Axial Ligand Exchange of *N*-heterocyclic Cobalt(III) Schiff Base Complexes, Part 1: Molecular Structure and NMR Solution Dynamics

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Supporting Information

PART 1. Synthesis and 1D/2D NMR Analysis of Co(III) Schiff base complexes

A Chemical Shift Data (**1-6**), Alkaline Conditions

B Chemical Shift Data (**1-6**), Acidic Conditions

C Chemical Shift Data (Free Ligands), Alkaline and Acidic Conditions

PART 2. DCl titration of cobalt(III) Schiff base complexes

A [Co(acacen)(4MeIm)$_2$]Br

B [Co(acacen)(NH$_3$)$_2$]Cl

C [Co(acacen)(2MeIm)$_2$]Br

D [Co(acacen)(NMeIm)$_2$]Br

E [Co(acacen)(Im)$_2$]Br

F [Co(acacen)(Py)$_2$]Br

PART 3. **pH/Temperature dependence of 4MeIm Exchange**

a [Co(acacen)$(Im)_2$]Br

b [Co(acacen)$(NMeIm)_2$]Br

c [Co(acacen)$(Py)_2$]Br

d [Co(acacen)$(NH_3)_2$]Cl

e [Co(acacen)$(2MeIm)_2$]Br

PART 4. **Reversibility of 4MeIm Exchange**

A [Co(acacen)$(4MeIm)_2$]Br and 2MeIm

B [Co(acacen)$(4MeIm)_2$]Br and NMeIm

C [Co(acacen)$(4MeIm)_2$]Br and Im

D [Co(acacen)$(4MeIm)_2$]Br and Py

PART 5. **Chemical Equilibrium - Variation in 4MeIm Equivalents**

A [Co(acacen)$(NH_3)_2$]Cl

B [Co(acacen)$(NMeIm)_2$]Br

C [Co(acacen)$(Im)_2$]Br

D [Co(acacen)$(Py)_2$]Br

PART 6. **Mass spectroscopy studies of Co(III) Schiff base complexes**

PART 7. **X-ray Crystallography studies of Co(III) Schiff base Complexes**

A [Co(acacen)$(NH_3)_2$]BPh_4

B [Co(acacen)$(2MeIm)_2$]Cl

C [Co(acacen)$(NMeIm)_2$]BPh_4

D [Co(acacen)$(Im)_2$]BPh_4

E [Co(acacen)$(Py)_2$]Br

PART 1. Synthesis

The following synthesis of [Co(acacen)(4MeIm)$_2$]Br (**1**) is given as an example.

[Co(acacen)(4MeIm)$_2$]Br (1)

2,4-pentadione (5.00 mL, 48.5 mmol) was combined with 5 mL of ethanol with stirring at room temperature. Ethylenediamine (1.6 mL, 23.8 mmol) was added neat dropwise via addition funnel causing the reaction to exotherm. The reaction mixture was stirred and allowed to cool to room temperature and then cooled at 4°C overnight. The crude solid was filtered under vacuum and titrated with ether three times to give H_2(acacen) as a crystalline white solid (3.423 g, 15.3 mmol, 64 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.01 (s, 2H), 3.45 (s, 4H), 2.01 (s, 6H), 1.91(s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 195.62, 163.14, 96.20, 43.64, 29.01, 18.84.

Methanolic solutions (5 mL) of H_2(acacen) (0.578 g, 2.58 mmol) and $CoBr_2{\cdot}6H_2O$ (0.561 g, 2.56 mmol) were combined and stirred at room temperature under nitrogen for two hours. The solution was opened to air and 4MeIm (0.433 g, 5.27 mmol) was added and the reaction mixture stirred overnight at room temperature. The solution was concentrated; addition of diethyl ether precipitated a brown solid. The product was filtered and washed with cold diethyl ether (0.657 g, 1.28 mmol, 49%). ^{1}H NMR (500 MHz, D_2O) δ: 7.33 (s, 2H), 6.38 (s, 2H), 3.45 (s, 2H), 2.09 (s, 6H), 2.27 (s, 6H), 2.14 (s, 6H). ^{13}C NMR (126 MHz, D_2O) δ: 180.03, 172.54, 138.96, 130.96, 126.35, 98.29, 55.68, 27.36, 24.70, 11.97.

