Supporting Information

Temperature dependence of the spin state and geometry in tricobalt paddlewheel complexes with halide axial ligands

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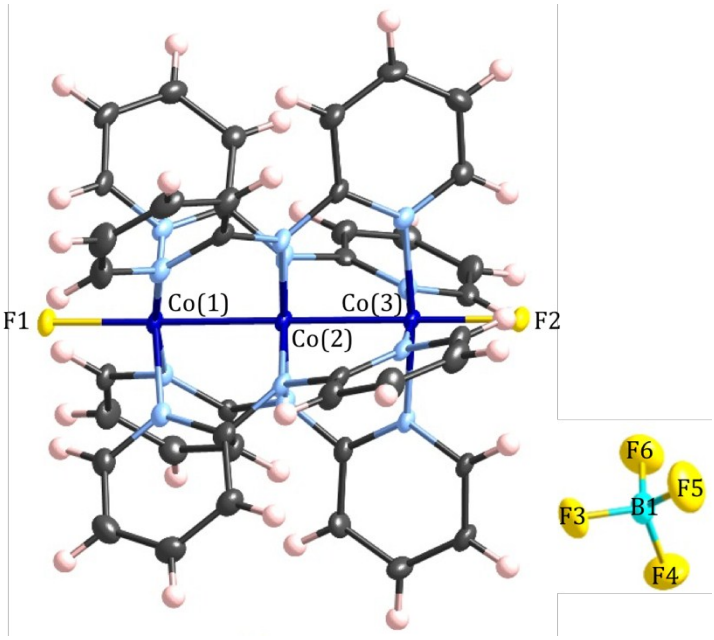

Figure S1. Thermal ellipsoid plot (50% probability) of **1**[BF_4]·4CH_2Cl_2. Dichloromethane atoms omitted.

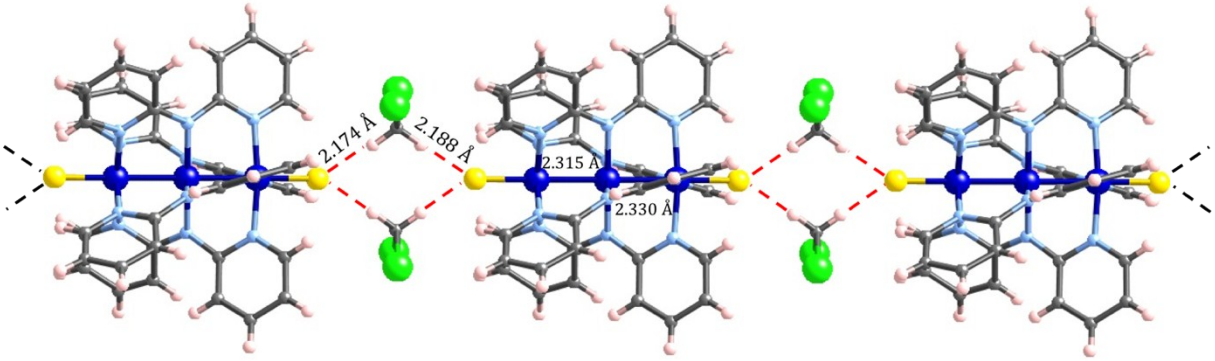

Figure S2. One-dimensional arrangement of **1**·2CH_2Cl_2 assembled by hydrogen bonding interactions with the dichloromethane solvent molecule. The slight difference in the length of the hydrogen bonds on either side of **1** may contribute to the slight asymmetry of the {Co_3} core.

