

Supporting Information for:

Substituent Effects of N4 Schiff Base Ligands on the Formation of Fluoride-Bridged Dicobalt(II) Complexes via B–F Abstraction: Structures and Magnetism

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X-ray Diffraction Data Collection and Crystal Structure Refinement. The data were collected on a Rigaku AFC12 diffractometer with a Saturn 724+ CCD using a graphite monochromator with MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). A total of 1220 frames of data were collected using ω -scans with a scan range of 0.5° and a counting time of 45 seconds per frame. The data were collected at 100 K using a Rigaku XStream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data reduction were performed using the Rigaku Americas Corporation's Crystal Clear version 1.40.¹ The structure was solved by direct methods using SIR2004² and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2014/7.³ Structure analysis was aided by use of the programs PLATON98⁴ and WinGX.⁵ The hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to $1.2 \times U_{eq}$ of the attached atom ($1.5 \times U_{eq}$ for methyl hydrogen atoms).

For complex **1**, The cobalt complex resides around a crystallographic two-fold rotation axis at $\frac{1}{2}$, y , $\frac{1}{4}$. The two-fold rotation axis passes through the bridging fluoride ion, F1. To maintain charge balance in the crystal, there are three BF₄ ions per dimeric complex. In the asymmetric unit, one of the tetrafluoroborate ions is given half-weight. This ion is disordered with a half-weighted molecule of acetonitrile. The two-fold symmetry of the complex results in the disorder of a molecule of water and a molecule of acetonitrile that are bound to the Co ion. By symmetry, the water and acetonitrile molecules are half-weighted in the refinement model. Because this disorder could be the result of imposing two-fold symmetry on the complex, a model in the lower symmetry space group, *Cc*, was considered. In *Cc*, there is no requirement that the water molecule and the acetonitrile molecule need be disordered. The refinement in *Cc* was reasonable. Predictably, the refinement model in *Cc* suffered from high correlation between parameters that would be related by the two-fold rotation axis. The agreement factors were also reasonable but significantly higher than those for the *C2/c* model. For the *Cc* model, $R1 = 0.0543$, while $wR2 = 0.149$ and $GOOF = 1.08$. When compared to the *C2/c* model, where $R1 = 0.0452$ and $wR2 = 0.112$, with a $GOOF = 1.07$, the *C2/c* model is superior.

The function, $\sum w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.0403 \cdot P)^2 + (19.6854 \cdot P)]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $Rw(F^2)$ refined to 0.112, with $R(F)$ equal to 0.0452 and a goodness of fit, S , = 1.07. Definitions used for calculating $R(F)$, $Rw(F^2)$ and the goodness of fit, S , are given below.⁶ The data were checked for secondary extinction effects but no correction was necessary.

Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).⁷ All figures were generated using SHELXTL/PC.⁸

X-ray refinement references

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- 4) Spek, A. L. (1998). *PLATON*, A Multipurpose Crystallographic Tool. Utrecht University, The Netherlands.
- 5) *WinGX 1.64*. (1999); An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-ray Diffraction Data. Farrugia, L. J. *J. Appl. Cryst.* 32. 837-838.
- 6) $R_w(F^2) = \{\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w(|F_o|^4)\}^{1/2}$, where w is the weight given each reflection.
 $R(F) = \sum(|F_o| - |F_c|) / \sum |F_o|$ for reflections with $F_o > 4(\sigma(F_o))$.
 $S = [\sum w(|F_o|^2 - |F_c|^2)^2 / (n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.
- 7) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.
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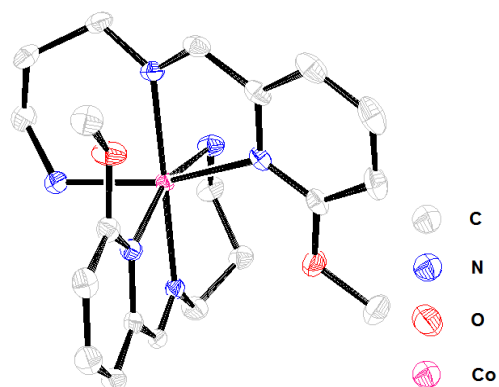


Figure S1. ORTEP diagram (50% ellipsoids) of the cation of **[Co(pnN₃-OMe)₂](BF₄)₂ (5)**. H's are not shown for sake of clarity.