PART 1A. 1D/2D NMR Analysis of Co(III) Schiff base complexes, ^{1}H and ^{13}C NMR assignment of $[Co(acacen)(X)_2]^+$ at alkaline pD.

$[Co(acacen)(X)_2]^+$	Species	Chemical Shifts	
		^{1}H (ppm)	^{13}C (ppm)
NH_3 (pD 8.69)	$[Co(acacen)(NH_3)_2]^+$	-	179.84, 173.26, 98.55,
		3.62 (s,4H,CH$_2$),	55.42,
	89% Abundance	2.09 (s,6H,CH$_3$),	27.34,
		2.26 (s,6H,CH$_3$)	24.63
		-	180.64, 174.09,
	$[Co(acacen)(NH_3)(D_2O)]^+$	-	98.76,
		3.80 (s,4H,CH$_2$),	55.82,
	11% Abundance	2.20 (s,6H,CH$_3$),	27.43,
		2.37 (s,6H,CH$_3$)	24.83
Im (pD 7.89)	$[Co(acacen)(Im)_2]^+$	-	180.13, 172.85, 98.36
		7.49 (s,2H,CH),	139.80,
		6.72 (s,2H,CH),	129.79,
		7.06 (s,2H,CH),	120.52,
	100% Abundance	3.46 (s,4H,CH$_2$),	55.75,
		2.10 (s,6H,CH$_3$),	27.35,
		2.29 (s,6H,CH$_3$)	24.75
4MeIm (pD 8.20)	$[Co(acacen)(4MeIm)_2]^+$	-	180.03, 172.54,
		-	130.96, 98.29,
		7.33 (s,2H,CH),	138.96,
		6.38 (s,2H,CH),	126.35,
	100% Abundance	3.45 (s,4H,CH$_2$),	55.68,
		2.09 (s,6H,CH$_3$),	27.36,
		2.27 (s,6H,CH$_3$),	24.70,
		2.14 (s,6H,CH$_3$)	11.97
NMeIm (pD 7.71)	$[Co(acacen)(NMeIm)_2]^+$	-	180.08, 172.85, 98.65,
		7.30 (s,2H,CH),	141.48,
		6.65 (s,2H,CH),	130.58,
		6.98 (s,2H,CH),	124.92,
	100% Abundance	3.47 (s,4H,CH$_2$),	55.69,
		3.67 (s,6H,CH$_3$),	37.18,
		2.10 (s,6H,CH$_3$),	27.38,
		2.29 (s,6H,CH$_3$)	24.78
2MeIm (pD 8.12)	$[Co(acacen)(2MeIm)_2]^+$	-	181.29, 173.38, 151.23,
		-	99.72,
		6.41 (s,2H,CH),	131.12,
		6.92 (s,2H,CH),	118.94,
	83% Abundance	3.66 (s,4H,CH$_2$),	54.53,
		2.07 (s,6H,CH$_3$),	26.99,
		2.22 (s,6H,CH$_3$),	23.92,
		2.29 (s,6H,CH$_3$)	14.37
	$[Co(acacen)(2MeIm)(D_2O)]^+$	-	99.39
		6.82 (s,2H,CH),	-
		6.16 (s,2H,CH),	-
	17% Abundance	3.87-3.51 (dm,4H,CH$_2$)	55.66
		2.23 (s,6H,CH$_3$),	27.28
		2.40 (s,6H,CH$_3$)	24.48
Py (pD 7.00)	$[Co(acacen)(Py)_2]Br$	-	181.03, 174.38
		8.04 [d (*J*=5.37),4H,CH)],	154.81,
		7.92 [t (*J*=7.60),2H,CH)],	142.34,
		7.37 [t (J=6.99),4H,CH)],	127.92,
	100% Abundance	3.76 (s,4H,CH$_2$),	54.71,
		2.08 (s,6H,CH$_3$),	27.59,
		2.30 (s,6H,CH$_3$	24.70

PART 1B. 1D/2D NMR Analysis of Co(III) Schiff base complexes, ^{1}H and ^{13}C NMR assignment of $[\mathrm{Co(acacen)(X)_2}]^+$ at acidic pD.