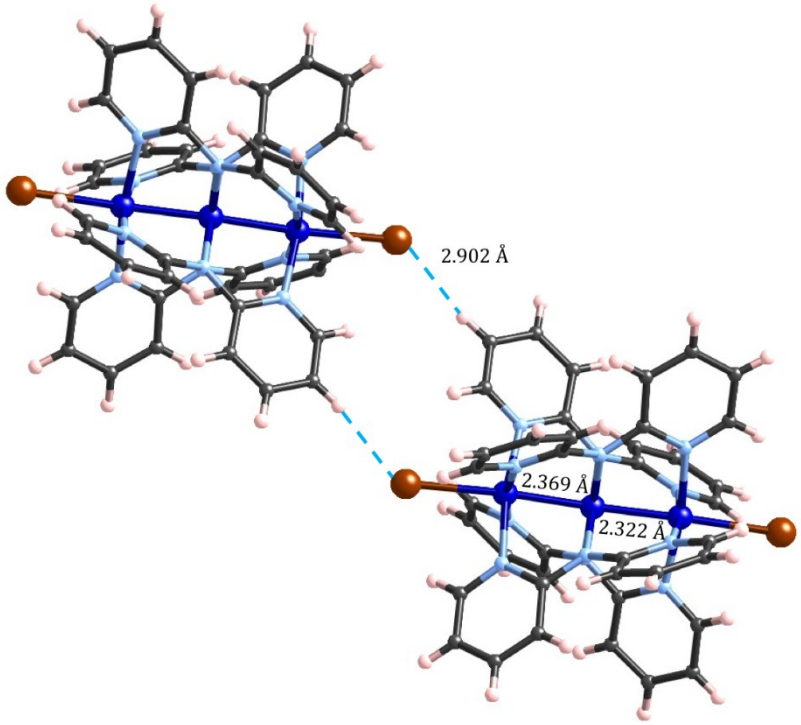

Figure S3. Pairwise arrangement of **3**·Et_2O assembled by H···Br–Co interactions. Similar interactions are observed in **2**·Et_2O.

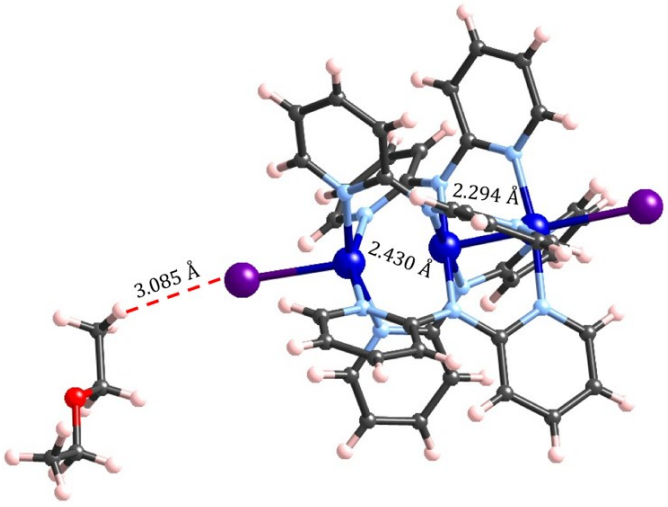

Figure S4. Interaction of axial iodide with the diethyl ether solvent molecule in **4**·Et_2O associated with the elongation of one Co–Co distance.

Table S1. Crystal data and structure refinement for **1**·2CH_2Cl_2.

formula	$C_{42}H_{36}Cl_4Co_3F_2N_{12}$		
FW	1065.42		
T, K	85(2)	120(2)	250(2)
crystal system	monoclinic	monoclinic	monoclinic
space group	*C*2/*c*	*C*2/*c*	*C*2/*c*
a, Å	20.362(5)	20.3854(6)	20.4657(15)
b, Å	13.838(3)	13.8382(6)	13.9159(8)
c, Å	17.100(7)	17.0652(7)	17.1718(12)
β, deg.	118.721(8)	118.457(3)	118.216(2)
V, Å^3	4225(2)	4232.4(3)	4309.4(5)
Z	4	4	4
d(calc), g cm^{-3}	1.675	1.672	1.642
data/restraints/paramet.	4321/0/287	4279/0/287	3954/0/287
R_1[a] ($I > 2\sigma(I)$)	0.0247	0.0341	0.0459
wR_2[b] ($I > 2\sigma(I)$)	0.0626	0.0940	0.1168

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$, $w = 1/\sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [\max(0 \text{ or } F_o^2) + 2(F_c^2)]/3$.

Table S2. Crystal data and structure refinement for **2**·Et_2O.

formula	$C_{44}H_{42}Cl_2Co_3N_{12}O$			
FW	1002.58			
T, K	85(2)	120(2)	298(2)	350(2)
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a, Å	15.8035(8)	15.8217(14)	15.9782(17)	16.0520(12)
b, Å	15.6410(8)	15.6581(12)	15.8417(18)	15.9094(11)
c, Å	16.9161(8)	16.9215(14)	17.110(2)	17.1371(11)
β, deg.	98.981(2)	98.916(3)	98.357(5)	97.995(3)
V, Å^3	4130.1(4)	4141.4(6)	4284.9(9)	4333.9(5)
Z	4	4	4	4
d(calc), g cm^{-3}	1.612	1.608	1.554	1.537
data/restraints/paramet.	9131/0/561	12158/0/559	10646/0/561	8839/3/559
R_1[a] ($I > 2\sigma(I)$)	0.0219	0.0246	0.0371	0.0404
wR_2[b] ($I > 2\sigma(I)$)	0.0539	0.0589	0.0868	0.1038

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$, $w = 1/\sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [\max(0 \text{ or } F_o^2) + 2(F_c^2)]/3$.

