Electronic supporting information

Both dielectrics and conductance anomalies in an open-framework cobalt phosphate

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References

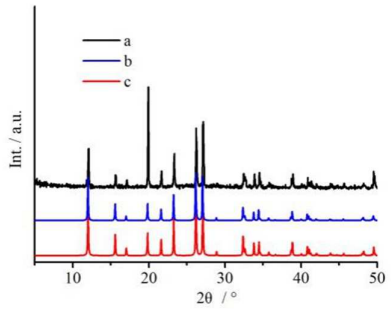


Fig. S1: Experimental and simulated PXRD patterns of **1** (a) as-prepared sample (b) obtained from single crystal data in literature[1] and (c) obtained from single crystal data in this work.

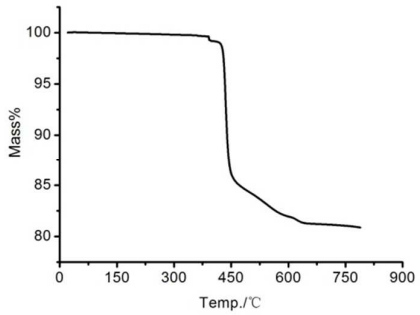


Fig. S2: TG curve of **1**.

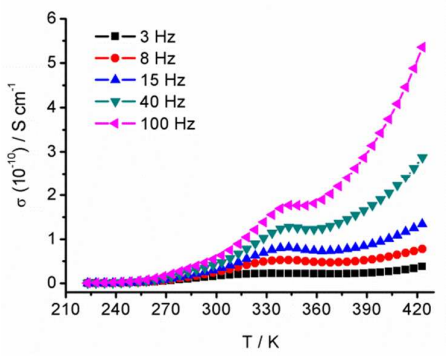


Fig. S3: Temperature dependent conductivity of **1** at the selected ac frequencies.

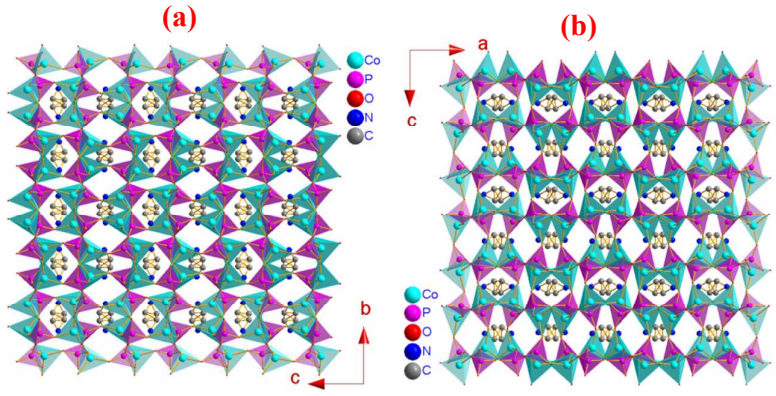


Fig. S4: Polyhedral packing diagrams of **1** at 293 K viewed along (a) *a*-axis/[100] and (b) *b*-axis/[010] directions, where the hydrogen atoms are omitted for clarity.