$[\mathrm{Co(acacen)(X)_2}]^+$	Species	Chemical Shifts	
		^{1}H (ppm)	^{13}C (ppm)
NH$_3$ (pD 2.96)	$[\mathrm{Co(acacen)(NH_3)(D_2O)}]^+$ 30% Abundance	- - 3.79 (s,4H,CH$_2$), 2.19 (s,6H,CH$_3$), 2.36 (s,6H,CH$_3$)	180.64, 174.21, 98.36, 55.90, 27.50, 24.95
	$[\mathrm{Co(acacen)(D_2O)_2}]^+$ 70% Abundance	- - 2.27 (s,4H,CH$_2$), 0.90 (s,6H,CH$_3$), 0.74 (s,6H,CH$_3$)	165.29, 155.78, 98.55, 51.26, 22.91, 20.70
Im (pD 3.74)	$[\mathrm{Co(acacen)(Im)_2}]^+$ 52% Abundance	- - 7.48 (s,2H,CH), 6.70 (s,2H,CH), 7.04 (s,2H,CH), 3.44 (s,4H,CH$_2$), 2.08 (s,6H,CH$_3$), 2.28 (s,6H,CH$_3$)	180.20, 172.95, 98.25, 139.86, 129.92, 120.86, 55.85, 27.44, 24.85
	$[\mathrm{Co(acacen)(Im)(D_2O)}]^+$ 48% Abundance	- - 7.10 (s,1H,CH), 6.30 (s,1H,CH), 6.92 (s,1H,CH), 3.83-3.53 [dq(J=141.0, 6.9 Hz),4H,CH$_2$], 2.21 (s,6H,CH$_3$), 2.40 (s,6H,CH$_3$)	180.66, 174.02, 98.75, 139.96, 129.83, 120.56, 56.22, 27.50, 25.07
4MeIm (pD 3.37)	$[\mathrm{Co(acacen)(4MeIm)_2}]^+$ 55% Abundance	- - 7.32 (s,2H,CH), 6.37 (s,2H,CH), 3.44 (s,4H,CH$_2$), 2.07 (s,6H,CH$_3$), 2.26 (s,6H,CH$_3$), 2.13 (s,6H,CH$_3$)	180.07, 172.61, 131.00, 98.41, 139.00, 126.41, 55.74, 27.42, 24.77, 11.96
	$[\mathrm{Co(acacen)(4MeIm)(H_2O)}]^+$ 45% Abundance	- - 6.95 (s,1H,CH), 5.98 (s,1H,CH), 3.82-3.54 [dq (J=141.3, 6.8 Hz), 4H,CH$_2$], 2.21 (s,6H,CH$_3$), 2.39 (s,6H,CH$_3$), 2.06 (s,3H,CH$_3$)	180.58, 173.84, 131.39, 98.21, 139.18 126.23 56.16 27.48 25.01 12.03
NMeIm (pD 3.80)	$[\mathrm{Co(acacen)(NMeIm)_2}]^+$ 62% Abundance	- - 7.29 (s,2H,CH), 6.63 (s,2H,CH), 6.97 (s,2H,CH), 3.46 (s,4H,CH$_2$), 3.65 (s,3H,CH$_3$), 2.08 (s,6H,CH$_3$), 2.28 (s,6H,CH$_3$)	180.12, 172.93, 98.74, 141.56, 130.65, 125.00, 55.78, 37.29, 27.47, 24.89
	$[\mathrm{Co(acacen)(NMeIm)(D_2O)}]^+$ 38% Abundance	- - 6.24 (s,1H,CH), 6.93 (s,1H,CH), 6.85 (s,1H,CH), 3.82-3.54 [dq, (J=140.6, 7.0 Hz), 4H,CH$_2$], 3.59 (s,3H,CH$_3$), 2.21 (s,6H,CH$_3$), 2.40 (s,6H,CH$_3$)	180.59, 174.01, 98.52, 141.53, 137.90, 125.33, 56.19, 37.44, 27.52, 25.09

