Electronic Supplementary Information

for

Increasing the Electron Donation in a Dinucleating Ligand Family: Molecular and Electronic Structures in a Series of $Co^{II}Co^{II}$ Complexes

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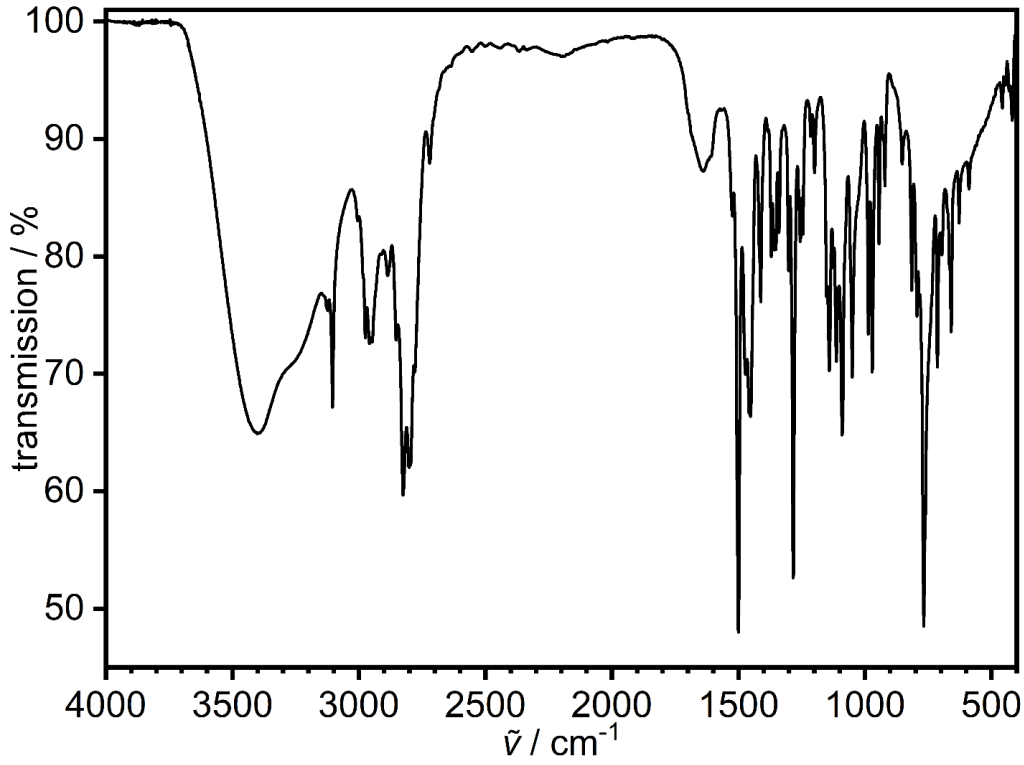

Figure S1. FTIR spectrum of cool.

