Counter Anion Dependent Gradual Spin Transition in a 1D Cobalt(II) Coordination Polymer

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1. Materials:

High purity 1,2-ethanediamine (Spectrochem, India), 2-benzoylpyridine (Lancaster, UK), sodium dicyanamide (Lancaster, UK), potassium hexafluorophosphate (Fluka, Germany) and cobalt(II) chloride hexahydrate (E. Merck, India) were used as received. All other chemicals and solvents used were AR grade. The synthetic reactions and work-up were done in open air.

2. Physical measurements:

Elemental analyses (carbon, hydrogen and nitrogen) were done using a Perkin-Elmer 2400 CHNS/O elemental analyzer. IR spectrum (KBr disk, 4000-400 cm^{-1}) was recorded using a Perkin-Elmer FTIR model RX1 spectrometer. Ground state absorption measurement (in MeOH) was made with a Shimadzu model UV-2450 UV-VIS spectrophotometer. The conventional magnetic characterization was carried out with a commercial MPMS-XL SQUID magnetometer operating between 300 and 2 K.

3. Isolation of $[Co(enbzpy)(\mu_{1,5}\text{-dca})]_n(PF_6)_n$ (1.PF_6):

Enbzpy (390 mg, 1 mmol) in methanol (10 mL) was added to $CoCl_2.6H_2O$ (238 mg, 1 mmol) dissolved (10 mL) in the same solvent. A methanolic solution (10 mL) of Na(dca) (89 mg, 1 mmol) was added drop by drop followed by the addition of KPF_6 (184 mg, 1 mmol) to this deep red reaction mixture. The final deep red solution was filtered and the supernatant liquid was kept undisturbed in open air for slow evaporation. After one day red crystalline product of **1.**PF_6 was isolated by filtration, washed with dehydrated ethanol and dried *in vacuo* over silica gel. Yield: 462 mg (70% based on cobalt); elemental analyses calcd (%): C 50.9, H 3.4, N 14.8; found: C 51.2, H 3.3, N 15.0%. IR (KBr in cm^{-1}): ν = 2313, 2237, 2182 (dca), 1636, 1598 (C=C + C=N), 841, 558 (PF_6^-). UV-Vis (MeOH, λ in nm): 280 (ligand-based transition), 535 [$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition].

4. X-ray crystallographic analysis:

Suitable single crystal (0.12 × 0.09 × 0.06) of **1.**PF_6 was mounted on a thin glass fiber and X-ray single crystal structural data of that single crystal were collected on Bruker D8 VENCTURE SCXRD at 298(2) K (**1.**PF_6^{RT}) and at 100(2) K (**1.**PF_6^{LT}) using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) operating at 50 kV and 30 mA. The program SAINT[1] was used for integration of diffraction profiles (for **1.**PF_6^{RT} and **1.**PF_6^{LT}) and absorption

corrections were made with SADABS programme[2]. Structures of **1.**PF_6^{RT} and **1.**PF_6^{LT} were solved using the programme SHELXS-97[3] and refined by SHELXL-97[3]. All non-hydrogen atoms were refined with anisotropic displacement parameters whereas all the hydrogen atoms were fixed by HFIX and placed in ideal positions. Two C atoms (C13 and C14) in **1.**PF_6^{LT} of the ethylenic arm of the Schiff base are disordered over two positions with fractional occupancies of 0.62 and 0.38 for C13 and C13A, and 0.62 and 0.38 for C14 and C14A, respectively. Later, during the refinement of the structure, a highly disordered electron density peaks were located which were believed to be disordered P and F. In **1.**PF_6^{LT}, the P atoms in the PF_6^- counter anion is in disordered state with occupancy factors 0.7110 and 0.2890 for P2 and P2A, respectively. Each F atom of PF_6^- counter anion is in disordered state over two positions with occupancy factors 0.7110 (F1, F2, F3, F4, F5 and F6) and 0.2890 (F1A, F2A, F3A, F4A, F5A and F6A). Additionally, some restraints such as EADP and ISOR were applied for a few atoms in **1.**PF_6^{LT}. Materials for publication were prepared using SHELXTL[3], PLATON[4], Mercury 1.4[5] and Diamond[6] programmes.

