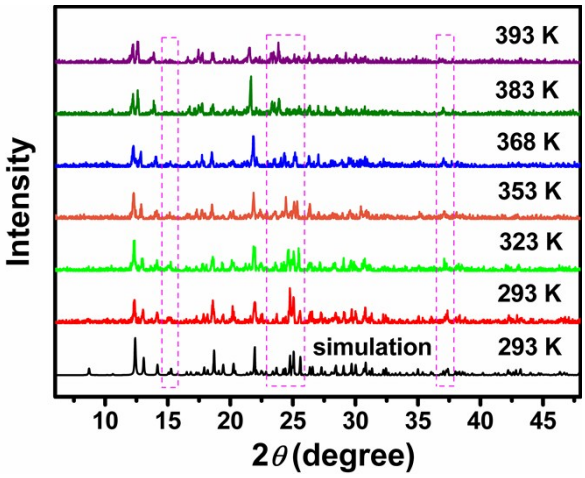

Fig. S4 Variable-temperature PXRD patterns of **2** measured in the heating mode. The PXRD patterns measured at 293 K matching very well with the simulated ones.

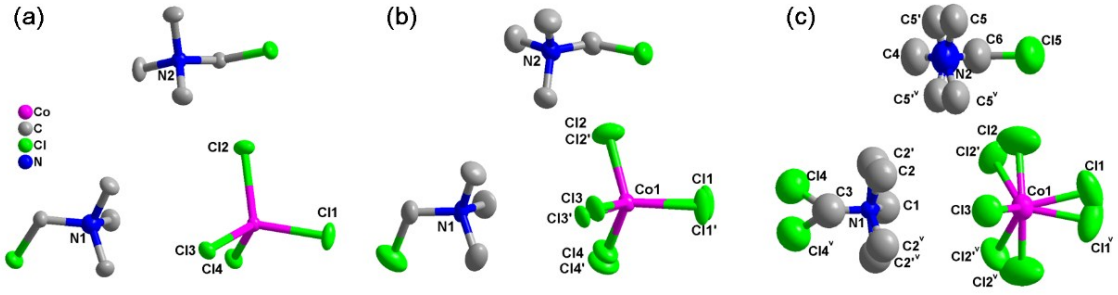

Fig. S5 Thermal ellipsoidal view of **1** at (a) 223 K, (b) at 293 K and (c) 353 K. Hydrogen atoms bonded to the C atoms are omitted for clarity. Thermal ellipsoids for the atoms are shown at 30% probability level.

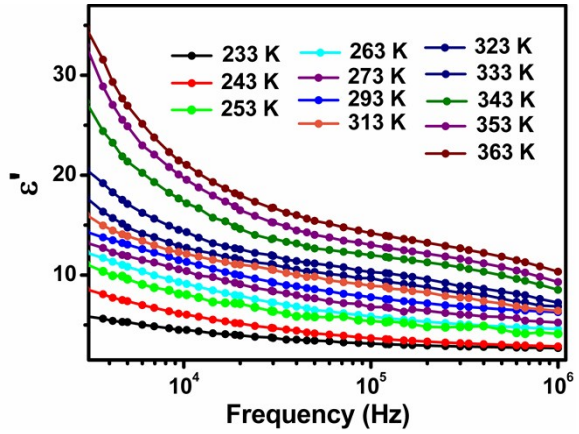

Fig. S6 Frequency dependence of the dielectric constant (ε') of **1** obtained at selected temperatures.

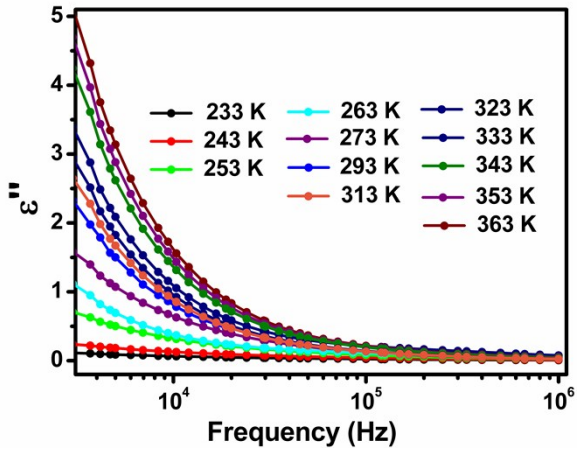

Fig. S7 Frequency dependence of the dielectric constant (ε'') of **1** obtained at selected temperatures.