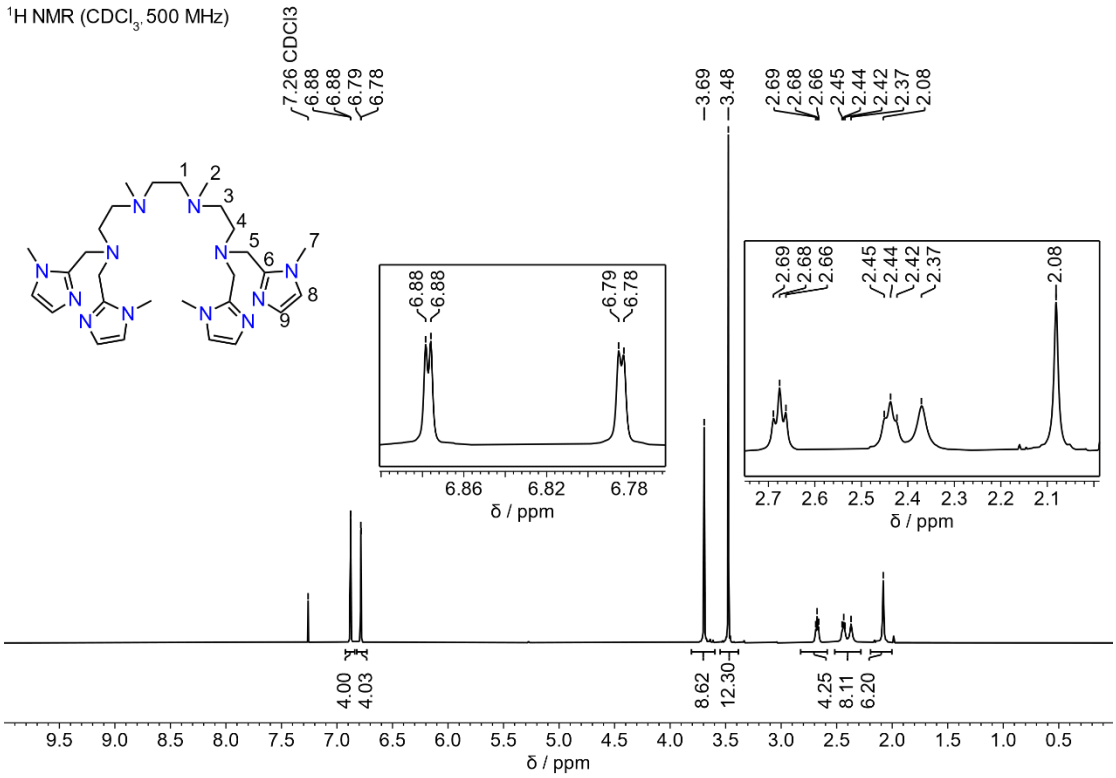

Figure S2. 500MHz ^{1}H NMR spectrum of cool in $CDCl_3$.