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Table S1. Selected bond lengths and bond angles (Å, °) for **1.**PF_6^{RT} and **1.**PF_6^{LT}

Bond distances of **1.**PF_6^{RT}		Bond angles of **1.**PF_6^{RT}	
Co1-N1	2.109(5)	N4-Co1-N2	156.84(17)
Co1-N2	2.045(4)	N4-Co1-N3	77.06(17)
Co1-N3	2.034(9)	N2-Co1-N3	79.84(17)
Co1-N4	2.097(4)	N4-Co1-N5	87.14(17)
Co1-N5	2.127(5)	N2-Co1-N5	95.75(18)
Co1-N7*	2.134(5)	N3-Co1-N5	93.0(2)
		N4-Co1-N7*	89.96(17)
		N2-Co1-N7*	91.20(18)
		N3-Co1-N7*	97.01(18)
		N5-Co1-N7*	168.7(2)
		N4-Co1-N1	126.10(17)
		N2-Co1-N1	77.02(17)
		N3-Co1-N1	156.83(17)
		N5-Co1-N1	88.13(18)
		N7-Co1-N1*	84.79(17)
		C28-N6-C27	130.1(6)
Bond distances of **1.**PF_6^{LT}		Bond angles of **1.**PF_6^{LT}	
Co1-N1	2.039(6)	N1-Co1-N5	85.7(3)
Co1-N2	1.921(6)	N1-Co1-N2	80.1(2)
Co1-N3	1.916(6)	N5-Co1-N2	90.6(3)
Co1-N4	2.043(7)	N1-Co1-N7*	87.2(3)
Co1-N5	2.163(7)	N5-Co1-N7*	171.3(3)
Co1-N7**	2.181(8)	N2-Co1-N7*	93.1(3)
		N1-Co1-N3	163.8(2)
		N5-Co1-N3	96.6(3)
		N2-Co1-N3	83.9(3)
		N7-Co1-N3*	91.6(3)
		N1-Co1-N4	115.9(3)
		N5-Co1-N4	90.9(3)
		N2-Co1-N4	164.1(3)
		N7-Co1-N4*	87.6(3)
		N3-Co1-N4	80.2(3)
		C28-N6-C27	124.4(7)

*x, 1+y, z; **x, -1+y, z.

Table S2. Hydrogen bonds and C-H···π interactions donor/acceptor scheme (Å, °) for **1.**PF_6^{RT}

D-H···A	D-H	H···A	D···A	D-H···A
C4-H4···N6^{i}	0.93	2.52	3.191(9)	129
C8-H8···Cg(4)^{ii}	0.93	2.97	3.802(9)	150
C21-H21···Cg(5)^{iii}	0.93	2.85	3.581(7)	136

Symmetry codes: i = 1-x, 1/2+y, 1/2-z, -1/2+z; ii = 1-x,-1/2+y,1/2-z; iii = -x,1/2+y,1/2-z

Cg(4) = N(1)-C(1)-C(2)-C(3)-C(4)-C(5)

Cg(5) = N(4)-C(22)-C(23)-C(24)-C(25)-C(26)

Table S3. π···π interactions donor/acceptor scheme (Å, °) for **1.**PF_6^{RT}

Cg-Cg	Cg-Cg distance	Dihedral angle (*i,j*)	Perpendicular distances between baricentres (i,j)
Cg(6)-Cg(6)^{iv}	4.235(5)	0.00	3.696(4)
Cg(7)-Cg(7)^{v}	4.937(4)	0.00	4.261(3)

Symmetry codes: iv = 1-x, -y, -z; v = -x, -y, -z.