Table S1. Crystal data and refinement parameters for of **5(ClO₄)**.

5	
Empirical formula	C ₂₀ H ₃₀ Cl ₂ CoN ₆ O ₁₀
Molecular formula	[Co ^{II} (pnN ₃ -OMe _{hydrolyzed}) ₂](ClO ₄) ₂
FW	644.33
Color	Reddish pink
Habit	Needles
Size (mm)	0.54 × 0.19 × 0.16
T (K)	100(2)
λ (Å)	0.71073
Lattice	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	9.9009(5)
<i>b</i> (Å)	17.9640(8)
<i>c</i> (Å)	15.9921(9)
α (°)	90.000
β (°)	105.467(2)
γ (°)	90.000
<i>V</i> (Å ³)	2741.3(2)
<i>Z</i>	4
<i>d</i> _{calc} (g/cm ³)	1.561
μ (mm ⁻¹)	0.884
GOF on <i>F</i> ²	1.010
<i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	R1 = 0.0355 wR2 = 0.0746
<i>R</i> indices all data	R1 = 0.0568 wR2 = 0.0855

Table S2. Selected bond distances (Å) and angles (°) for dimers with μ -F bridge(s) reported here and in literature.

Reference No.	Chemical Formula	M...M	M-N*	M-N _{py}	M-N _{pyr}	M-F	\angle M-F-M
This work	[Co ^{II} ₂ (μ -F)(pnN ₄ -PhCl) ₂ (OH ₂)(MeCN)](BF ₄) ₃ (1)	4.003	*Schiff-base: 2.103(2) 2.107(2)	2.2559(19) 2.282(2)	–	2.034(5)	159.47(11)
EDEVEG ¹	[Co ₂ (μ -F)(μ -L _m [*]) ₂](BF ₄) ₃	4.13	–	–	*pyrazole: avg: 2.099	2.0626(4)	180.00
HUQHOR ²	[Co ₂ (μ -F)(μ -L _m) ₂](BF ₄) ₃	3.90	–	–	*pyrazole: avg: 2.09	1.9521(4) 1.9774(4) avg: 1.96	180
NIDBAD ³	[Co ₂ (μ -Br)L ¹](BPh ₄) ₂	3.577	–	–	1.944(1), 1.945(4)	2.077(3)	118.9(2)
DISTAA ⁴	[Co ₃ (μ -F) ₂ (detrH) ₆ (NCS) ₄](H ₂ O) ₂	3.3726(3)	–	–	*triazole: 2.137(2)- 2.206(2)	1.992(1)- 2.019(1) avg: 2.006	114.44(7)
DOMHIW ⁵	[Co ₃ (μ -F) ₂ (tmtr) ₄ (NCS) ₄](H ₂ O) ₂ (H ₂ O) ₄	3.4015(3)	–	–	*triazole: 2.131(2), 2.152(2), 2.168(2), 2.172(2)	2.023(1) 2.058(2) avg: 2.041	112.92(7)