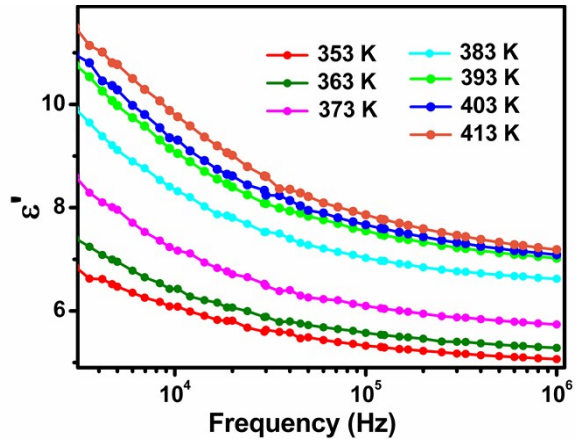

Fig. S8 Frequency dependence of the dielectric constant (ε') of **2** obtained at selected temperatures.

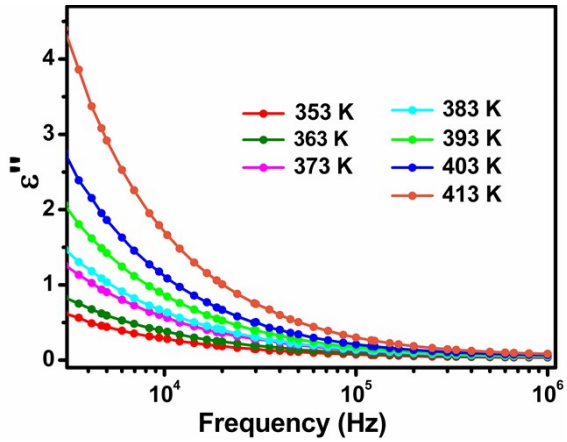

Fig. S9 Frequency dependence of the dielectric constant (ε'') of **2** obtained at selected temperatures.

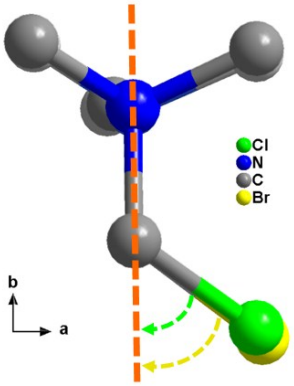

Fig. S10 The cations in **1** and **2** at RTP.

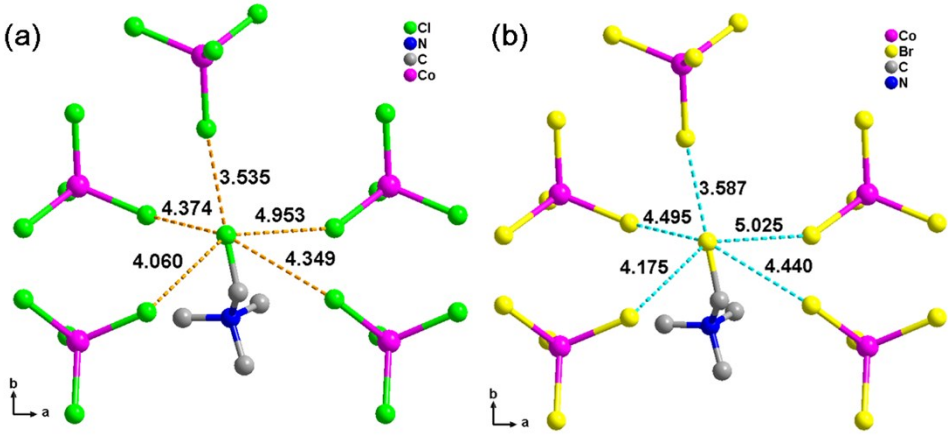

Fig. S11 The C-X…X interaction of (a) **1** (X=Cl). (b) **2** (X=Br).

Table S1 Crystal Data and Structure Refinement Details for **1** and **2.**

	$[Me_3NCH_2Cl]_2[CoCl_4]$			$[Me_3NCH_2Br]_2[CoBr_4]$
T (K)	223 K	293 K	353 K	293 K
Formula	417.91	417.91	417.91	684.61
Crystal system	orthorhombic	monoclinic	orthorhombic	monoclinic
Space group	$P2_12_12_1$	$P2_1/c$	*Pnma*	$P2_1/c$
a/Å	8.979(4)	9.199(7)	12.156(13)	9.4935(8)
b/Å	12.077(5)	16.828(14)	9.164(10)	17.3888(13)
c/Å	16.673(7)	12.10(1)	16.939(19)	12.4983(8)
β (deg)	90	93.47(2)	90	93.438(7)
V/Å^3	1808(13)	1870(3)	1887(4)	2059.5(3)
Z	4	4	4	4
F(000)	852	852	852	1284
Collected reflections	13385	11508	11575	12747
Unique reflections	4125	3382	1876	3733
Parameters refined	162	193	128	161
GOF	1.028	1.045	1.023	1.007
R_1	0.050	0.099	0.137	0.113
wR_2	0.115	0.217	0.258	0.311

Table S2 Selected bond lengths [Å] and angles [°] for **1** at 223 K, 293 K and 353 K.