Cg(6) = C(7)-C(8)-C(9)-C(10)-C(11)-C(12)

Cg(7) = C(16)-C(17)-C(18)-C(19)-C(20)-C(21)

Table S4. Hydrogen bonds and C-H···π interactions donor/acceptor scheme (Å, °) for **1.**PF_6^{LT}

D-H···A	D-H	H···A	D···A	D-H···A
C1-H55···F3^{vi}	0.95	2.54	3.347(17)	143
C4-H2···N6^{i}	0.95	2.43	3.210(10)	140
C23-H23···N5^{vii}	0.95	2.56	3.418(10)	150
C8-H8···Cg(5)^{i}	0.95	2.99	3.817(12)	147
C21-H21···Cg(6)^{viii}	0.95	2.88	3.545(11)	128

Symmetry codes: vi = x, 3/2-y, -1/2+z; vii = 2-x, 1/2+y, 1/2-z; viii = 2-x, -1/2+y, 1/2-z.

Cg(5) = N(1)-C(1)-C(2)-C(3)-C(4)-C(5)

Cg(6) = N(4)-C(22)-C(23)-C(24)-C(25)-C(26)

Table S5. π···π interactions donor/acceptor scheme (Å, °) for **1.**PF_6^{LT}

Cg-Cg	Cg-Cg distance	Dihedral angle (*i,j*)	Perpendicular distances between baricentres (i,j)
Cg(7)-Cg(7)^{ix}	3.955(6)	0.00	3.473(4)
Cg(8)-Cg(8)^{x}	5.222(5)	0.00	4.515(4)

Symmetry codes: ix = 1-x, 1-y, 1-z; x = 2-x, 1-y, 1-z.

Cg(7) = C(7)-C(8)-C(9)-C(10)-C(11)-C(12)

Cg(8) = C(16)-C(17)-C(18)-C(19)-C(20)-C(21)

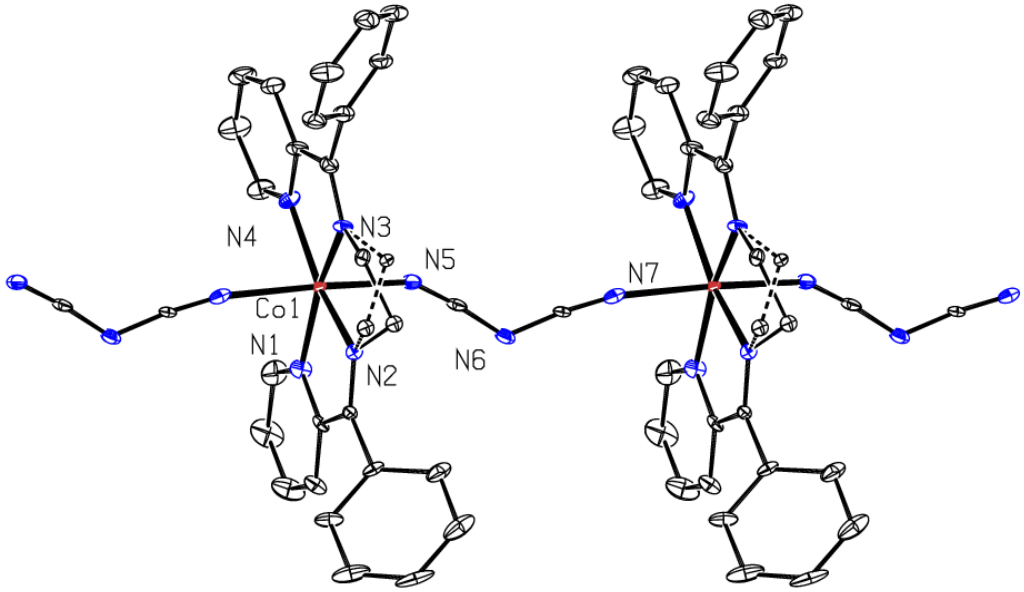

Fig. S1. A view of 1D chain in **1**.PF_6^{LT} (ORTEP, 30% thermal ellipsoid probability).

