Supporting Information
For

Synthesis and structure of 2,5-bis[*N*-(2,6-mesityl)iminomethyl]pyrrolylcobalt(II): Evidence for one-electron-oxidized, redox-non-innocent ligand behavior.

Garvin M. Peters,[a†] Jacob B. Winegrad,[†] Michael R. Gau, Gregory H. Imler,[b] Beibei Xu,[c] Shenqiang Ren,[c] Bradford B. Wayland*, and Michael J. Zdilla*

Department of Chemistry, Temple University, 1901 N. 13th St., Philadelphia, PA 19122

Contents

ATR-FTIR Spectrum

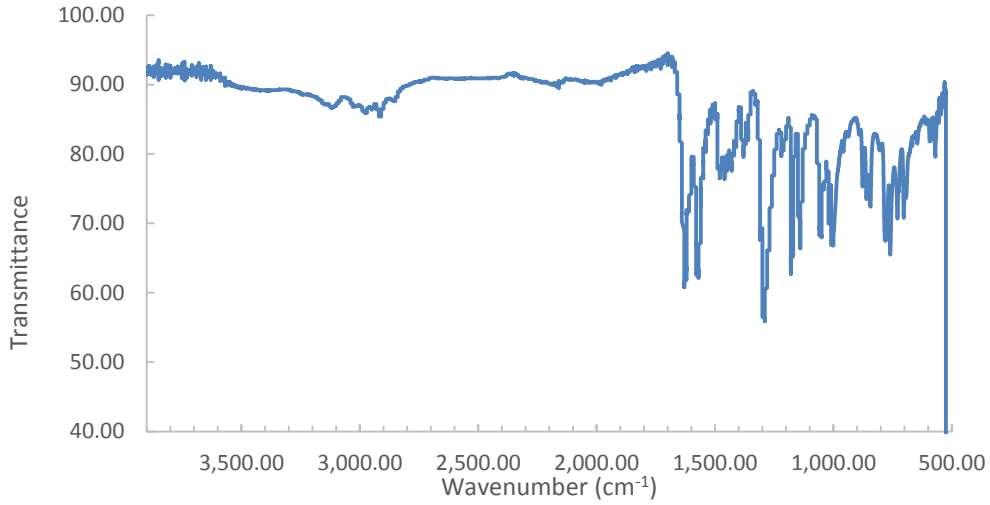

Figure S.1. ATR-FTIR spectrum of solid $Mes_2pyrCoCl_2$

UV-Visible Spectroscopy

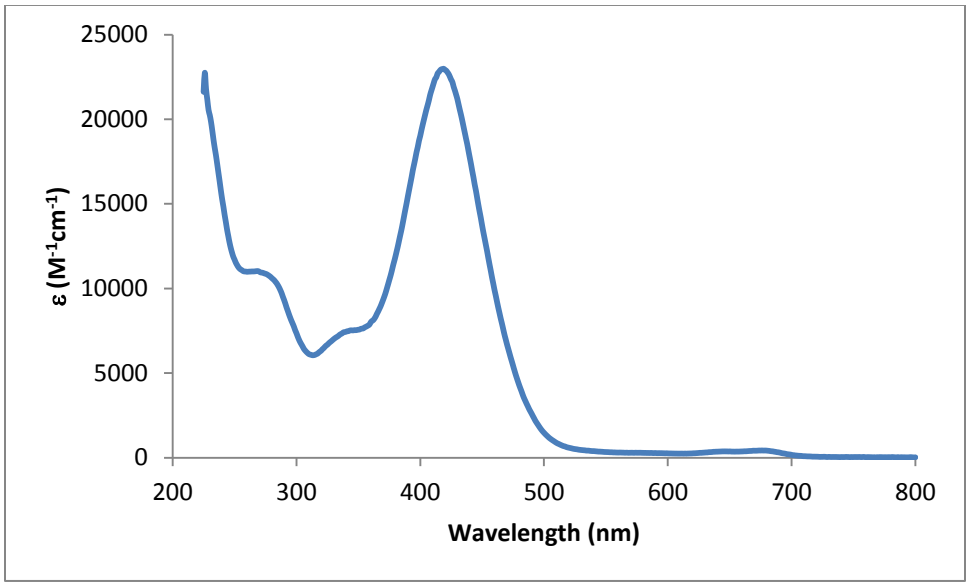

Figure S2. UV-Visible Absorption spectrum for $Mes_2pyrCoCl_2$ in dichloromethane exhibiting an intense band at 410 nm assigned as an MLCT between *d*-based electrons in the *e* orbitals and the vacancy in the ligand π orbitals (See Fig 7)