223 K	Co1-Cl3	2.271(2)	Co1-Cl2	2.2692(19)
	Co1-Cl1	2.27(19)	Co1-Cl4	2.2792(18)
	C4-Cl5	1.76(7)	C8-Cl6	1.752(7)
	Cl2-Co1-Cl3	110.26(8)	Cl2-Co1-Cl1	110.69(8)
	Cl3-Co1-Cl1	107.17(9)	Cl2-Co1-Cl4	107.52(7)
	Cl3-Co1-Cl4	108.62(8)	Cl1-Co1-Cl4	112.57(8)
	N1-C4-Cl5	112.3(4)	N2-C8-Cl6	113.0(5)
293 K	Co1-Cl4	2.19(2)	Co1-Cl2	2.208(19)
	Co1-Cl1'	2.25(3)	Co1-Cl3	2.29(2)
	Co1-Cl3'	2.28(2)	Co1-Cl1	2.30(2)
	Co1-Cl4'	2.34(2)	Co1-Cl2'	2.363(19)
	Cl5-C4	1.762(18)	Cl6-C8	1.747(17)
	Cl4-Co1-Cl1'	119.2(11)	Cl4-Co1-Cl3	110.2(10)
	Cl2-Co1-Cl1'	102.0(16)	Cl2-Co1-Cl3	112.9(7)
	Cl2-Co1-Cl3'	121.8(7)	Cl1'-Co1-Cl3	107.7(15)
	Cl1'-Co1-Cl3'	109.8(14)	Cl4-Co1-Cl1	108.8(8)
	Cl2-Co1-Cl4'	108.8(8)	Cl2-Co1-Cl1	109.4(11)
	Cl3-Co1-Cl4'	114.8(10)	Cl3-Co1-Cl1	110.7(14)

	Cl1'-Co1-Cl4'	109.9(9)	Cl3'-Co1-Cl1	110.6(14)
	Cl3'-Co1-Cl4'	104.3(8)	Cl4-Co1-Cl2	104.7(12)
	Cl4-Co1-Cl2'	109.2(9)	Cl4'-Co1-Cl2'	114.5(11)
	Cl1-Co1-Cl2'	114.6(14)	Cl1'-Co1-Cl2'	106.1(10)
	Cl3'-Co1-Cl2'	112.3(7)	Cl3-Co1-Cl2'	103.3(7)
	N1-C4-Cl5	112.7(12)	N2-C8-Cl6	112.6(11)
353 K	Co1-Cl1^{i}	2.207(11)	Co1-Cl2''^{i}	2.209(12)
	Co1-Cl1	2.207(11)	Co1-Cl2'	2.209(12)
	Co1-Cl2^{i}	2.25(2)	Co1-Cl2	2.25(2)
	Co1-Cl3	2.258(7)	C6-Cl5	1.75(3)
	C3-Cl4	1.65(3)	C3-Cl4^{ii}	1.65(3)
	Cl1^{i}-Co1-Cl2''^{i}	107.9(7)	Cl1-Co1-Cl2^{i}	105.3(9)
	Cl1-Co1-Cl2''^{i}	126.8(6)	Cl2'-Co1-Cl2^{i}	112.7(8)
	Cl1^{i}-Co1-Cl2'	126.8(6)	Cl3-Co1-Cl2^{i}	109.3(6)
	Cl1-Co1-Cl2'	107.9(7)	Cl1^{i}-Co1-Cl2	105.3(9)
	Cl1^{i}-Co1-Cl3	113.4(4)	Cl2''^{i}-Co1-Cl2	112.7(8)
	Cl1-Co1-Cl3	113.4 (4)	Cl3-Co1-Cl2	109.3(6)
	Cl2''^{i}-Co1-Cl3	108.3(4)	Cl2'-Co1-Cl3	108.3(4)
	N1-C3-Cl4	130(3)	N1-C3-Cl4^{ii}	13(3)
	N2-C6-Cl5	125(4)		

Symmetry codes: (i) x, −y+3/2, z; (ii) x, −y+1/2, z.

Table S3 Selected bond lengths [Å] and angles [°] for **2** at 293 K.

293K	Co1-Br2	2.403(3)	Co1-Br1	2.405(3)
	Co1-Br3	2.405(3)	Co1-Br4	2.412(3)
	Br5-C1	1.89(3)	Br6-C5	1.85(2)
	Br2-Co1-Br1	108.98(14)	Br2-Co1-Br3	107.97(15)
	Br1-Co1-Br3	109.06(13)	Br2-Co1-Br4	112.57(13)
	Br1-Co1-Br4	107.15(12)	Br3-Co1-Br4	111.07(13)
	N1-C1-Br5	114.2(15)	N2-C5-Br6	116.7(16)