2MeIm (pD 3.63)	$[Co(acacen)(2MeIm)(D_2O)]^+$ 39% Abundance	- - 6.15 (s,1H,CH), 6.80 (s,1H,CH), 3.86-3.49 (dm,4H,CH_2), 2.22 (m,6H,CH_3), 2.40 (m,6H,CH_3), 2.04 (m,3H,CH_3)	181.16, 180.16 174.79, 174.47 131.06, 119.50, 56.05, 55.97 27.61, 27.56, 27.36 25.23, 25.19, 24.58 13.93
	$[Co(acacen)(D_2O)_2]^+$ 61% Abundance	- 2.23 (s,4H,CH_2), 0.91 (s,6H,CH_3), 0.80 (s,6H,CH_3)	165.44, 155.89 51.30 22.94, 20.72
Py (pD 3.00)	$[Co(acacen)(Py)_2]^+$ 94% Abundance	- 8.02 [d (J = 5.3 Hz),4H,CH)], 7.90 [t (J = 7.6 Hz),2H,CH)], 7.38 – 7.32 (m,4H,CH), 3.74 (s,4H,CH_2), 2.06 (s,6H,CH_3), 2.28 (s,6H,CH_3)	181.03, 174.38 154.91, 128.02, 54.83, 27.69, 24.83
	$[Co(acacen)(Py)(H_2O)]^+$ 6% Abundance	- 7.79 [t (J = 7.6 Hz),2H,CH], 7.43 [d (J = 5.6 Hz),1H,CH], 7.20 [t (J = 6.9 Hz),2H,CH], 3.93-3.49 [dq (J = 202.9, 6.5 Hz), 1H], 2.24 (s,6H,CH_3), 2.44 (s,6H,CH_3)	180.75, 174.66, 142.46, 155.57, 128.23, 56.32 27.58, 25.22

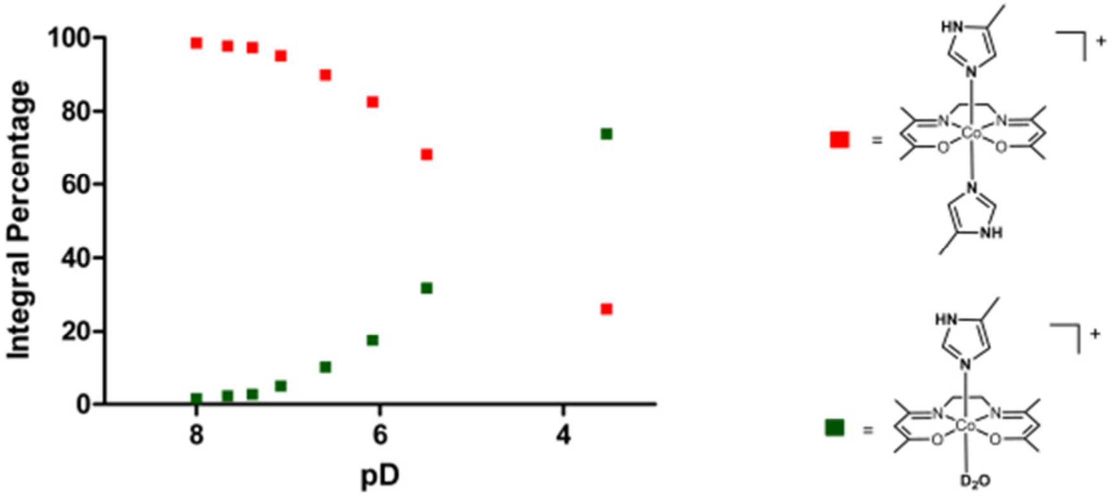
PART 1C. 1D/2D NMR Analysis of Co(III) Schiff base complexes, ^{1}H and ^{13}C NMR assignment of free ligands at alkaline and acidic pD.