Frontier Orbitals of (Mes_2pyr)$CoCl_2$ from DFT

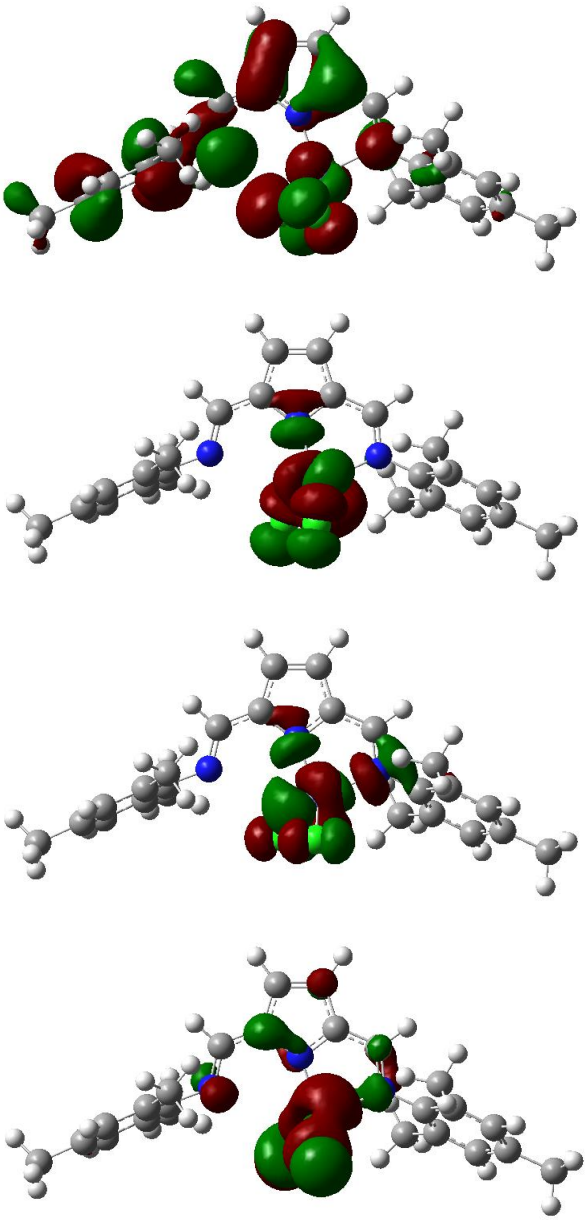

Figure S3. The four biorthogonolized SOMO orbitals of (Mes_2pyr)$CoCl_2$ from single-point calculations on the X-ray crystallographic geometry. (B3LYP, 6-311G/TZVP(Co)). The topmost orbital is predominantly ligand based and resembles the free ligand HOMO (Figure 6) and is assigned as the ligand radical orbital. The other three SOMO's are metal *d*-orbital based.

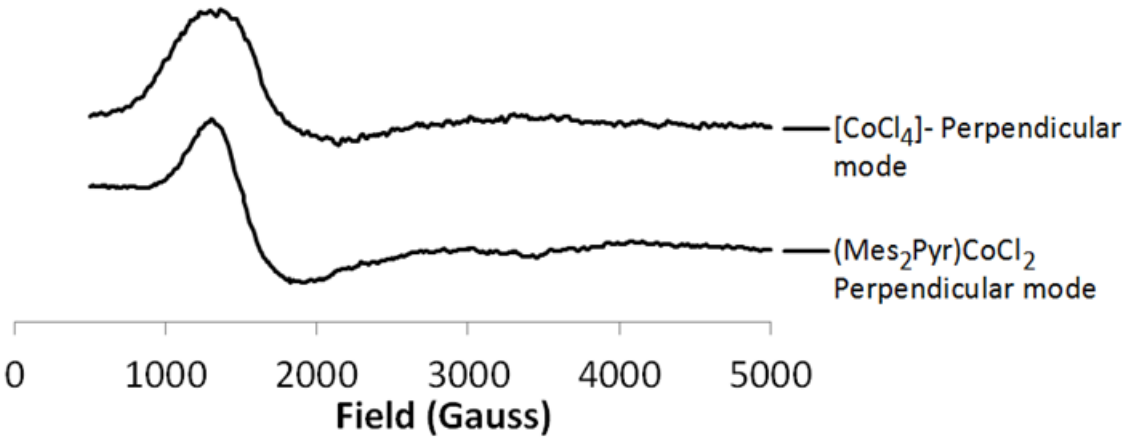

Figure S4. EPR spectra of $Mes_2pyrCoCl_2$ in perpendicular mode: MW Freq. 9.635 GHz, power 0.201 mW, Mod Amplitude 7.0 G, Mod. Freq. 100 kHz, Conversion time 92 ms, time const 164 ms.

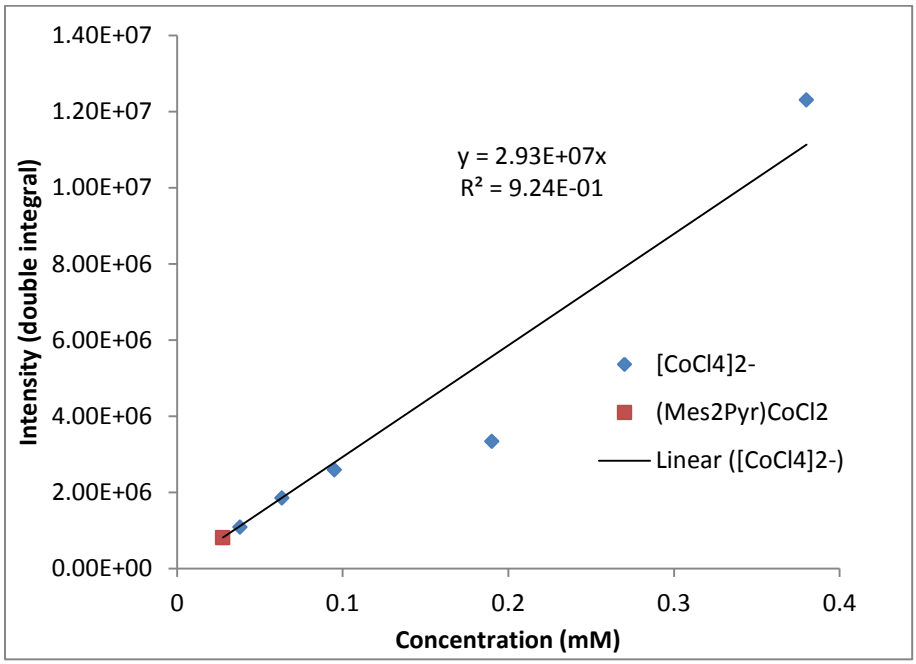

Figure S5. Calibration plot (blue) for double integral intensity vs. concentration of $[CoCl_4]^{2-}$ and EPR intensity of a 0.21 mM $Mes_2pyrCoCl_2$, giving ~13% S = 3/2 species.