Table S3. Crystal data and structure refinement for **3**·Et_2O.

formula	$C_{44}H_{42}Br_2Co_3N_{12}O$			
FW	1091.51			
T, K	85(2)	120(2)	298(2)	350(2)
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a, Å	16.0028(4)	16.0223(3)	16.1426(14)	16.1914(13)
b, Å	15.7192(4)	15.7356(3)	15.8923(14)	15.9355(12)
c, Å	17.0322(4)	17.0502(3)	17.1821(15)	17.2266(14)
β, deg.	100.4800(10)	100.4460(10)	99.607(4)	99.293(4)
V, Å^3	4213.00(18)	4227.46(14)	4346.1(7)	4386.4(6)
Z	4	4	4	4
d(calc), g cm^{-3}	1.721	1.715	1.668	1.653
data/restraints/paramet.	20493/0/561	20351/0/559	11240/0/561	10059/0/561
R_1[a] ($I > 2\sigma(I)$)	0.0263	0.0291	0.0431	0.0491
wR_2[b] ($I > 2\sigma(I)$)	0.0655	0.0683	0.1293	0.1389

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$, $w = 1/\sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [\max(0 \text{ or } F_o^2) + 2(F_c^2)]/3$.

Table S4. Crystal data and structure refinement for **4**·$C_2H_4Cl_2$.

formula	$C_{42}H_{36}Cl_2Co_3I_2N_{12}$		
FW	1210.32		
T, K	85(2)	120(2)	298(2)
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2/n$	$P2/n$	$P2/n$
a, Å	13.0572(5)	13.0708(7)	13.127(3)
b, Å	11.4574(4)	11.5118(6)	11.755(2)
c, Å	14.2468(5)	14.2242(8)	14.317(3)
β, deg.	94.467(2)	94.580(2)	94.369(8)
V, Å^3	2124.87(13)	2133.5(2)	2202.9(7)
Z	2	2	2
d(calc), g cm^{-3}	1.892	1.884	1.806
data/restraints/paramet.	4881/2/280	4914/56/321	4531/60/331
R_1[a] ($I > 2\sigma(I)$)	0.0252	0.0226	0.0268
wR_2[b] ($I > 2\sigma(I)$)	0.0566	0.0505	0.0637

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$, $w = 1/\sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [\max(0 \text{ or } F_o^2) + 2(F_c^2)]/3$.

Table S5. Crystal data and structure refinement for **4**·Et_2O.

formula	$C_{44}H_{42}I_2Co_3N_{12}O$			
FW	1185.48			
T, K	85(2)	170(2)	240(2)	298(2)
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	*C*2/*c*	*C*2/*c*	*C*2/*c*	*C*2/*c*
a, Å	37.112(3)	37.280(4)	37.3975(17)	37.533(9)
b, Å	12.6154(9)	12.6433(11)	12.7054(5)	12.746(6)
c, Å	18.8581(14)	18.8935(19)	18.9980(8)	19.056(2)
β, deg.	91.526(4)	91.748(5)	91.748(2)	91.61(1)
V, Å^3	8825.8(11)	8901.2(5)	9022.7(7)	9113(5)
Z	8	8	8	8
d(calc), g cm^{-3}	1.784	1.769	1.745	1.728
data/restraints/paramet.	13501/0/561	8155/0/561	8265/0/561	8370/0/537
R_1[a] ($I > 2\sigma(I)$)	0.0231	0.0371	0.0212	0.0493
wR_2[b] ($I > 2\sigma(I)$)	0.0499	0.0675	0.0482	0.0844

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$, $w = 1/\sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [\max(0 \text{ or } F_o^2) + 2(F_c^2)]/3$.