Species	pD	Chemical Shifts	
		^{1}H (ppm)	^{13}C (ppm)
Im	9.19	7.80 (s,1H,CH)	138.87
		7.15 (s,2H,CH)	124.58
	3.50	8.74 (s,1H,CH)	136.31
		7.51 (d,2H,CH)	121.87
4MeIm	9.53	-	135.25
		7.67 (s,1H,CH)	138.14
		6.82 (s,1H,CH)	120.26
		2.21 (s,3H,CH_3)	13.41
	3.14	-	132.57
		8.56 (s,1H,CH)	135.31
		7.19 (s,1H,CH)	118.30
		2.35 (s,3H,CH_3)	11.86
NMeIm	9.40	7.59 (s,1H,CH)	141.25
		7.07 (s,1H,CH)	130.27
		7.00 (s,1H,CH)	124.14
		3.68 (s,1H,CH)	35.83
	3.38	8.72 (s,1H,CH)	137.87
		7.48 (t,2H,CH)	125.87
		-	122.37
		3.96 (s,3H,CH_3)	38.45
2MeIm	9.85	-	148.69
		6.98 (s,2H,CH)	124.09
		2.37 (s,3H,CH_3)	15.27
	3.79	-	147.12
		7.32 (s,2H,CH)	121.05
		2.65 (s,3H,CH_3)	13.54
Py	7.00	8.55 [dt (J = 4.5, 1.7 Hz,2H, CH)	150.94
		7.93 (tt, J = 7.7, 1.8 Hz, 1H, CH)	141.08
		7.50 [ddd (J = 7.7, 4.5, 1.5 Hz,) 2H,CH]	127.49
	2.16	8.89 – 8.75 (m, 2H, CH)	150.16
		8.64 [tt, (J = 7.9, 1.6 Hz), 1H, CH]	144.04
		8.17 – 8.01 (m, 2H,CH)	130.39

PART 2A. DCl titration of Co(III) Schiff base complexes, DCl titration of [Co(acacen)(4MeIm)$_2$]Br

(A) Integral percentage of each Co(III) Schiff base complex in solution as a function of pD: **(B)** complete NMR spectrum, **(C)** alkyl NMR region **(D)** aromatic NMR region.

(A)



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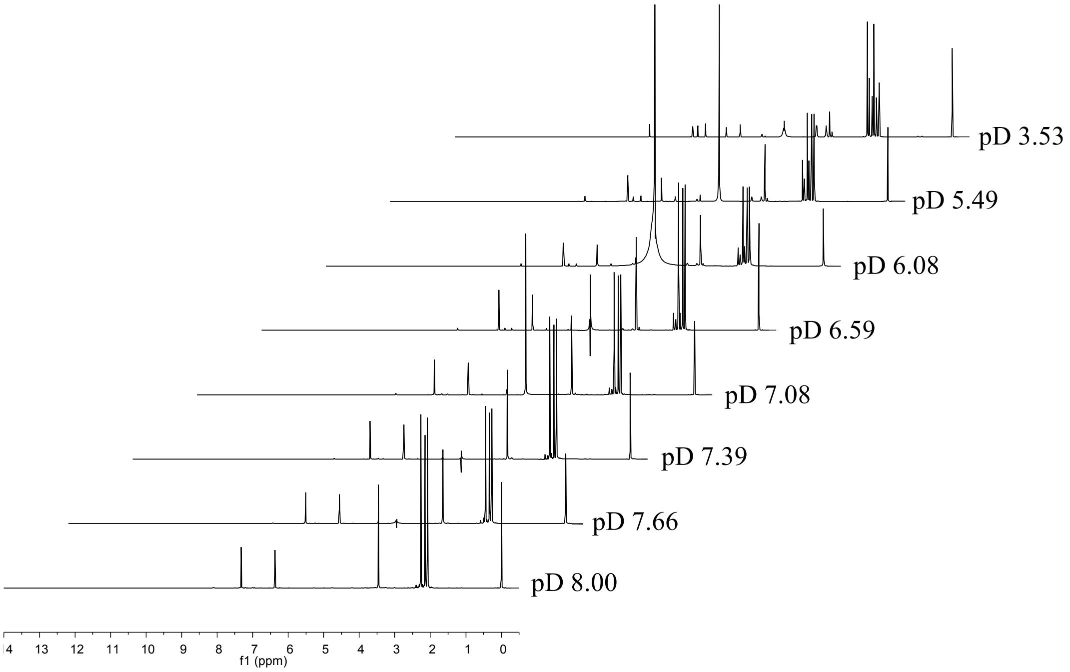