Solid state magnetometry on $(Mes_2pyr)CoCl_2$

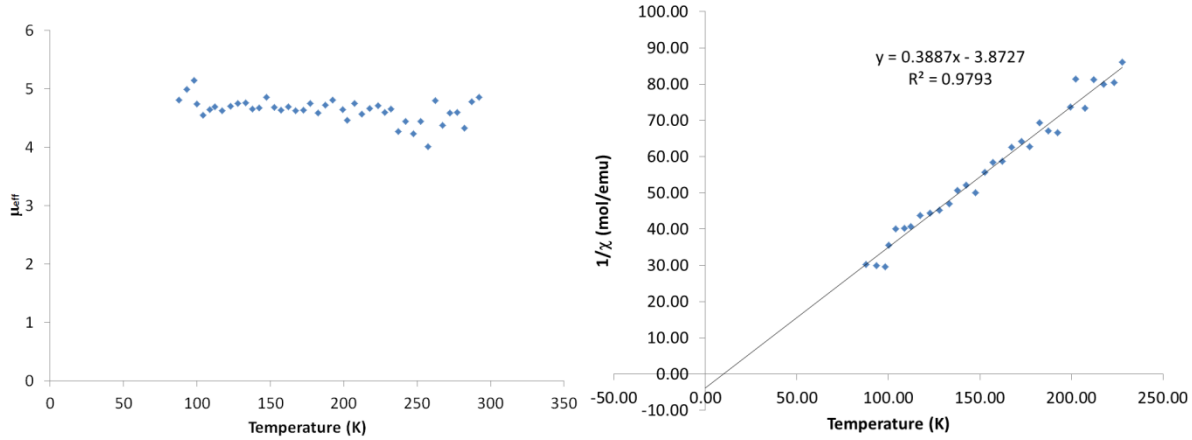

Figure S6. Solid state magnetometry on $Mes_2pyrCoCl_2$ demonstrating temperature invariability. Left: μ_{eff} vs. T. Right: Curie-Weiss plot of $1/\chi$ vs. T.

Table 1 Crystal data and structure refinement for Mes2pyrH.

Identification code	Mes2pyrH
Empirical formula	$C_{24}H_{27}N_3$
Formula weight	357.48
Temperature/K	100.02
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.1829(14)
b/Å	34.929(6)
c/Å	8.2568(15)
α/°	90
β/°	118.462(4)
γ/°	90
Volume/Å^3	2074.7(6)
Z	4
ρ_{calc}g/cm^3	1.144
μ/mm^{-1}	0.068
F(000)	768.0
Crystal size/mm^3	0.198 × 0.164 × 0.04
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.664 to 52.708
Index ranges	$-9 \leq h \leq 10$, $-43 \leq k \leq 31$, $-10 \leq l \leq 10$
Reflections collected	11993
Independent reflections	4232 [R_{int} = 0.0585, R_{sigma} = 0.0790]
Data/restraints/parameters	4232/0/254
Goodness-of-fit on F^2	1.006
Final R indexes [I>=2σ (I)]	R_1 = 0.0534, wR_2 = 0.1050
Final R indexes [all data]	R_1 = 0.1052, wR_2 = 0.1222
Largest diff. peak/hole / e Å^{-3}	0.27/-0.26

Table 2 Bond Lengths for Mes2pyrH.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N2	C2	1.366(2)	C20	C19	1.389(3)
N2	C5	1.364(3)	C19	C18	1.395(3)
N1	C1	1.276(2)	C19	C23	1.512(3)
N1	C7	1.420(3)	C18	C17	1.391(3)
N3	C6	1.282(2)	C17	C22	1.517(3)
N3	C16	1.432(3)	C7	C8	1.402(3)
C2	C3	1.384(3)	C7	C12	1.403(3)
C2	C1	1.451(3)	C8	C9	1.391(3)
C3	C4	1.396(3)	C8	C13	1.506(3)
C4	C5	1.381(3)	C9	C10	1.391(3)
C5	C6	1.442(3)	C10	C11	1.389(3)
C16	C21	1.404(3)	C10	C14	1.506(3)
C16	C17	1.404(3)	C11	C12	1.394(3)
C21	C20	1.388(3)	C12	C15	1.510(3)
C21	C24	1.501(3)			