Table S6. Crystal data and structure refinement for **1**[BF_4]·4CH_2Cl_2.

formula	C44 H40 B Cl8 Co3 F6 N12
FW	1322.08
T, K	120(2)
crystal system	triclinic
space group	P-1
a, Å	11.5876(4)
b, Å	14.3205(5)
c, Å	17.8580(5)
α, deg.	71.833(1)
β, deg.	76.570(1)
γ, deg.	67.623(1)
V, Å^3	2581.78(15)
Z	2
d(calc), g cm^{-3}	1.701
data/restraints/paramet.	9460/0/667
R_1[a] ($I > 2\sigma(I)$)	0.0423
wR_2[b] ($I > 2\sigma(I)$)	0.1116

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$, $w = 1/\sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [\max(0 \text{ or } F_o^2) + 2(F_c^2)]/3$.

Table S7. Selected bond distances (Å) and angles (°) for **1**·2CH_2Cl_2.

T (K)	85(2)	120(2)	250(2)
Co(1)–Co(2)	2.3265(6)	2.3257(6)	2.3304(9)
Co(2)–Co(3)	2.3156(6)	2.3157(6)	2.3153(9)
Co(1)–F(1)	2.0108(14)	2.0084(19)	2.016(3)
Co(3)–F(2)	2.0054(14)	2.005(2)	2.007(3)
Co(1)–N(1)	1.9650(14)	1.964(2)	1.965(3)
Co(1)–N(1A)[#]	1.9649(14)	1.964(2)	1.965(3)
Co(1)–N(2)	1.9712(16)	1.964(2)	1.969(3)
Co(1)–N(2A)[#]	1.9711(16)	1.964(2)	1.969(3)
Co(2)–N(3)	1.9198(14)	1.917(2)	1.919(3)
Co(2)–N(3A)[#]	1.9197(14)	1.917(2)	1.919(3)
Co(2)–N(4)	1.9388(15)	1.932(2)	1.936(3)
Co(2)–N(4A)[#]	1.9388(15)	1.932(2)	1.936(3)
Co(3)–N(5)	1.9554(15)	1.950(2)	1.956(3)
Co(3)–N(5A)[#]	1.9544(14)	1.950(2)	1.956(3)
Co(3)–N(6)	1.9528(14)	1.951(2)	1.949(3)
Co(3)–N(6A)[#]	1.9528(14)	1.9507(19)	1.949(3)
Co(1)–Co(2)–Co(3)	180.00	180.00	180.00
Co(1)–Co(2)–F(1)	180.00	180.00	180.00
Co(2)–Co(3)–F(2)	180.00	180.00	180.00

[#] Symmetry transformations used to generate equivalent atoms: 1-x+1, y, -z+1/2

Table S8. Selected bond distances (Å) and angles (°) for **2**·Et_2O.

T (K)	85(2)	120(2)	298(2)	350(2)
Co(1)–Co(2)	2.3323(2)	2.3312(3)	2.3752(5)	2.3964(6)
Co(2)–Co(3)	2.3209(2)	2.3198(3)	2.3299(5)	2.3397(6)
Co(1)–Cl(1)	2.4816(3)	2.4823(4)	2.4574(7)	2.4350(9)
Co(3)–Cl(2)	2.4430(3)	2.4443(4)	2.4471(7)	2.4412(9)
Co(1)–N(1)	1.9910(11)	1.9827(10)	2.028(2)	2.054(3)
Co(1)–N(2)	1.9908(11)	1.9784(11)	2.027(2)	2.049(3)
Co(1)–N(3)	1.9779(11)	1.9892(11)	2.027(2)	2.050(3)
Co(1)–N(4)	1.9831(11)	1.9915(11)	2.027(2)	2.049(3)
Co(2)–N(5)	1.9063(11)	1.9128(10)	1.9125(19)	1.913(2)
Co(2)–N(6)	1.9064(11)	1.9018(10)	1.911(2)	1.917(3)
Co(2)–N(7)	1.9023(11)	1.9039(10)	1.9098(19)	1.916(2)
Co(2)–N(8)	1.9143(11)	1.9076(10)	1.918(2)	1.917(3)
Co(3)–N(9)	1.9723(11)	1.9764(11)	1.991(2)	2.016(3)
Co(3)–N(10)	1.9699(11)	1.9956(10)	1.982(2)	2.004(3)
Co(3)–N11)	1.9966(11)	1.9682(11)	2.006(2)	1.997(3)
Co(3)–N(12)	1.9772(11)	1.9722(10)	1.991(2)	1.993(3)
Co(1)–Co(2)–Co(3)	177.557(10)	177.665(10)	178.454(19)	178.55(2)
Co(1)–Co(2)–Cl(1)	178.267(12)	178.340(12)	178.86(3)	178.98(4)
Co(2)–Co(3)–Cl(2)	177.013(12)	177.099(11)	177.73(2)	177.96(3)

Table S9. Selected bond distances (Å) and angles (°) for **3**·Et_2O.