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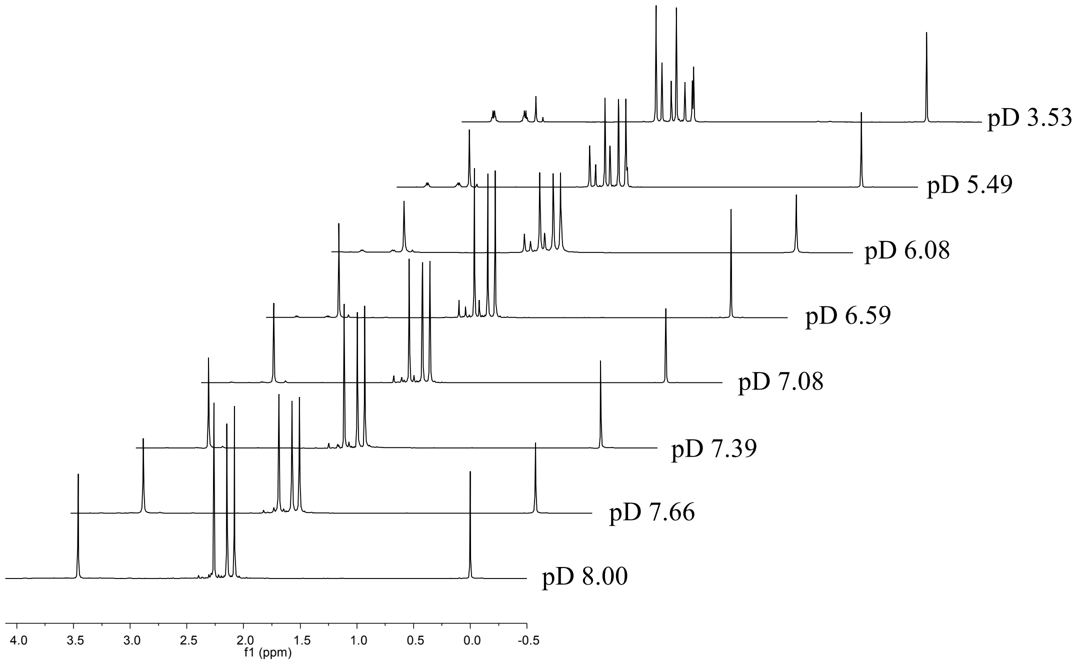
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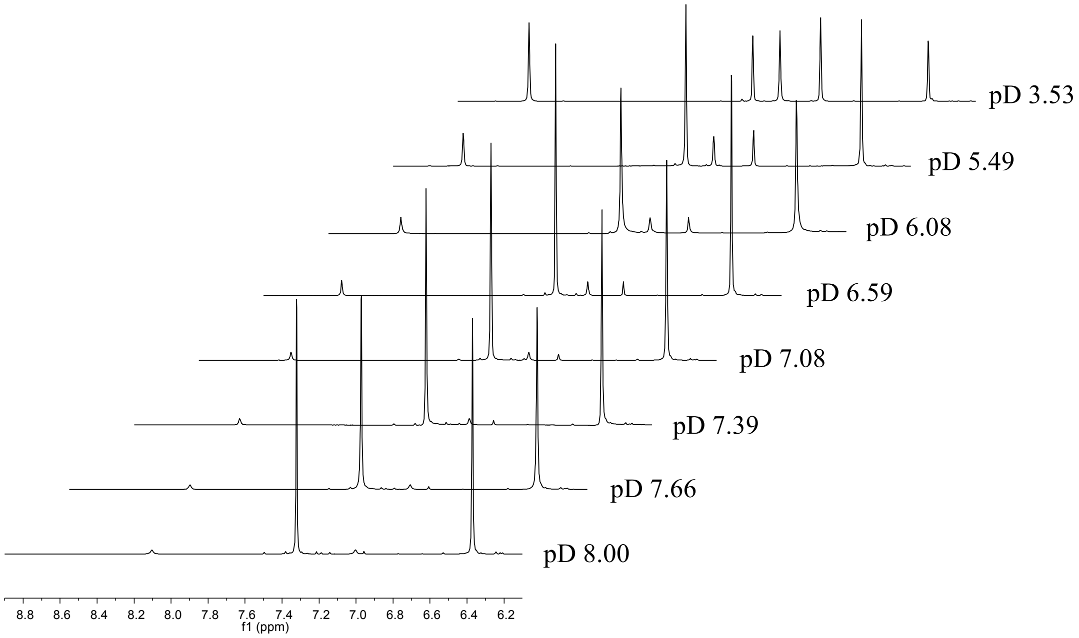
(D)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7.2
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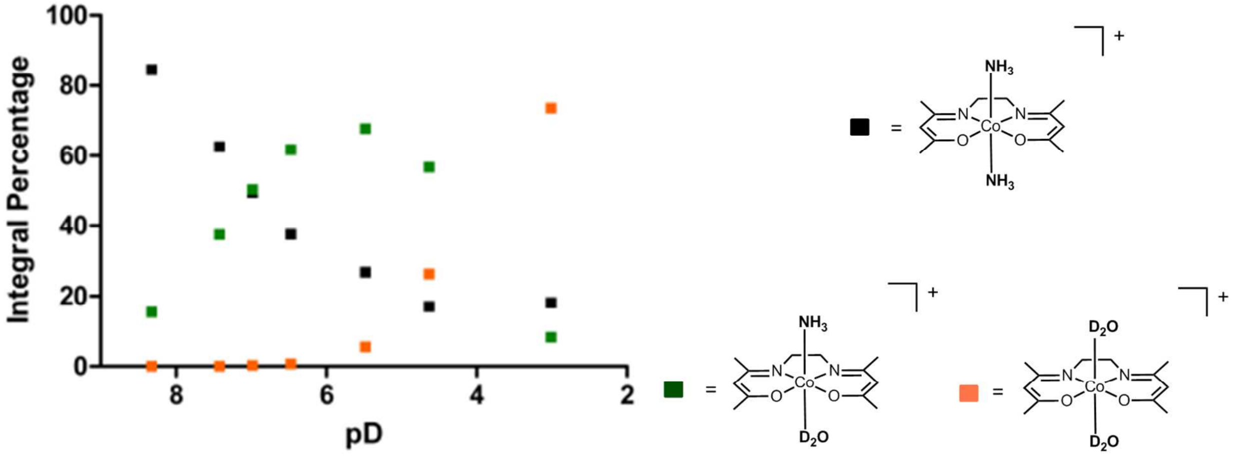
6.6
6.4
6.2
f1 (ppm)