Table 3 Bond Angles for Mes2pyrH.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C5	N2	C2	110.03(17)	C18	C19	C23	121.2(2)
C1	N1	C7	120.93(17)	C17	C18	C19	122.0(2)
C6	N3	C16	116.18(18)	C16	C17	C22	120.87(19)
N2	C2	C3	107.50(19)	C18	C17	C16	118.73(18)
N2	C2	C1	120.36(18)	C18	C17	C22	120.38(19)
C3	C2	C1	132.13(19)	N1	C1	C2	118.80(19)
C2	C3	C4	107.22(18)	C8	C7	N1	117.23(18)
C5	C4	C3	108.18(19)	C8	C7	C12	120.82(19)
N2	C5	C4	107.08(18)	C12	C7	N1	121.63(18)
N2	C5	C6	122.83(18)	C7	C8	C13	119.43(19)
C4	C5	C6	129.9(2)	C9	C8	C7	118.72(19)
N3	C6	C5	123.5(2)	C9	C8	C13	121.85(18)
C21	C16	N3	119.11(19)	C10	C9	C8	121.85(19)
C17	C16	N3	120.50(18)	C9	C10	C14	121.1(2)
C17	C16	C21	120.35(19)	C11	C10	C9	118.1(2)
C16	C21	C24	120.62(19)	C11	C10	C14	120.9(2)

C20	C21	C16	118.5(2)	C10	C11	C12	122.3(2)
C20	C21	C24	120.82(18)	C7	C12	C15	121.84(19)
C21	C20	C19	122.55(19)	C11	C12	C7	118.13(18)
C20	C19	C18	117.64(19)	C11	C12	C15	120.02(19)
C20	C19	C23	121.11(19)				

Table 4 Torsion Angles for Mes2pyrH.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N2	C2	C3	C4	0.3(2)	C21	C20	C19	C18	-1.8(3)
N2	C2	C1	N1	-0.6(3)	C21	C20	C19	C23	178.88(19)
N2	C5	C6	N3	-0.4(3)	C20	C19	C18	C17	1.8(3)
N1	C7	C8	C9	175.96(17)	C19	C18	C17	C16	1.1(3)
N1	C7	C8	C13	-4.3(3)	C19	C18	C17	C22	-177.35(18)
N1	C7	C12	C11	-174.08(17)	C17	C16	C21	C20	4.2(3)
N1	C7	C12	C15	5.7(3)	C17	C16	C21	C24	-177.26(19)
N3	C16	C21	C20	-177.94(18)	C23	C19	C18	C17	-178.85(19)
N3	C16	C21	C24	0.6(3)	C24	C21	C20	C19	-179.7(2)
N3	C16	C17	C18	178.00(18)	C1	N1	C7	C8	116.4(2)
N3	C16	C17	C22	-3.5(3)	C1	N1	C7	C12	-70.0(3)
C2	N2	C5	C4	0.2(2)	C1	C2	C3	C4	-178.2(2)
C2	N2	C5	C6	175.81(18)	C7	N1	C1	C2	179.74(18)
C2	C3	C4	C5	-0.2(2)	C7	C8	C9	C10	-1.7(3)
C3	C2	C1	N1	177.7(2)	C8	C7	C12	C11	-0.7(3)
C3	C4	C5	N2	0.0(2)	C8	C7	C12	C15	179.03(17)
C3	C4	C5	C6	-175.2(2)	C8	C9	C10	C11	-0.5(3)
C4	C5	C6	N3	174.1(2)	C8	C9	C10	C14	179.3(2)
C5	N2	C2	C3	-0.3(2)	C9	C10	C11	C12	2.2(3)
C5	N2	C2	C1	178.40(18)	C10	C11	C12	C7	-1.6(3)
C6	N3	C16	C21	111.7(2)	C10	C11	C12	C15	178.66(17)
C6	N3	C16	C17	-70.4(2)	C12	C7	C8	C9	2.3(3)
C16	N3	C6	C5	-179.90(18)	C12	C7	C8	C13	-177.92(17)
C16	C21	C20	C19	-1.2(3)	C14	C10	C11	C12	-177.6(2)
C21	C16	C17	C18	-4.2(3)	C13	C8	C9	C10	178.53(18)
C21	C16	C17	C22	174.30(19)					

Crystal Data for $C_{24}H_{27}N_3$ (M =357.48 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 8.1829(14) Å, b = 34.929(6) Å, c = 8.2568(15) Å, β = 118.462(4)°, V = 2074.7(6) Å^3, Z = 4, T = 100.02 K, μ(MoKα) = 0.068 mm^{-1}, *Dcalc* = 1.144 g/cm^3, 11993 reflections measured (4.664° ≤ 2Θ ≤ 52.708°), 4232 unique (R_{int} = 0.0585, R_{sigma} = 0.0790) which were used in all calculations. The final R_1 was 0.0534 (I > 2σ(I)) and wR_2 was 0.1222 (all data).

Refinement model description

Number of restraints - 0

Details:

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1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups
 At 1.5 times of:
  All C(H,H,H) groups
2.a Aromatic/amide H refined with riding coordinates:
 C3(H3), C4(H4), C6(H6), C20(H20), C18(H18), C1(H1), C9(H9), C11(H11)
2.b Idealised Me refined as rotating group:
 C22(H22A,H22B,H22C), C23(H23A,H23B,H23C), C24(H24A,H24B,H24C),
C15(H15A,H15B,
 H15C), C14(H14A,H14B,H14C), C13(H13A,H13B,H13C)
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Table 5 Crystal data and structure refinement for CoMes2pyrCl2.