T (K)	85(2)	120(2)	298(2)	350(2)
Co(1)–Co(2)	2.3303(2)	2.3295(2)	2.3691(6)	2.3862(7)
Co(2)–Co(3)	2.3162(2)	2.3162(2)	2.3218(5)	2.3308(7)
Co(1)–Br(1)	2.68524(19)	2.6890(2)	2.6363(6)	2.6096(7)
Co(3)–Br(2)	2.61670(18)	2.6205(2)	2.6081(6)	2.6002(7)
Co(1)–N(1)	1.9780(10)	1.9790(11)	2.025(3)	2.042(4)
Co(1)–N(2)	1.9843(9)	1.9967(10)	2.029(3)	2.047(3)
Co(1)–N(3)	1.9898(10)	1.9912(11)	2.029(3)	2.046(3)
Co(1)–N(4)	1.9988(9)	1.9853(11)	2.033(3)	2.049(4)
Co(2)–N(5)	1.9016(9)	1.9021(10)	1.916(2)	1.916(3)
Co(2)–N(6)	1.9128(9)	1.9038(10)	1.914(3)	1.915(3)
Co(2)–N(7)	1.9013(9)	1.9010(10)	1.914(2)	1.910(3)
Co(2)–N(8)	1.9033(9)	1.9111(10)	1.913(3)	1.912(3)
Co(3)–N(9)	1.9998(9)	1.9670(10)	2.007(3)	2.011(3)
Co(3)–N(10)	1.9816(9)	1.9789(10)	1.997(3)	2.009(3)
Co(3)–N(11)	1.9771(9)	1.9824(11)	1.993(3)	2.003(3)
Co(3)–N(12)	1.9685(9)	1.9986(10)	1.977(3)	1.989(3)
Co(1)–Co(2)–Co(3)	177.165(9)	177.343(10)	178.29(2)	178.49(3)
Co(1)–Co(2)–Br(1)	177.811(8)	177.919(9)	178.42(2)	178.54(3)
Co(2)–Co(3)–Br(2)	176.380(8)	176.499(9)	177.04(2)	177.30(3)

Table S10. Selected bond distances (Å) and angles (°) for **4**·Et_2O.

T (K)	85(2)	170(2)	240(2)	298(2)
Co(1)–Co(2)	2.4295(3)	2.4504(8)	2.4645(4)	2.4680(15)
Co(2)–Co(3)	2.2942(3)	2.2928(8)	2.2937(4)	2.3047(14)
Co(1)–I(1)	2.7728(3)	2.7535(7)	2.7449(3)	2.7542(13)
Co(3)–I(2)	2.8620(3)	2.8620(7)	2.8719(3)	2.8702(13)
Co(1)–N(1)	2.1372(15)	2.158(4)	2.1691(19)	2.176(6)
Co(1)–N(2)	2.0896(15)	2.106(4)	2.1232(19)	2.116(5)
Co(1)–N(3)	2.0939(15)	2.123(4)	2.1380(18)	2.150(6)
Co(1)–N(4)	2.0933(16)	2.109(4)	2.1253(19)	2.126(6)
Co(2)–N(5)	1.8845(14)	1.889(3)	1.8941(17)	1.896(5)
Co(2)–N(6)	1.9077(14)	1.909(3)	1.9116(17)	1.912(5)
Co(2)–N(7)	1.8974(13)	1.898(3)	1.9005(17)	1.902(5)
Co(2)–N(8)	1.9010(14)	1.904(3)	1.9090(17)	1.907(5)
Co(3)–N(9)	1.9768(14)	1.979(4)	1.9787(18)	1.982(5)
Co(3)–N(10)	1.9838(14)	1.981(3)	1.9855(17)	1.990(5)
Co(3)–N(11)	1.9840(14)	1.984(3)	1.9881(17)	1.995(5)
Co(3)–N(12)	1.9799(14)	1.986(3)	1.9830(16)	1.988(5)
Co(1)–Co(2)–Co(3)	176.858(13)	177.26(3)	177.724(17)	178.17(5)
Co(1)–Co(2)–I(1)	178.635(12)	178.85(3)	178.990(15)	179.25(5)
Co(2)–Co(3)–I(2)	179.55(12)	179.49(3)	179.626(15)	179.61(5)

Table S11. Selected bond distances (Å) and angles (°) for **4**·$C_2H_4Cl_2$.