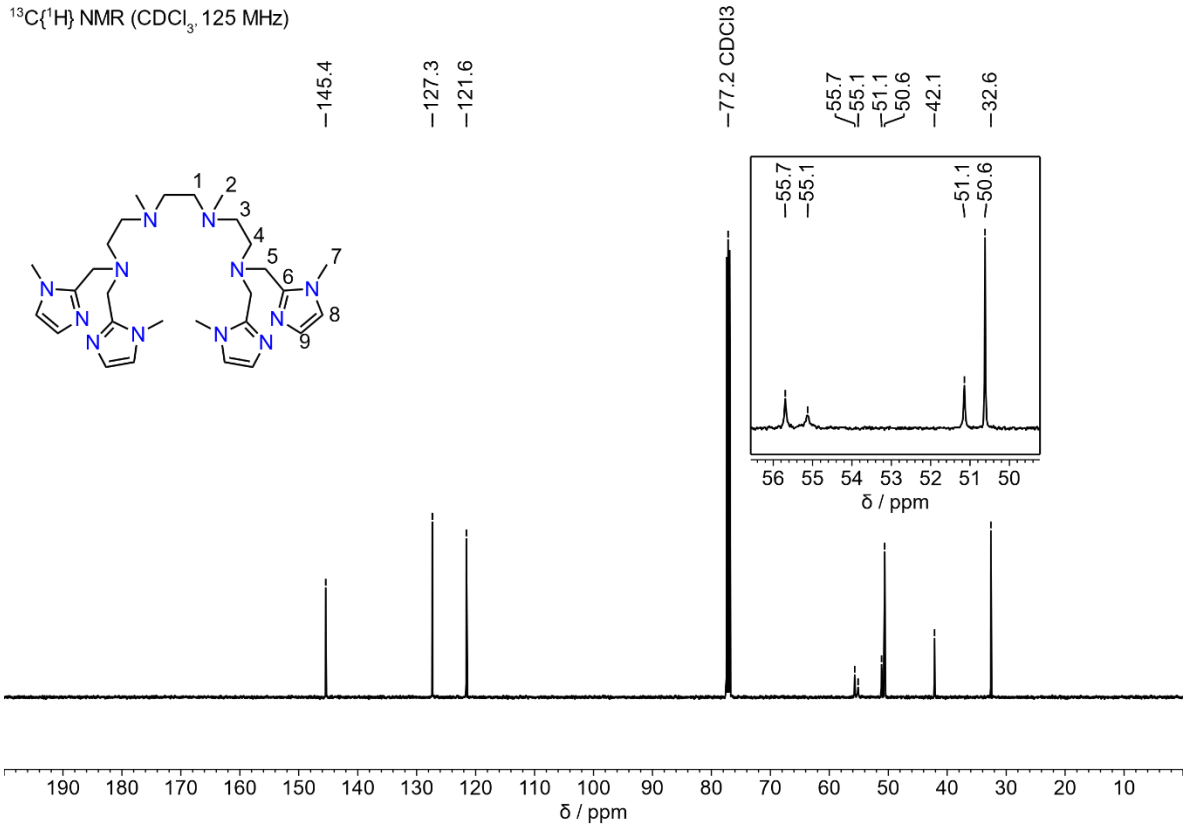

Figure S3. 125MHz $^{13}C\{^{1}H\}$ NMR spectrum of cool in $CDCl_3$.