Identification code	CoMes2pyrCl2
Empirical formula	$C_{24}H_{27}Cl_2CoN_3$
Formula weight	487.31
Temperature/K	100.03
Crystal system	monoclinic
Space group	C2/c
a/Å	21.2416(14)
b/Å	14.4875(9)
c/Å	16.1470(11)
α/°	90
β/°	107.5572(10)
γ/°	90
Volume/Å^3	4737.6(5)
Z	8
ρ_{calc}g/cm^3	1.366
μ/mm^{-1}	0.966
F(000)	2024.0
Crystal size/mm^3	0.11 × 0.09 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.456 to 55.714
Index ranges	$-27 \leq h \leq 27$, $-16 \leq k \leq 19$, $-20 \leq l \leq 21$
Reflections collected	26149
Independent reflections	5621 [R_{int} = 0.0205, R_{sigma} = 0.0148]
Data/restraints/parameters	5621/6/305
Goodness-of-fit on F^2	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0278, wR_2 = 0.0698
Final R indexes [all data]	R_1 = 0.0308, wR_2 = 0.0715
Largest diff. peak/hole / e Å^{-3}	0.91/-0.33

Table 6 Bond Lengths for CoMes2pyrCl2.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Co1	Cl1	2.2350(8)	C5	C4	1.416(2)
Co1	Cl2	2.2452(6)	C5	C6	1.4100(19)
Co1	N1	2.0768(12)	C15	C16	1.399(2)
Co1	N2	2.0240(12)	C15	C14	1.396(2)
N1	C11	1.4408(17)	C13	C12	1.398(2)
N1	C1	1.2918(19)	C13	C14	1.394(2)
N3	C31	1.4404(17)	C17	C16	1.5086(19)
N3	C6	1.3041(19)	C34	C35	1.396(2)
N3	Co1A	2.136(3)	C34	C33	1.391(2)
N2	C5	1.3723(18)	C34	C38	1.510(2)
N2	C2	1.3609(18)	C12	C19	1.507(2)
N2	Co1A	2.088(3)	C3	C4	1.388(2)
C11	C16	1.401(2)	C3	C2	1.408(2)
C11	C12	1.400(2)	C33	C32	1.394(2)
C36	C37	1.5076(19)	C14	C18	1.511(2)
C36	C31	1.400(2)	C39	C32	1.511(2)
C36	C35	1.3918(19)	Co1A	Cl1A	2.261(11)
C1	C2	1.4453(19)	Co1A	Cl2A	2.181(12)
C31	C32	1.401(2)			

Table 7 Bond Angles for CoMes2pyrCl2.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cl1	Co1	Cl2	108.36(4)	C14	C13	C12	122.06(13)
N1	Co1	Cl1	109.76(4)	C35	C34	C38	120.88(14)
N1	Co1	Cl2	127.14(5)	C33	C34	C35	118.67(13)
N2	Co1	Cl1	119.52(4)	C33	C34	C38	120.44(14)
N2	Co1	Cl2	108.43(4)	C11	C16	C17	120.24(13)
N2	Co1	N1	82.51(5)	C15	C16	C11	117.88(13)
C11	N1	Co1	129.69(9)	C15	C16	C17	121.84(13)
C1	N1	Co1	109.71(10)	C11	C12	C19	121.02(13)
C1	N1	C11	119.46(12)	C13	C12	C11	117.59(13)
C31	N3	Co1A	130.93(12)	C13	C12	C19	121.39(13)
C6	N3	C31	124.18(12)	C4	C3	C2	105.81(13)
C6	N3	Co1A	101.82(12)	C3	C4	C5	106.39(13)

C5	N2	Co1	144.42(10)	N2	C2	C1	117.68(12)
C5	N2	Co1A	102.28(11)	N2	C2	C3	111.84(12)
C2	N2	Co1	109.65(9)	C3	C2	C1	130.47(13)
C2	N2	C5	105.20(11)	C36	C35	C34	121.52(13)
C2	N2	Co1A	152.15(12)	C34	C33	C32	122.32(14)
C16	C11	N1	118.44(12)	N3	C6	C5	123.79(13)
C12	C11	N1	119.26(13)	C15	C14	C18	121.25(14)
C12	C11	C16	122.27(13)	C13	C14	C15	118.53(13)
C31	C36	C37	120.49(13)	C13	C14	C18	120.21(14)
C35	C36	C37	121.75(13)	C31	C32	C39	123.16(13)
C35	C36	C31	117.74(13)	C33	C32	C31	116.95(14)
N1	C1	C2	118.96(13)	C33	C32	C39	119.78(13)
C36	C31	N3	116.90(12)	N3	Co1A	Cl1A	136.6(4)
C36	C31	C32	122.77(13)	N3	Co1A	Cl2A	104.6(4)
C32	C31	N3	120.27(13)	N2	Co1A	N3	85.96(11)
N2	C5	C4	110.75(12)	N2	Co1A	Cl1A	102.7(4)
N2	C5	C6	122.59(13)	N2	Co1A	Cl2A	122.9(4)
C6	C5	C4	126.59(13)	Cl2A	Co1A	Cl1A	105.6(5)
C14	C15	C16	121.62(14)				