T (K)	85(2)	120(2)	298(2)
Co(1)–Co(2)	2.3144(3)	2.3111(4)	2.3557(6)
Co(1)–I(1)	2.8905(4)	2.8926(5)	2.8449(7)
Co(1)–N(1)	1.9947(18)	1.9958(19)	2.047(2)
Co(1)–N(2)	1.9922(17)	1.9931(19)	2.039(2)
Co(1)–N(3)	2.0078(18)	2.0017(19)	2.040(2)
Co(1)–N(4)	1.9910(17)	1.9892(18)	2.029(2)
Co(2)–N(5)	1.8929(18)	1.8921(19)	1.895(2)
Co(2)–N(6)	1.8888(18)	1.8898(19)	1.899(2)
Co(1)–Co(2)–Co(1A)[#]	178.99(2)	179.44(2)	179.49(3)
Co(1)–Co(2)–I(1)	178.902(16)	179.119(16)	179.246(17)

[#] Symmetry transformations used to generate equivalent atoms: 1-x+3/2, y, -z+1/2.

Table S12. Selected bond distances (Å) and angles (°) for **1**[BF_4]·4CH_2Cl_2 at 120 K.

Co(1)–Co(2)	2.3191(6)	Co(2)–N(7)	1.886(3)
Co(2)–Co(3)	2.3192(6)	Co(2)–N(8)	1.888(3)
Co(1)–F(1)	1.9560(19)	Co(3)–N(9)	1.957(3)
Co(3)–F(2)	1.9521(19)	Co(3)–N(10)	1.951(3)
Co(1)–N(1)	1.951(3)	Co(3)–N(11)	1.958(3)
Co(1)–N(2)	1.950(3)	Co(3)–N12)	1.953(3)
Co(1)–N(3)	1.942(3)	Co(1)–Co(2)–Co(3)	179.53(3)
Co(1)–N(4)	1.948(3)	Co(1)–Co(2)–F(1)	179.25(6)
Co(2)–N(5)	1.883(3)	Co(2)–Co(3)–F(2)	179.08(7)
Co(2)–N(6)	1.882(3)		

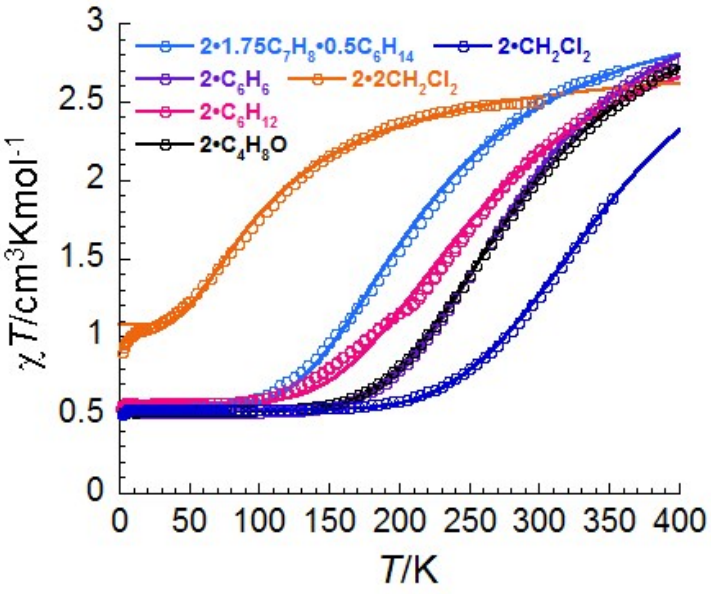

Figure S5. χT versus T plots for the previously published chloride adducts measured at 1000 Oe, where χ is the magnetic susceptibility equal to M/H per mole of complex. Lines are the fits to the ideal solution model (Eq. 1, see main text).