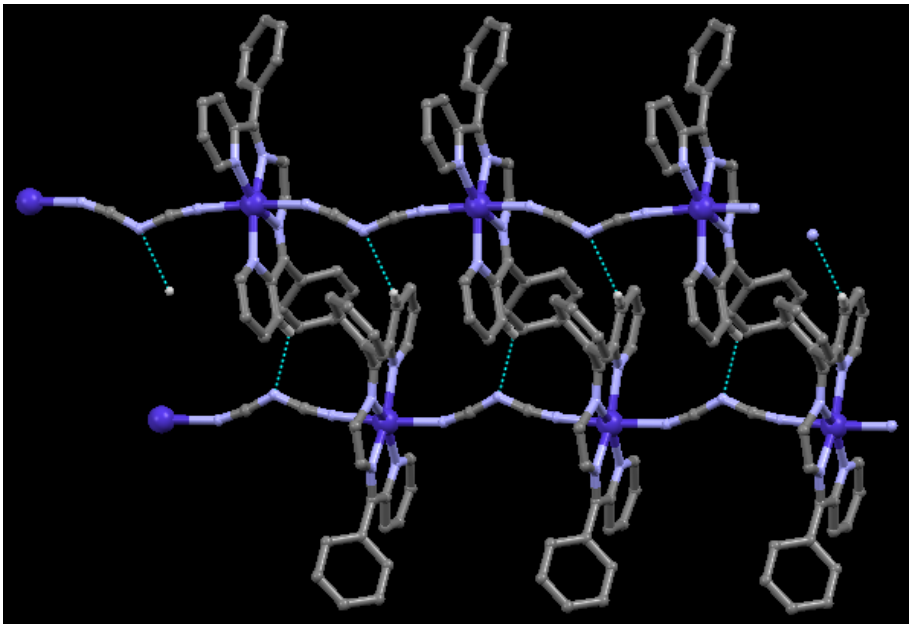

Fig. S2. Association of two 1D chains in **1**.PF_6^{RT} by C-H···N hydrogen bonds.

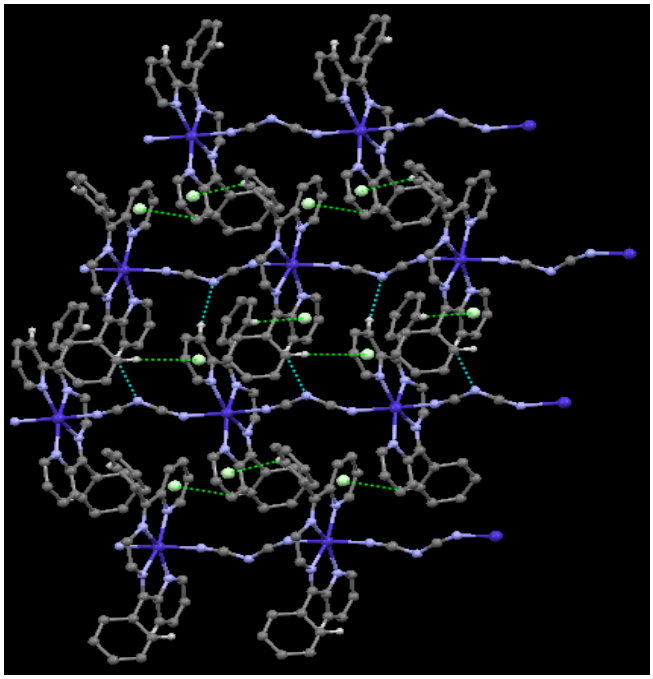

Fig. S3. 2D sheet structure in **1.**PF_6^{RT} formed through C-H···N hydrogen bonds and C-H···π interactions.