DOTBUK ⁶	[Cr ₂ (μ -F)(F) ₂ (TPyA) ₂](BF ₄) ₃	3.862	*amine 2.059 2.065	2.016 2.042	–	1.977(16) 1.9347(16)	179.85(12)
This work	[Co ^{II} ₂ (μ -F) ₂ (pnN ₄ -PhCl) ₂](BF ₄) ₂ (2)	3.109	*Schiff-base: 2.2.115(4) 2.127(4)	2.288(4) 2.326(4)	–	2.045(4) 2.049(4)	98.8(2) 99.1(2)
CIBGOL ⁷	[Co ₄ (L ^{Mix}) ₂ (F) ₄](BF ₄) ₄	3.114(9)	*amine: 2.127(5) 2.139(4) mean: 2.129	2.100(4)- 2.162(4) mean: 2.129	*pyrimidine: 2.233(4) 2.227(4) mean: 2.230	1.987(3)- 2.086(3) mean: 2.036	100.0(1) 99.4(1)
VEDTAB ⁸	[Co ₄ (L ^{Et}) ₂ (F) ₄](BF ₄) ₄	3.194(5)	2.161(2) 2.177(2) mean: 2.169	2.134(2)- 2.198(2) avg: 2.155	*pyrimidine: 2.390(2) 2.316(2) mean: 2.353	1.992(1)- 2.095(1), mean: 2.049	100.64(5) 104.29(5)
FMPZCO ⁹	[Co ₂ F ₂ (dmpz) ₆](BF ₄) ₂	3.092(2)	–	–	2.033(5), 2.040(5), 2.042(6)	1.924(4) 2.146(4)	98.8(2)
UZEYOO ¹⁰	[L ^{tBu} Co(μ -F)] ₂	3.062	*amine: 1.952 1.974	–	–	1.860 1.988	105.43
XUJTOM ¹¹	[Co ₆ L ₄ (μ -F) ₂](BF ₄) ₁₀	3.143	–	2.127(6)- 2.208(13) avg: 2.172	2.093(12)- 2.190(9)	2.035(6)- 2.058(5) avg: 2.047	100.18 100.36
BOMTII ¹²	[Co ₂ (μ -F) ₂ L ₂](BF ₄) ₂	3.157	*amine: 2.124(3)	2.143(3) 2.249(3) 2.251(3)	–	1.985(2), 2.098(2) avg: 2.196	101.24
NASHUL ¹³	[L ^{Me} Fe(μ -F)] ₂	3.0831(6)	*diketiminate 2.0081(18) 2.0161(17)	–	–	1.9757(12) 1.9774(14)	102.44(10) 102.56(9)
CENJIO ¹⁴	[Cu ₂ (μ -F) ₂ (tmpz) ₆](BF ₄) ₂	3.0141(8)	–	–	2.103(3) 2.009(3) 1.965(3)	2.183(2) 1.911(2)	94.59(7)
PIBPEV ¹⁵	[Cu ₂ F ₂ (bnpy ₂) ₂](PF ₆) ₂	3.137(1)	*amine: 2.064	2.014 2.019	–	1.918(2) 2.232(2)	97.97
This work	[Co ^{II} ₂ (pnN ₄) ₃](BF ₄) ₄ (3)	6.801	*Schiff-base: 2.141(7) 2.144(7) 2.168(7)	2.154(7) 2.160(7) 2.166(7)	–	–	–
This work	[Co ^{II} (py) ₄ (MeCN) ₂](BF ₄) ₂ (4)	–	–	2.156(8)	–	–	–