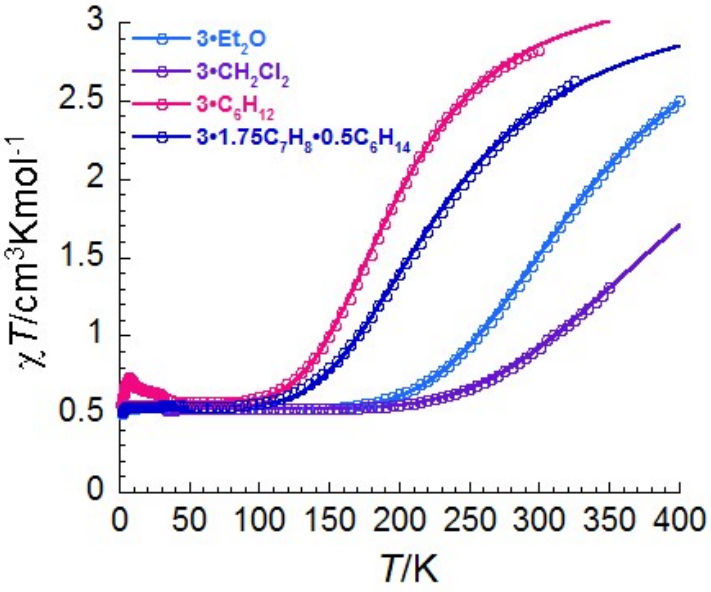

Figure S6. χT versus T plots for the previously published bromide adducts and **3**·Et_2O measured at 1000 Oe, where χ is the magnetic susceptibility equal to M/H per mole of complex. Lines are the fits to the ideal solution model (Eq. 1, see main text).

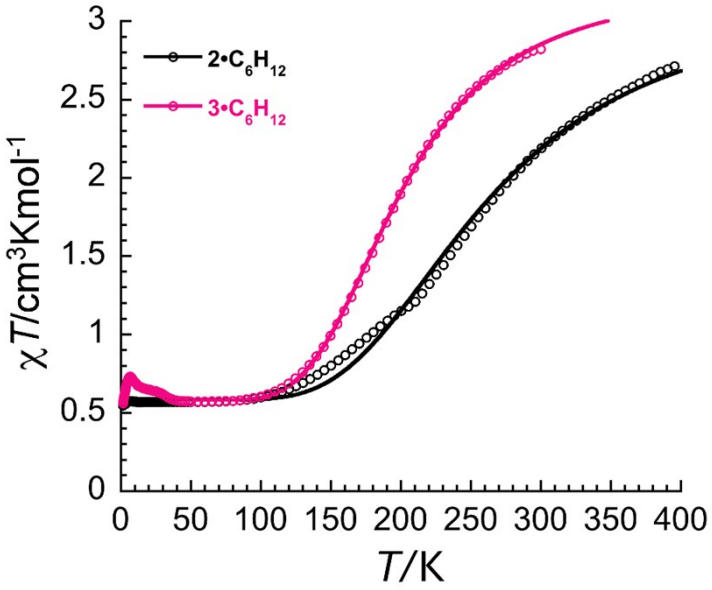

Figure S7. χT versus T plots for the cyclohexane solvates of chloride **2** and bromide **3** measured at 1000 Oe, where χ is the magnetic susceptibility equal to M/H per mole of complex. Lines are the fits to the ideal solution model (Eq. 1, see main text).

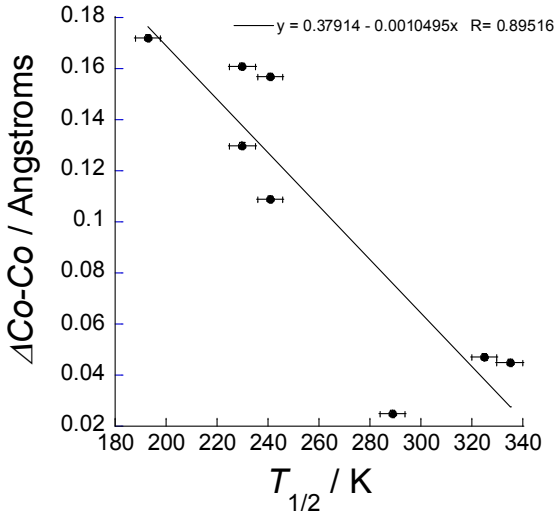

Figure S8. Correlation between $T_{1/2}$ and the difference in Co-Co bond distances for structures obtained close to room temperature. In this plot, the differences in the Co-Co distances for both molecules in the asymmetric unit for **2**·1.75toluene·0.5hexane and **2**·1.75toluene·0.5hexane are included.