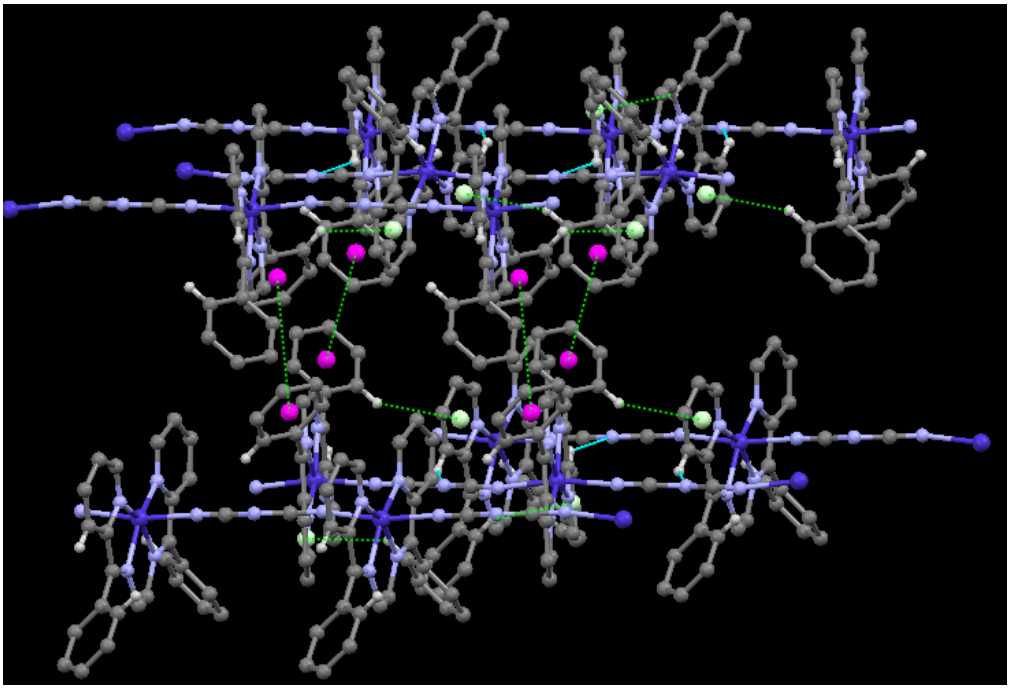

Fig. S4. 3D network structure in **1.**PF_6^{RT} formed through C-H···N hydrogen bonds and C-H···π and π···π interactions.

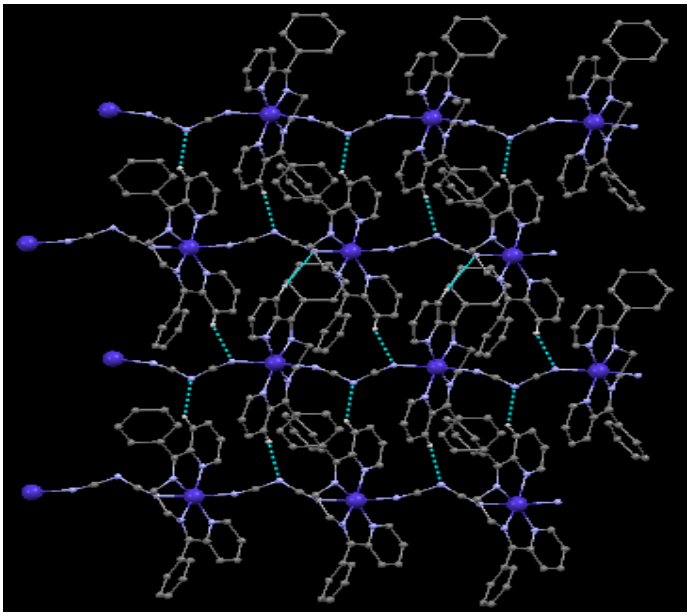

Fig. S5. 2D sheet structure in **1.**PF_6^{LT} formed through C-H···N hydrogen bonds.