Table S2 references

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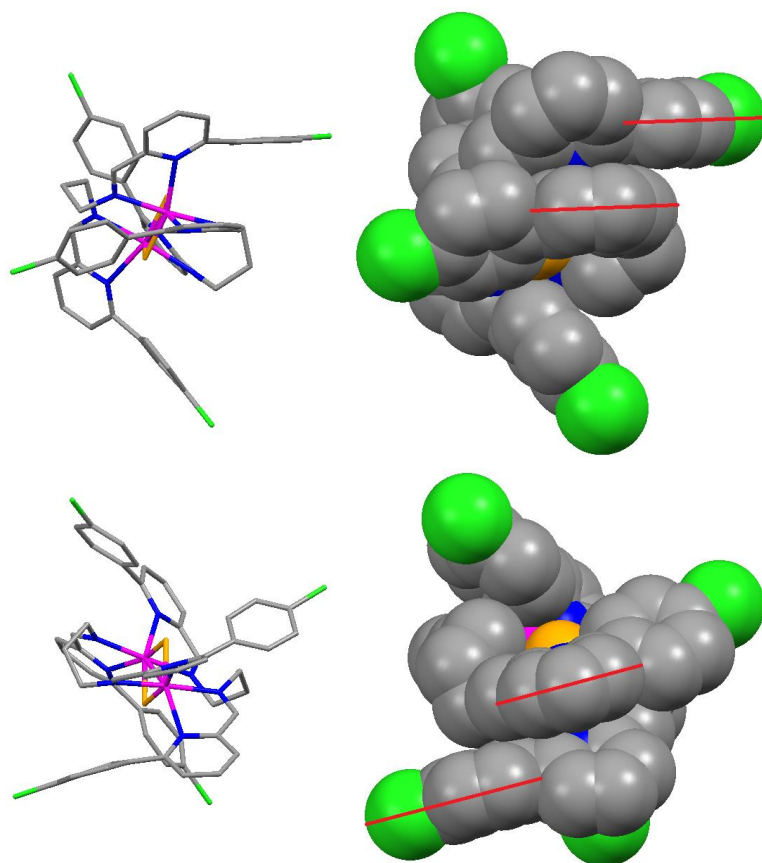


Figure S2. Capped stick and space-filling representations of complex **2**, illustrating the π - π interactions between ligands. Red lines represent the plane of the aromatic ring. The closest C \cdots C distance is 3.616 Å.

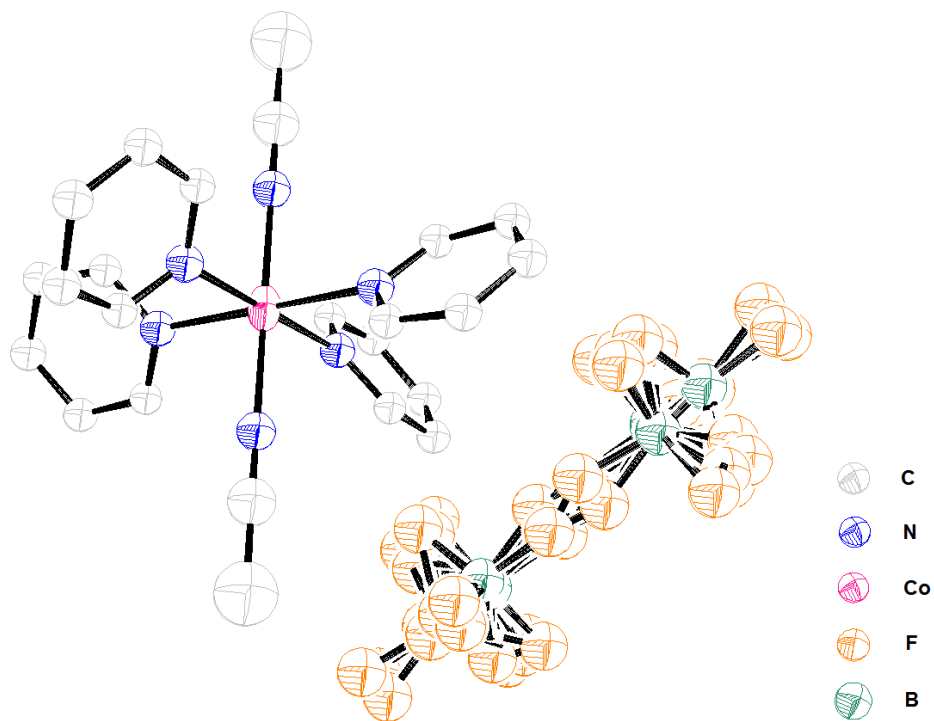


Figure S3. Full ORTEP diagram (50% ellipsoids) of [Co^{II}(py)₄(MeCN)₂](BF₄)₂ (**4**) including disorder model of the BF₄ counterions. H's are not shown for sake of clarity.