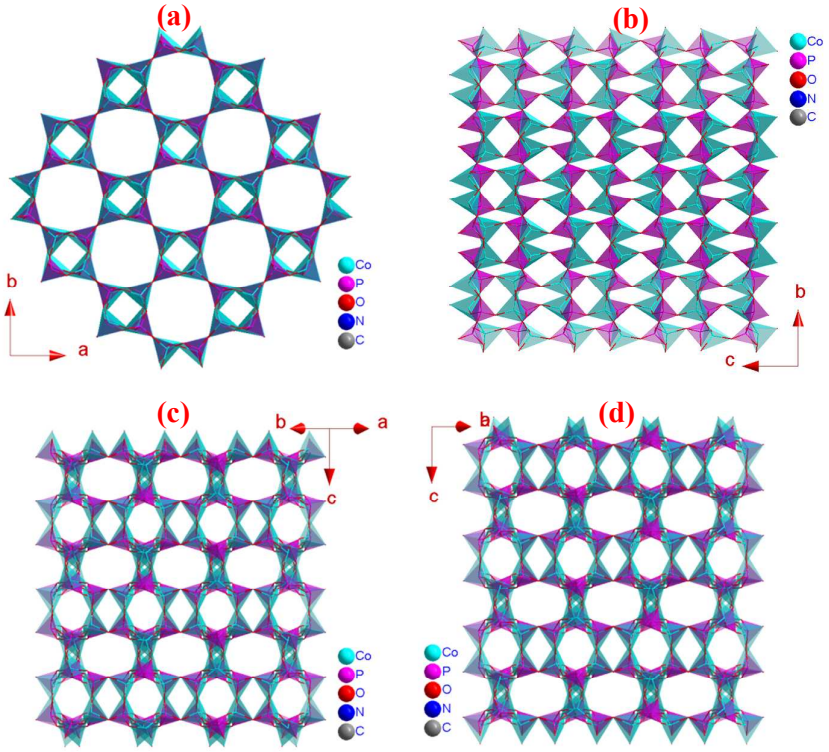


Fig. S5: Polyhedral open-framework diagrams of **1** at 293 K viewed along (a) [001] (b) [100] (c) [110] and (d) [-110] where the hydrogen atoms are omitted for clarity.

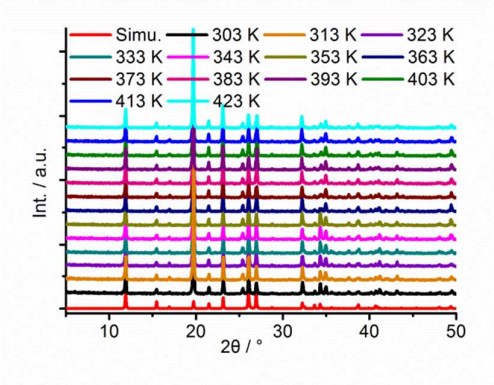


Fig. S6: Variable-temperature PXRD patterns in the 2θ range of 5-50° at the selected temperatures for **1**.

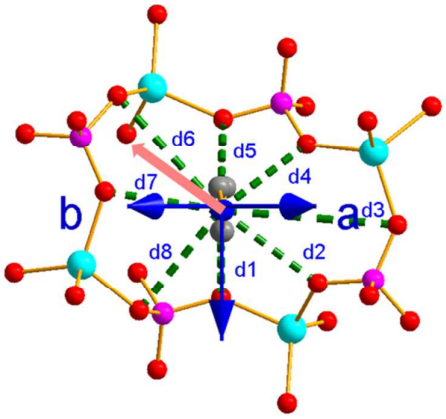
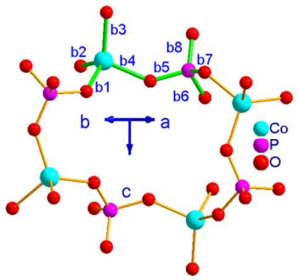


Fig. S7: Illustration for the neighboring N…O distances between the cation and framework viewed along the [110] direction for **1**, where the red arrow indicates the approximate direction that the cations are located off-center of channels upon heating from low-temperature phase to high-temperature phase.