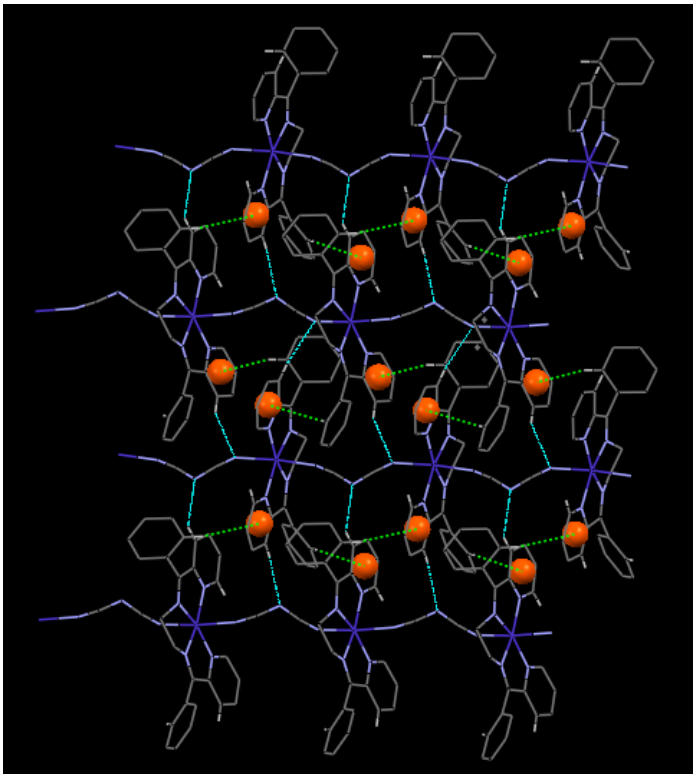

Fig. S6. 2D sheet structures in **1.**PF_6^{LT} formed through C-H···N hydrogen bonds and C-H···π interactions

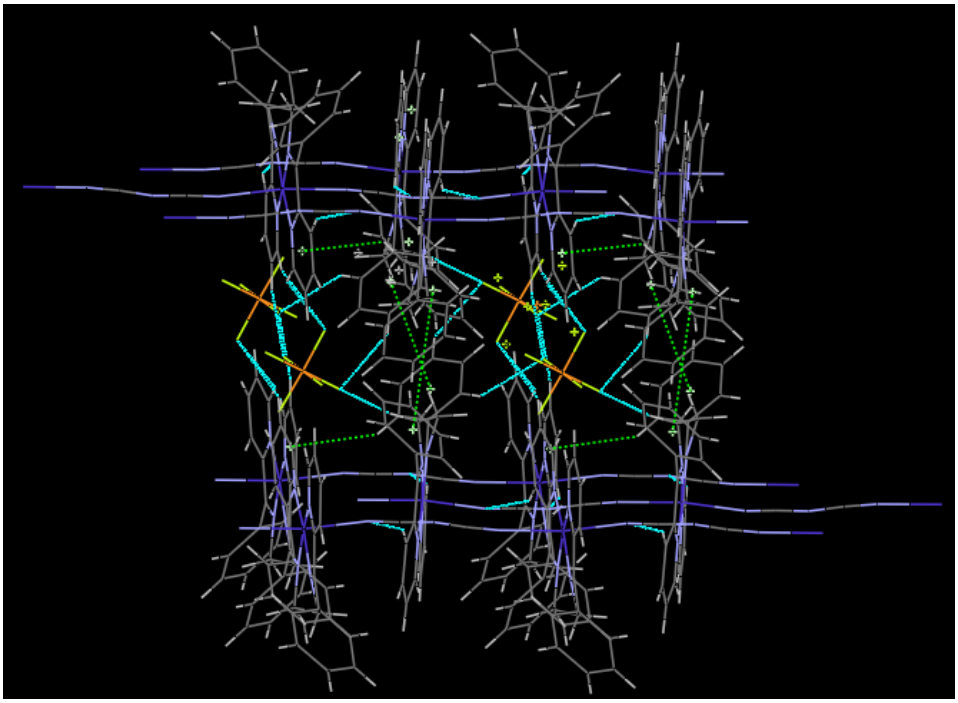

Fig. S7. 3D network structure in **1.**PF_6^{LT} formed through C-H···N and C-H···F hydrogen bonds and C-H···π and π···π interactions.