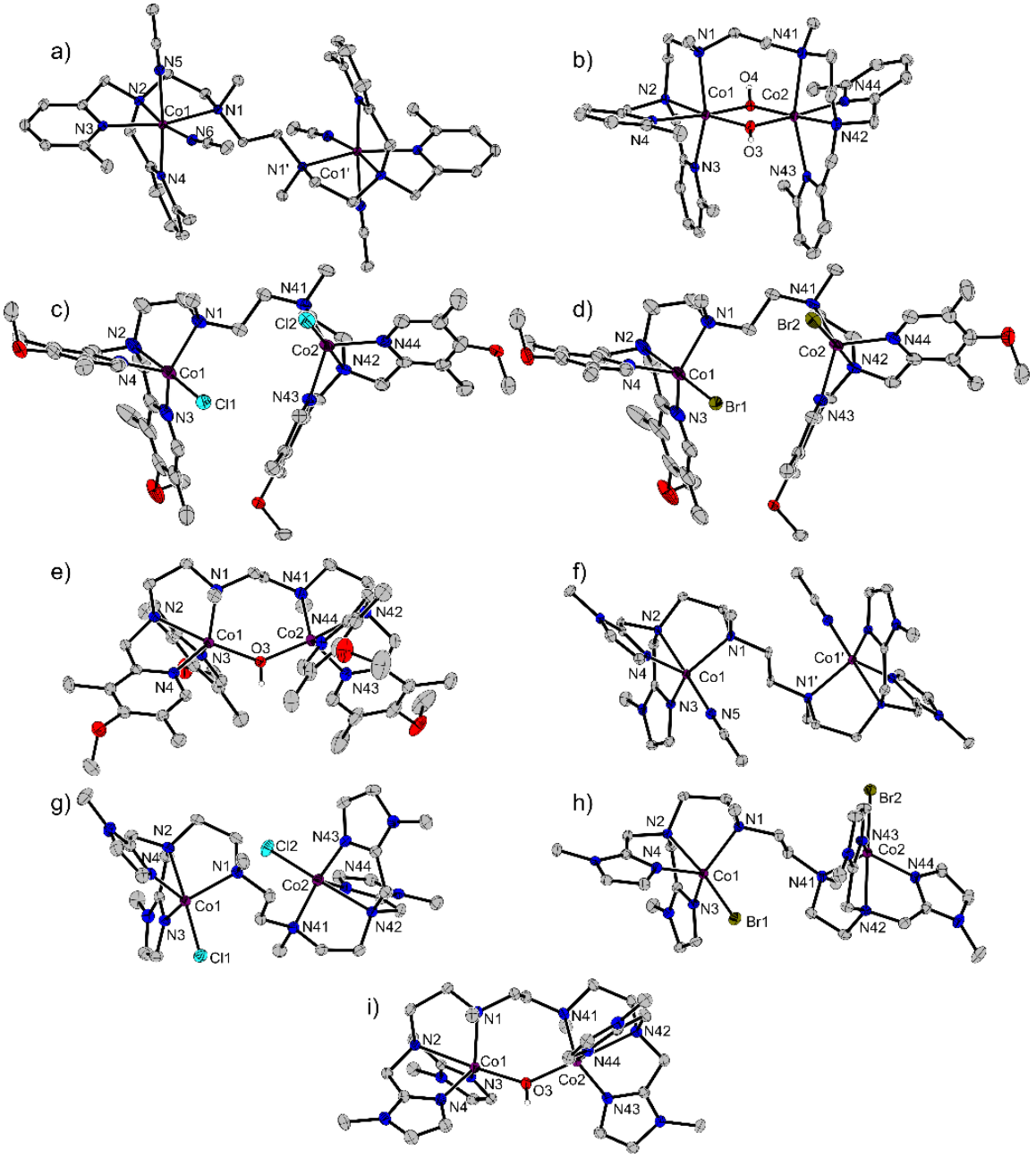

Figure S4. Thermal ellipsoid plots drawn at 50% probability level of a) $[(susan^{6\text{-}Me})\{Co^{II}(CH_3CN)_2\}_2]^{4+}$ in single-crystals of $[(susan^{6\text{-}Me})\{Co^{II}(CH_3CN)_2\}_2](ClO_4)_4$, b) $[(susan^{6\text{-}Me})\{Co^{II}(\mu\text{-}OH)_2Co^{II}\}]^{2+}$ in single-crystals of $[(susan^{6\text{-}Me})\{Co^{II}(\mu\text{-}OH)_2Co^{II}\}](ClO_4)_2$•MeOH, c) $[(susan^{OMe})\{Co^{II}Cl\}_2]^{2+}$ in single-crystals of $[(susan^{OMe})\{Co^{II}Cl\}_2](ClO_4)_2$•3MeOH, d) $[(susan^{OMe})\{Co^{II}Br\}_2]^{2+}$ in single-crystals of $[(susan^{OMe})\{Co^{II}Br\}_2](ClO_4)_2$•3MeOH, e) $[(susan^{OMe})Co^{II}(\mu\text{-}OH)Co^{II}]^{3+}$ in single-crystals of $[(susan^{OMe})Co^{II}(\mu\text{-}OH)Co^{II}](ClO_4)_3$•$3CH_3CN$, f) $[(cool)\{Co^{II}(CH_3CN)\}_2]^{4+}$ in single-crystals of $[(cool)\{Co^{II}(CH_3CN)\}_2](ClO_4)_4$•$2CH_3CN$, g) $[(cool)\{Co^{II}Cl\}_2]^{2+}$ in single-crystals of $[(cool)\{Co^{II}Cl\}_2](ClO_4)_2$, h) $[(cool)\{Co^{II}Br\}_2]^{2+}$ in single-crystals of $[(cool)\{Co^{II}Br\}_2](ClO_4)_2$, and i) $[(cool)Co^{II}(\mu\text{-}OH)Co^{II}]^{3+}$ in single-crystals of $[(cool)Co^{II}(\mu\text{-}OH)Co^{II}](BPh_4)_2(CF_3SO_3)$-•$2CH_3CN$. Hydrogen atoms, counter ions and solvent molecules are omitted for clarity.