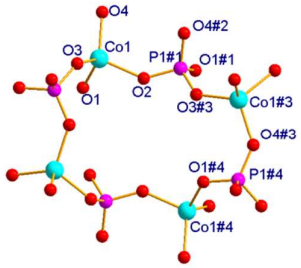
Table S1: Comparison of typical bond lengths in the CoO_4 and PO_4 tetrahedra of inorganic framework at 293, 323 and 373 K



$D_{Co/P...O}$ / Å	T = 293 K	T = 323 K	T = 373 K	Δd_1 / Å	Δd_2 / Å
b1	1.965(3)	1.965(3)	1.961(3)	0.000	-0.004
b2	1.951(3)	1.951(3)	1.957(3)	0.000	0.006
b3	1.941(2)	1.941(2)	1.945(3)	0.000	0.004
b4	1.918(3)	1.916(3)	1.922(3)	-0.002	0.006
b5	1.516(3)	1.520(3)	1.522(3)	0.004	0.002
b6	1.525(3)	1.526(3)	1.529(3)	0.001	0.003
b7	1.525(3)	1.527(3)	1.527(3)	0.002	0.000
b8	1.522(3)	1.521(3)	1.524(3)	-0.001	0.003

Notes: $\Delta d_1 = d_{Co/P...O}(T = 323K) - d_{Co/P...O}$ (T = 293K); $\Delta d_2 = d_{Co/P...O}$ (T = 373K) – $d_{Co/P...O}$ (T = 323K)

Table S2: Comparison of typical bond angles within the CoO_4 and PO_4 tetrahedra as well as between CoO_4 and PO_4 tetrahedra in the inorganic framework at 293, 323 and 373 K

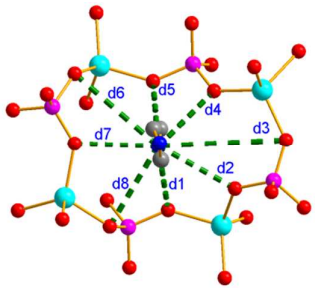


Bond angle / °	T = 293 K	T = 323 K	T = 373 K	$\Delta\angle i_1$ / °	$\Delta\angle i_2$ / °
∠O1-Co1-O2	97.52(13)	97.39(14)	97.24(13)	-0.13	-0.15
∠O1-Co1-O3	116.03(15)	116.09(16)	115.19(15)	0.06	-0.90
∠O1-Co1-O4	110.87(13)	110.88(14)	111.52(13)	0.01	0.64
∠O2-Co1-O3	107.57(17)	107.70(17)	107.74(15)	0.13	0.04
∠O2-Co1-O4	110.79(13)	110.54(13)	110.39(12)	-0.25	-0.15
∠O3-Co1-O4	112.90(12)	113.03(12)	113.46(11)	0.13	0.43
∠O2-P1#1-O1#1	108.0(2)	107.7(2)	108.1(2)	-0.1	0.4
∠O2-P1#1-O4#2	111.02(16)	110.89(17)	111.26(16)	-0.13	0.37
∠O2-P1#1-O3#3	104.97(18)	105.12(19)	104.89(17)	0.15	-0.23
∠O1#1-P1#1-O4#2	111.89(17)	112.02(18)	111.80(18)	0.13	-0.22
∠O1#1-P1#1-O3#3	110.5(2)	110.6(2)	110.7(2)	0.1	0.1
∠O3#3-P1#1-O4#2	110.28(16)	110.24(17)	109.92(17)	-0.04	-0.32
∠Co1-O2-P1#1	140.81(19)	141.12(19)	141.26(17)	0.31	0.14
∠P1#1-O3#3-Co1#3	135.39(18)	135.49(19)	135.29(19)	0.1	-0.20
∠Co1#3-O4#3-P1#4	139.08(17)	139.13(18)	138.48(18)	0.05	-0.65
∠P1#4-O1#4-Co1#4	128.9(2)	128.7(2)	129.0(2)	-0.2	0.3

Symmetry codes: #1 = y, 0.5-x, 0.5-z; #2 = 1-x, 1-y, -z; #3 = 1.5-y, x, 0.5-z; #4 = 1-x, 1-y, 1-z.