Table 8 Torsion Angles for CoMes2pyrCl2.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Co1	N1	C11	C16	88.51(15)	C16	C15	C14	C13	0.0(2)
Co1	N1	C11	C12	-89.47(16)	C16	C15	C14	C18	179.14(14)
Co1	N1	C1	C2	-10.09(16)	C12	C11	C16	C15	2.4(2)
Co1	N2	C5	C4	168.05(12)	C12	C11	C16	C17	-175.41(14)
Co1	N2	C5	C6	-14.8(2)	C12	C13	C14	C15	1.6(2)
Co1	N2	C2	C1	7.32(15)	C12	C13	C14	C18	-177.57(15)
Co1	N2	C2	C3	-173.06(10)	C4	C5	C6	N3	168.34(14)
N1	C11	C16	C15	-175.55(12)	C4	C3	C2	N2	0.66(17)
N1	C11	C16	C17	6.7(2)	C4	C3	C2	C1	-179.78(15)
N1	C11	C12	C13	177.01(13)	C2	N2	C5	C4	-0.13(15)
N1	C11	C12	C19	-3.0(2)	C2	N2	C5	C6	177.06(13)
N1	C1	C2	N2	2.1(2)	C2	C3	C4	C5	-0.69(16)
N1	C1	C2	C3	-177.41(15)	C35	C36	C31	N3	-177.77(12)
N3	C31	C32	C33	178.96(13)	C35	C36	C31	C32	-0.6(2)

N3	C31	C32	C39	2.7(2)	C35	C34	C33	C32	0.5(2)
N2	C5	C4	C3	0.53(17)	C33	C34	C35	C36	0.9(2)
N2	C5	C6	N3	-8.4(2)	C6	N3	C31	C36	-122.12(15)
C11	N1	C1	C2	-179.06(12)	C6	N3	C31	C32	60.6(2)
C36	C31	C32	C33	1.8(2)	C6	C5	C4	C3	-176.52(14)
C36	C31	C32	C39	-174.42(14)	C38	C34	C35	C36	179.61(13)
C1	N1	C11	C16	-105.02(16)	C38	C34	C33	C32	-178.24(14)
C1	N1	C11	C12	76.99(18)	C14	C15	C16	C11	-1.9(2)
C37	C36	C31	N3	3.92(19)	C14	C15	C16	C17	175.83(14)
C37	C36	C31	C32	-178.87(14)	C14	C13	C12	C11	-1.1(2)
C37	C36	C35	C34	177.45(13)	C14	C13	C12	C19	178.92(14)
C31	N3	C6	C5	179.99(13)	Co1A	N3	C31	C36	34.3(2)
C31	C36	C35	C34	-0.8(2)	Co1A	N3	C31	C32	-142.98(15)
C5	N2	C2	C1	-179.95(12)	Co1A	N3	C6	C5	17.98(18)
C5	N2	C2	C3	-0.33(16)	Co1A	N2	C5	C4	175.32(12)
C34	C33	C32	C31	-1.8(2)	Co1A	N2	C5	C6	-7.49(17)
C34	C33	C32	C39	174.58(15)	Co1A	N2	C2	C1	9.6(3)
C16	C11	C12	C13	-0.9(2)	Co1A	N2	C2	C3	-170.8(2)
C16	C11	C12	C19	179.06(14)					

Crystal Data for $C_{24}H_{27}Cl_2CoN_3$ (M =487.31 g/mol): monoclinic, space group C2/c (no. 15), a = 21.2416(14) Å, b = 14.4875(9) Å, c = 16.1470(11) Å, β = 107.5572(10)°, V = 4737.6(5) Å^3, Z = 8, T = 100.03 K, μ(MoKα) = 0.966 mm^{-1}, *Dcalc* = 1.366 g/cm^3, 26149 reflections measured (3.456° ≤ 2Θ ≤ 55.714°), 5621 unique (R_{int} = 0.0205, R_{sigma} = 0.0148) which were used in all calculations. The final R_1 was 0.0278 (I > 2σ(I)) and wR_2 was 0.0715 (all data).

Number of restraints - 6

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups
 At 1.5 times of:
  All C(H,H,H) groups
2. Rigid bond restraints
 Cl2, Cl2A
 with sigma for 1-2 distances of 0.002 and sigma for 1-3 distances of 0.002
3. Uiso/Uaniso restraints and constraints
Cl2 ≈ Cl2A: within 2A with sigma of 0.002 and sigma for terminal atoms of
0.002
4. Others
 Sof(Co1A)=Sof(Cl1A)=Sof(Cl2A)=1-FVAR(1)
 Sof(Co1)=Sof(Cl1)=Sof(Cl2)=FVAR(1)
5.a Aromatic/amide H refined with riding coordinates:
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C1(H1), C15(H15), C13(H13), C3(H3), C4(H4), C35(H35), C33(H33), C6(H6)
5.b Idealised Me refined as rotating group:
C37(H37A,H37B,H37C), C17(H17A,H17B,H17C), C19(H19A,H19B,H19C),
C38(H38A,H38B,
H38C), C39(H39A,H39B,H39C), C18(H18A,H18B,H18C)

Table 9 Crystal data and structure refinement for CoMes2pyrCl2DCM.