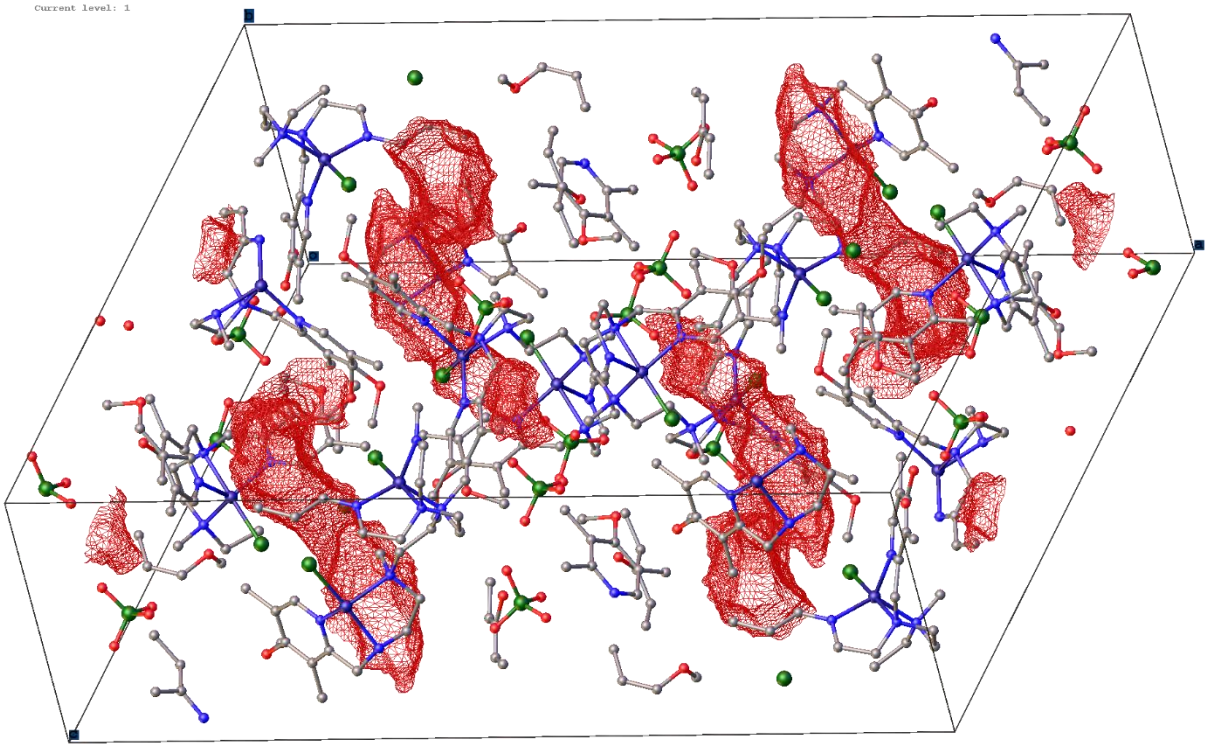

Figure S5. Calculated voids 0.1 Å from van der Waals surface in the unit cell of [(susan^{OMe}){CoCl}$_2$](ClO$_4$)$_2$•3MeOH. The channels are oriented along the 2_1 screw axis, i.e. parallel to the crystallographic *b*-axis. Hydrogen atoms were omitted for clarity.

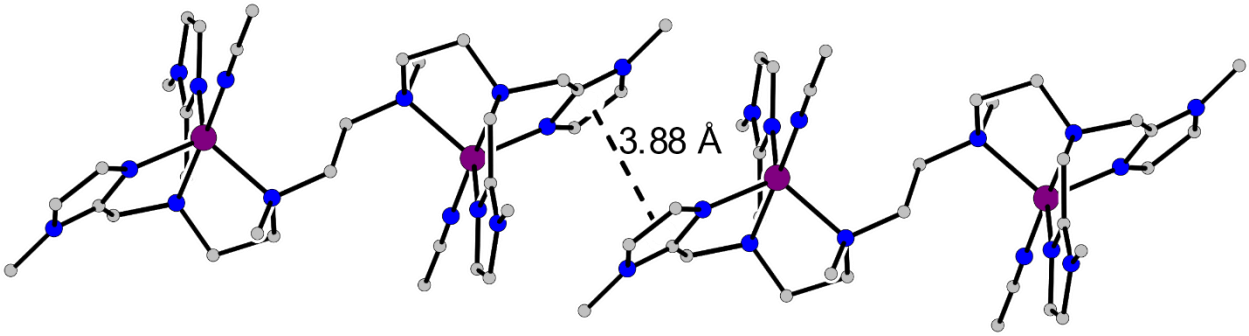

Figure S6. Intermolecular π-π interaction between two neighboring imidazoles in single crystals of [(cool){$Co^{II}(CH_3CN)$}$_2$]$(ClO_4)_4$•2CH_3CN. Hydrogen atoms, counter ions and solvent molecules are omitted for clarity.

Table S1. Crystal data and refinement parameters.