Notes: $\Delta\angle i_1 = \angle i(T = 323K) - \angle i(T = 293K)$; $\Delta\angle i_2 = \angle i(T = 373K) - \angle i(T = 323K)$

Table S3: Comparison of typical interatomic distances (Å) between N atom in H_2en^{2+} cation and O atoms in the inorganic framework at 293, 323 and 373 K



$d_{N...O}$ / Å	T = 293 K	T = 323 K	T = 373 K	Δd_1 / Å	Δd_2 / Å
d1	2.869(5)	2.870(5)	2.888(5)	0.001	0.018
d2	3.072(5)	3.070(5)	3.088(5)	-0.002	0.018
d3	4.465(5)	4.467(5)	4.490(5)	0.002	0.023
d4	2.840(5)	2.845(5)	2.855(5)	0.005	0.010
d5	2.912(5)	2.920(5)	2.934(5)	0.008	0.014
d6	3.904(5)	3.901(5)	3.884(5)	-0.003	-0.017
d7	2.958(5)	2.961(5)	2.941(5)	0.003	-0.020
d8	3.296(5)	3.296(5)	3.339(5)	0.000	0.043

Notes: $\Delta d_1 = d_{N...O}(T = 323K) - d_{N...O}(T = 293K)$; $\Delta d_2 = d_{N...O}(T = 373K) - d_{N...O}(T = 323K)$

Table S4: Atom displacement parameters (U_{eq}, U_{11}, U_{22}, and U_{33} / (10^{-2}) Å^2) at the selected temperatures

Atom	Tem./K	U_{eq}	U_{11}	U_{22}	U_{33}
Co(1)	293	1.34(2)	1.50(3)	1.19(3)	1.33(3)
	323	1.49(3)	1.65(3)	1.31(3)	1.49(4)
	373	1.87(2)	1.55(3)	1.90(3)	2.16(3)
P(1)	293	1.18(3)	1.31(5)	1.03(4)	1.22(5)
	323	1.31(3)	1.43(5)	1.16(5)	1.35(5)
	373	1.70(3)	1.46(5)	1.86(5)	1.79(5)
O(1)	293	4.60(9)	2.21(16)	8.2(3)	3.41(16)
	323	4.69(9)	2.32(17)	8.0(3)	3.70(17)
	373	4.33(9)	2.18(15)	8.1(2)	2.74(16)
O(2)	293	3.76(8)	3.53(17)	5.6(2)	2.17(13)
	323	3.83(9)	3.74(18)	5.4(2)	2.33(13)
	373	3.73(7)	5.38(18)	3.26(15)	2.55(14)
O(3)	293	4.02(9)	8.3(3)	1.73(15)	2.03(13)
	323	4.26(9)	8.5(3)	2.04(16)	2.19(14)
	373	4.64(8)	7.0(2)	2.44(16)	4.51(17)
O(4)	293	2.36(6)	2.62(14)	3.17(15)	1.29(11)
	323	2.57(6)	2.79(15)	3.38(16)	1.54(12)
	373	2.82(6)	3.20(14)	3.38(14)	1.87(13)
C(1)	293	2.1(2)	2.4(4)	2.3(4)	1.7(5)
	323	2.3(2)	2.5(5)	2.5(4)	1.8(4)
	373	2.82(2)	2.8(5)	3.5(5)	2.1(5)
C(1)’	293	2.0(2)	2.1(4)	2.4(4)	1.3(4)
	323	2.4(2)	3.2(5)	2.7(4)	1.5(5)
	373	3.1(2)	3.4(4)	3.6(5)	2.4(5)
N(1)	293	2.28(8)	2.7(2)	2.10(18)	2.02(17)
	323	2.59(9)	3.3(2)	2.4(2)	2.11(19)
	373	3.07(8)	2.95(19)	3.09(19)	3.2(2)

References

1. Chen, J.; Jones, R. H.; Natarajan, S.; Hursthouse, M. B.; Thomas, J. M. A Novel Open-Framework Cobalt Phosphate Containing a Tetrahedrally Coordinated Cobalt(I1) Center: $CoPO_4 \cdot 0.5C_2H_{10}N_2$. *Angw. Chem. Int. Ed.* **1994**, *33*, 639–640.