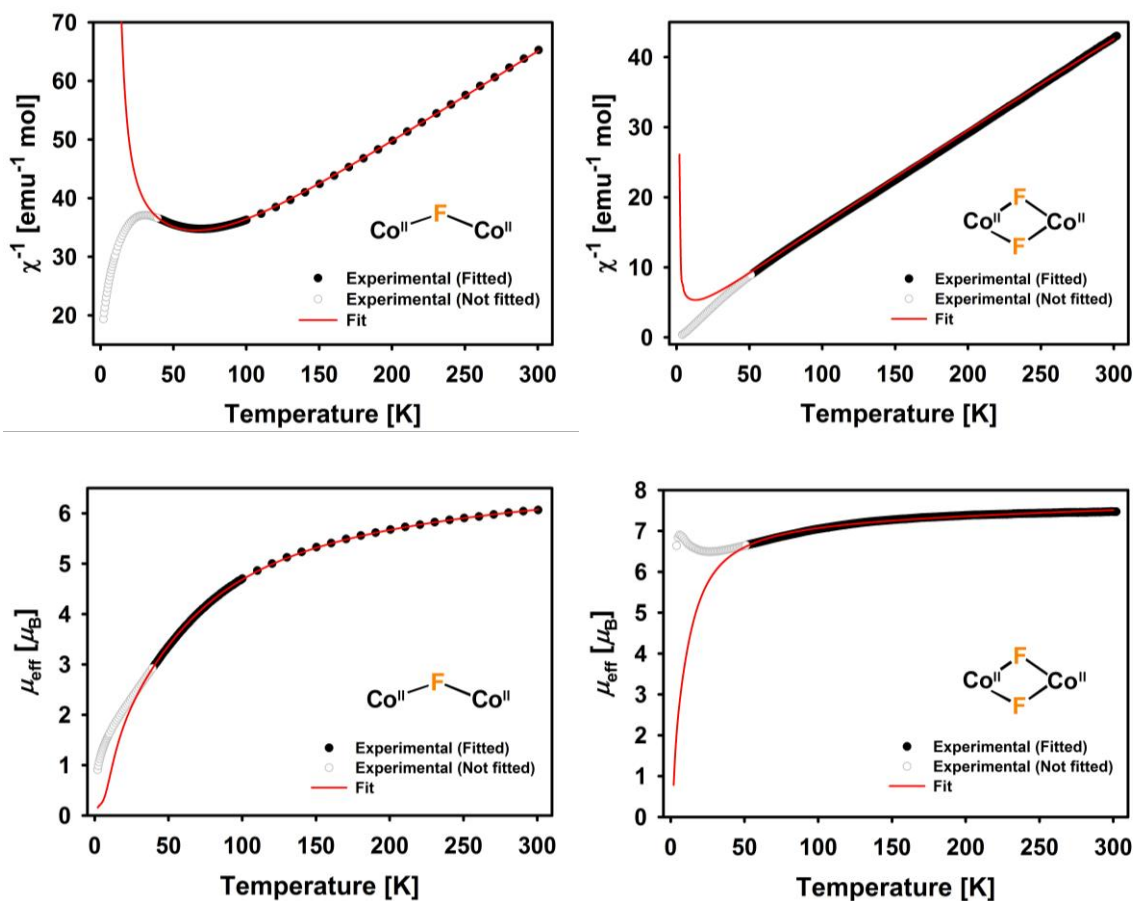


Figure S4. The reciprocal χ vs T and μ_{eff} vs T plots for complexes 1 and 2 obtained 1000 G; filled circles represent experimental data that is well-modeled by the magnetic simulation (red line). Open black circles are experimental data that deviates from the simulation.