	[(susan$^{6\text{-Me}}$){Co^{II}(CH$_3$CN)$_2$}$_2$](ClO$_4$)$_4$	[(susan$^{6\text{-Me}}$){Co^{II}(μ-OH)$_2$Co^{II}}](ClO$_4$)$_2$•MeOH	[(susan^{OMe}){Co^{II}Cl}$_2$](ClO$_4$)$_2$•3MeOH	[(susan^{OMe}){Co^{II}Br}$_2$](ClO$_4$)$_2$•3MeOH	[(susan^{OMe}){Co^{II}(μ-OH)Co^{II}}](ClO$_4$)$_3$•3CH$_3$CN
Empirical formula	$C_{44}H_{62}Cl_4Co_2N_{12}O_{16}$	$C_{37}H_{56}Cl_2Co_2N_8O_{11}$	$C_{47}H_{78}Cl_4Co_2N_8O_{15}$	$C_{47}H_{78}Br_2Cl_2Co_2N_8O_{15}$	$C_{50}H_{76}Cl_3Co_2H_{76}N_{11}O_{17}$
Formula weight	1274.71	977.65	1254.83	1343.75	1327.42
Crystal system	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$C2/c$	$C2/c$	$P2_1/c$
a [Å]	11.4940(6)	10.0649(2)	34.6570(13)	34.7597(14)	12.1162(16)
b [Å]	11.7996(7)	32.2086(5)	14.4542(9)	14.4732(6)	38.977(5)
c [Å]	12.1256(7)	13.7980(2)	24.3699(13)	24.5591(8)	12.8849(16)
α [°]	70.583(2)	90	90	90	90
β [°]	64.862(2)	110.8920(10)	105.2390(10)	106.4700(10)	93.902(2)
γ [°]	67.714(2)	90	90	90	90
V [Å^3]	1348.44(14)	4178.90(12)	11778.6(11)	11848.3(8)	6070.8(13)
Z	1	4	8	8	4
ρ [g cm^{-3}]	1.570	1.554	1.415	1.507	1.452
μ [mm^{-1}]	7.319	7.980	0.813	2.067	0.754
F(000)	660.0	2040.0	5264.0	5552.0	2776.0
Crystal size [mm^3]	0.17 × 0.13 × 0.07	0.36 × 0.08 × 0.04	0.25 × 0.18 × 0.14	0.31 × 0.26 × 0.08	0.46 × 0.22 × 0.05
Radiation	CuKα (λ = 1.54178Å)	CuKα (λ = 1.54178Å)	MoKα (λ = 0.71073 Å)	MoKα (λ = 0.71073 Å)	MoKα (λ = 0.71073 Å)
2Θ range [°]	8.23 to 136.71°	5.49 to 137.09°	3.36 to 52.04	3.07 to 60.07	3.34 to 60.19
	-13 ≤ h ≤ 12	-12 ≤ h ≤ 12	-42 ≤ h ≤ 42	-48 ≤ h ≤ 48	-17 ≤ h ≤ 17
hkl ranges	-14 ≤ k ≤ 14	-38 ≤ k ≤ 38	-17 ≤ k ≤ 17	-20 ≤ k ≤ 20	-54 ≤ k ≤ 54
	-14 ≤ l ≤ 14	-16 ≤ l ≤ 16	-29 ≤ l ≤ 30	-34 ≤ l ≤ 34	-18 ≤ l ≤ 18
Collected refl.	36906	31286	63771	131671	114260
Unique refl., R_{int}	4933, 0.0307	7669, 0.0415	11596, 0.0527	17357, 0.0444	17790, 0.0529
Observed refl.($I > 2\sigma(I)$)	4854	6684	8513	13535	13451
Completeness	0.994	0.997	1.000	1.000	0.997
Data/restraints/param.	4933/0/357	7669/2/557	11596/168/721	17357/234/721	17790/211/778
Goodness-of-fit on F^2	1.047	1.036	1.031	1.017	1.012
R_1, wR_2 ($I > 2\sigma(I)$)	0.0278, 0.0723	0.0401, 0.0977	0.0378, 0.0862	0.0391, 0.0838	0.0403, 0.0875
R_1, wR_2 (all data)	0.0282, 0.0725	0.0489, 0.1023	0.0602, 0.0953	0.0561, 0.0905	0.0619, 0.0951
Largest peak/hole [e Å^{-3}]	0.74/-0.38	0.64/-0.52	0.58/-0.51	0.84/-0.61	0.59/-0.54
CCDC numbers	2341023	2341024	2341025	2341026	2341027

Continuation of Table S1.