Identification code	CoMes2pyrCl2DCM
Empirical formula	$C_{24}H_{26}Cl_2CoN_3$
Formula weight	486.31
Temperature/K	100.02
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	16.453(2)
b/Å	11.3132(17)
c/Å	15.240(2)
α/°	90
β/°	108.344(3)
γ/°	90
Volume/Å^3	2692.6(7)
Z	4
ρ_{calc}g/cm^3	1.200
μ/mm^{-1}	0.849
F(000)	1008.0
Crystal size/mm^3	0.4 × 0.3 × 0.06
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.446 to 56.034
Index ranges	$-21 \leq h \leq 19$, $-14 \leq k \leq 14$, $-19 \leq l \leq 20$
Reflections collected	18378
Independent reflections	6463 [R_{int} = 0.0321, R_{sigma} = 0.0381]
Data/restraints/parameters	6463/6/305
Goodness-of-fit on F^2	1.093
Final R indexes [I>=2σ (I)]	R_1 = 0.0609, wR_2 = 0.1205
Final R indexes [all data]	R_1 = 0.0795, wR_2 = 0.1290
Largest diff. peak/hole / e Å^{-3}	0.67/-0.35

Table 10 Bond Lengths for CoMes2pyrCl2DCM.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N3	C6	1.306(4)	C16	C15	1.389(7)
N3	C31	1.437(4)	C16	C17	1.518(7)
N3	Co1A	2.262(4)	C14	C15	1.362(8)
N2	C5	1.365(4)	C14	C13	1.411(8)
N2	C2	1.370(4)	C14	C18	1.540(7)
N2	Co1	2.020(3)	C36	C31	1.401(4)
N2	Co1A	2.015(3)	C36	C37	1.514(4)
N1	C1	1.280(5)	C36	C35	1.379(5)
N1	C11	1.446(5)	C31	C32	1.395(4)
N1	Co1	2.076(3)	C34	C35	1.404(5)
C6	C5	1.401(5)	C34	C33	1.402(5)
C5	C4	1.417(4)	C34	C38	1.499(5)
C3	C2	1.405(5)	C33	C32	1.393(5)
C3	C4	1.368(6)	C39	C32	1.511(4)
C2	C1	1.428(5)	Co1	Cl1	2.250(3)
C12	C11	1.397(6)	Co1	Cl2	2.222(3)
C12	C19	1.529(8)	Co1A	Cl1A	2.243(14)
C12	C13	1.395(7)	Co1A	Cl2A	2.258(12)
C11	C16	1.385(6)			

Table 11 Bond Angles for CoMes2pyrCl2DCM.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C6	N3	C31	123.2(3)	C15	C14	C18	122.8(6)
C6	N3	Co1A	100.9(2)	C13	C14	C18	120.2(6)
C31	N3	Co1A	133.23(19)	C14	C15	C16	123.4(6)
C5	N2	C2	105.8(3)	C12	C13	C14	122.3(5)
C5	N2	Co1	144.9(2)	C31	C36	C37	119.9(3)
C5	N2	Co1A	107.4(2)	C35	C36	C31	118.0(3)
C2	N2	Co1	109.3(2)	C35	C36	C37	122.0(3)
C2	N2	Co1A	146.8(3)	C36	C31	N3	118.3(3)
C1	N1	C11	120.1(3)	C32	C31	N3	119.3(3)
C1	N1	Co1	110.2(3)	C32	C31	C36	122.3(3)
C11	N1	Co1	129.2(2)	C35	C34	C38	121.3(3)
N3	C6	C5	123.9(3)	C33	C34	C35	117.6(3)

N2	C5	C6	122.4(3)	C33	C34	C38	121.2(3)
N2	C5	C4	109.9(3)	C36	C35	C34	122.3(3)
C6	C5	C4	127.6(3)	C32	C33	C34	122.3(3)
C4	C3	C2	106.5(3)	C31	C32	C39	121.7(3)
N2	C2	C3	110.8(3)	C33	C32	C31	117.5(3)
N2	C2	C1	118.3(3)	C33	C32	C39	120.7(3)
C3	C2	C1	130.9(3)	N2	Co1	N1	82.61(12)
C3	C4	C5	107.0(3)	N2	Co1	Cl1	106.34(11)
N1	C1	C2	119.2(3)	N2	Co1	Cl2	123.22(10)
C11	C12	C19	120.2(5)	N1	Co1	Cl1	123.29(11)
C13	C12	C11	117.4(5)	N1	Co1	Cl2	111.39(11)
C13	C12	C19	122.4(5)	Cl2	Co1	Cl1	108.96(12)
C12	C11	N1	117.5(4)	N2	Co1A	N3	83.94(13)
C16	C11	N1	120.7(4)	N2	Co1A	Cl1A	114.0(5)
C16	C11	C12	121.8(5)	N2	Co1A	Cl2A	110.9(3)
C11	C16	C15	118.1(5)	Cl1A	Co1A	N3	112.3(4)
C11	C16	C17	121.5(5)	Cl1A	Co1A	Cl2A	107.5(5)
C15	C16	C17	120.4(5)	Cl2A	Co1A	N3	126.4(3)
C15	C14	C13	117.0(5)				

Table 12 Torsion Angles for CoMes2pyrCl2DCM.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N3	C6	C5	N2	-8.2(5)	C13	C14	C15	C16	-1.8(8)
N3	C6	C5	C4	166.8(3)	C18	C14	C15	C16	177.7(5)
N3	C31	C32	C33	-176.4(3)	C18	C14	C13	C12	-177.1(5)
N3	C31	C32	C39	2.3(5)	C36	C31	C32	C33	1.6(5)
N2	C5	C4	C3	0.9(4)	C36	C31	C32	C39	-179.7(3)
N2	C2	C1	N1	3.1(5)	C31	N3	C6	C5	176.1(3)
N1	C11	C16	C15	179.6(4)	C31	C36	C35	C34	0.9(5)
N1	C11	C16	C17	0.1(7)	C34	C33	C32	C31	-0.1(5)
C6	N3	C31	C36	108.8(3)	C34	C33	C32	C39	-178.9(3)
C6	N3	C31	C32	-73.1(4)	C37	C36	C31	N3	-5.7(4)
C6	C5	C4	C3	-174.6(3)	C37	C36	C31	C32	176.3(3)
C5	N2	C2	C3	-0.6(3)	C37	C36	C35	C34	-177.3(3)
C5	N2	C2	C1	-178.6(3)	C35	C36	C31	N3	176.1(3)
C3	C2	C1	N1	-174.6(3)	C35	C36	C31	C32	-1.9(5)