	$[(cool)\{Co^{II}(CH_3CN)\}_2](ClO_4)_4 \cdot 2CH_3CN$	$[(cool)\{Co^{II}Cl\}_2](ClO_4)_2$	$[(cool)\{Co^{II}Br\}_2](ClO_4)_2$	$[(cool)\{Co^{II}(\mu\text{-}OH)Co^{II}\}](BPh_4)_2(CF_3SO_3) \cdot 2CH_3CN$
Empirical formula	$C_{36}H_{58}N_{16}O_{16}Cl_4Co_2$	$C_{28}H_{46}Cl_4Co_2N_{12}O_8$	$C_{28}H_{46}Br_2Cl_2Co_2N_{12}O_8$	$C_{81}H_{93}B_2Co_2F_3N_{14}O_4S$
Formula weight	1230.64	938.43	1027.35	1555.23
Crystal system	monoclinic	orthorhombic	orthorhombic	triclinic
Space group	$P2_1/n$	$P2_12_12_1$	$P2_12_12_1$	$P\bar{1}$
a [Å]	11.730(3)	12.505(2)	12.4043(6)	13.3763(5)
b [Å]	17.852(4)	12.7850(19)	13.0584(7)	15.5871(7)
c [Å]	13.124(4)	24.509(4)	24.6003(11)	19.1171(8)
α [°]	90	90	90	90.4780(10)
β [°]	112.367(15)	90	90	94.2380(10)
γ [°]	90	90	90	105.7960(10)
V [Å^3]	2541.6(12)	3918.4(11)	3984.8(3)	3823.2(3)
Z	2	4	4	2
ρ [g cm^{-3}]	1.608	1.591	1.712	1.351
μ [mm^{-1}]	0.946	1.182	3.034	0.529
$F(000)$	1272.0	1936.0	2080.0	1632.0
Crystal size [mm^3]	0.09 × 0.09 × 0.07	0.19 × 0.18 × 0.04	0.39 × 0.22 × 0.18	0.50 × 0.25 × 0.08
Radiation	MoKα (λ= 0.71073 Å)	MoKα (λ = 0.71073 Å)	MoKα (λ = 0.71073 Å)	MoKα (λ = 0.71073 Å)
2Θ range [°]	5.67 to 54.00	3.32 to 60.21	3.53 to 65.90	2.72 to 60.39
	$-14 \le h \le 14$	$-17 \le h \le 17$	$-18 \le h \le 18$	$-18 \le h \le 18$
hkl ranges	$-22 \le k \le 22$	$-18 \le k \le 17$	$-19 \le k \le 19$	$-21 \le k \le 22$
	$-16 \le l \le 16$	$-34 \le l \le 34$	$-32 \le l \le 37$	$-26 \le l \le 27$
Collected refl.	48437	72831	246620	237268
Unique refl., R_{int}	5538, 0.0720	11494, 0.0434	14231, 0.0319	22561, 0.0387
Observed refl.($I > 2\sigma(I)$)	4105	10423	13612	18521
Completeness	0.999	0.997	0.971	0.995
Data/restraints/param.	5538/0/339	11494/93/521	14231/21/521	22561/1/1019
Goodness-of-fit on F^2	1.007	1.027	1.029	1.018
R_1, wR_2 ($I > 2\sigma(I)$)	0.0393, 0.0799	0.0330, 0.0791	0.0211, 0.0508	0.0356, 0.0894
R_1, wR_2 (all data)	0.0661, 0.0904	0.0392, 0.0822	0.0231, 0.0515	0.0479, 0.0970
Largest peak/hole [e Å^{-3}]	0.96/-0.74	0.73/-0.41	0.77/-0.39	0.57/-0.36
Flack parameter		-0.008(4)	-0.0069(10)	
CCDC numbers	2341028	2341029	2341030	2341031