C2	N2	C5	C6	175.6(3)	C35	C34	C33	C32	-0.9(6)
C2	N2	C5	C4	-0.2(3)	C33	C34	C35	C36	0.5(6)
C2	C3	C4	C5	-1.2(4)	C38	C34	C35	C36	-179.8(4)
C4	C3	C2	N2	1.1(4)	C38	C34	C33	C32	179.4(4)
C4	C3	C2	C1	178.9(3)	Co1	N2	C5	C6	-5.6(5)
C1	N1	C11	C12	-112.6(4)	Co1	N2	C5	C4	178.6(3)
C1	N1	C11	C16	68.9(5)	Co1	N2	C2	C3	-179.8(2)
C12	C11	C16	C15	1.1(7)	Co1	N2	C2	C1	2.1(3)
C12	C11	C16	C17	-178.3(5)	Co1	N1	C1	C2	-6.3(4)
C11	N1	C1	C2	-179.4(3)	Co1	N1	C11	C12	75.8(5)
C11	C12	C13	C14	-1.3(7)	Co1	N1	C11	C16	-102.7(4)
C11	C16	C15	C14	0.0(8)	Co1A	N3	C6	C5	12.4(3)
C19	C12	C11	N1	1.9(6)	Co1A	N3	C31	C36	-93.5(3)
C19	C12	C11	C16	-179.6(5)	Co1A	N3	C31	C32	84.6(4)
C19	C12	C13	C14	177.7(5)	Co1A	N2	C5	C6	-2.9(3)
C15	C14	C13	C12	2.4(8)	Co1A	N2	C5	C4	-178.7(2)
C17	C16	C15	C14	179.5(5)	Co1A	N2	C2	C3	176.8(3)
C13	C12	C11	N1	-179.0(4)	Co1A	N2	C2	C1	-1.3(5)
C13	C12	C11	C16	-0.5(6)					

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for CoMes2pyrCl2DCM.

Atom	***x***	***y***	***z***	**U(eq)**
H6	6018	8243	2286	38
H3	4028	8674	-778	57
H4	5468	8726	429	56
H1	2372	7990	-688	50
H19A	767	9840	1088	149
H19B	1583	9755	734	149
H19C	1574	9055	1643	149
H15	-101	5644	-1032	103
H17A	1732	5843	-1159	141
H17B	1288	4803	-762	141
H17C	2115	5461	-97	141
H13	-420	8579	299	98
H18A	-1634	7004	-305	174
H18B	-1538	6148	-1103	174

H18C	-1645	7542	-1280	174
H37A	5641	10377	3664	64
H37B	5619	10620	4691	64
H37C	4869	9874	3983	64
H35	6624	9449	5807	49
H33	7270	6158	5226	50
H39A	5642	5697	3236	67
H39B	6568	5210	3820	67
H39C	6472	6114	2986	67
H38A	7585	8349	7013	98
H38B	8253	7692	6611	98
H38C	7565	6940	6920	98

Crystal Data for $C_{25}H_{28}Cl_4CoN_3$ (M =486.31 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 16.453(2) Å, b = 11.3132(17) Å, c = 15.240(2) Å, β = 108.344(3)°, V = 2692.6(7) Å^3, Z = 4, T = 100.02 K, μ(MoKα) = 0.849 mm^{-1}, $Dcalc$ = 1.200 g/cm^3, 18378 reflections measured (4.446° ≤ 2Θ ≤ 56.034°), 6463 unique (R_{int} = 0.0321, R_{sigma} = 0.0381) which were used in all calculations. The final R_1 was 0.0609 (I > 2σ(I)) and wR_2 was 0.1290 (all data).

Refinement model description

Number of restraints - 6

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups
 At 1.5 times of:
  All C(H,H,H) groups
2. Rigid bond restraints
 Cl1, Cl1A
 with sigma for 1-2 distances of 0.002 and sigma for 1-3 distances of 0.002
3. Uiso/Uaniso restraints and constraints
Cl1 ≈ Cl1A: within 2A with sigma of 0.002 and sigma for terminal atoms of
0.005
4. Others
 Sof(Co1A)=Sof(Cl1A)=Sof(Cl2A)=1-FVAR(1)
 Sof(Co1)=Sof(Cl1)=Sof(Cl2)=FVAR(1)
5.a Aromatic/amide H refined with riding coordinates:
 C6(H6), C3(H3), C4(H4), C1(H1), C15(H15), C13(H13), C35(H35), C33(H33)
5.b Idealised Me refined as rotating group:
 C19(H19A,H19B,H19C), C17(H17A,H17B,H17C), C18(H18A,H18B,H18C),
C37(H37A,H37B,
 H37C), C39(H39A,H39B,H39C), C38(H38A,H38B,H38C)
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