PART 2B. DCl titration of Co(III) Schiff base complexes, DCl titration of [Co(acacen)$(NH_3)_2$]Cl

(A) Integral percentage of each Co(III) Schiff base complex in solution as a function of pD: **(B)** complete NMR spectrum, **(C)** alkyl NMR region.

(A)



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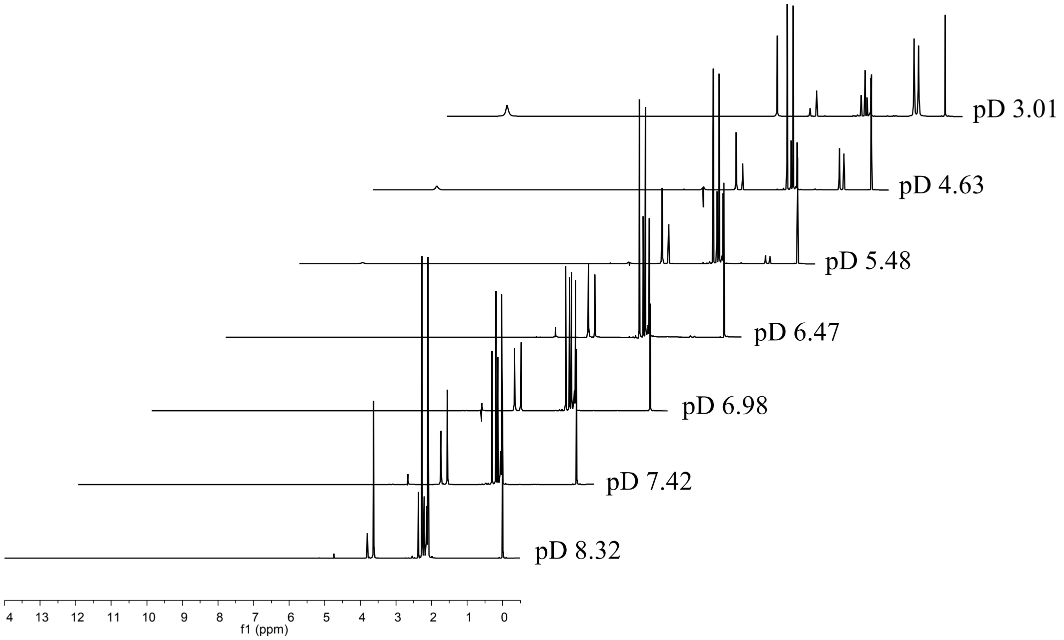

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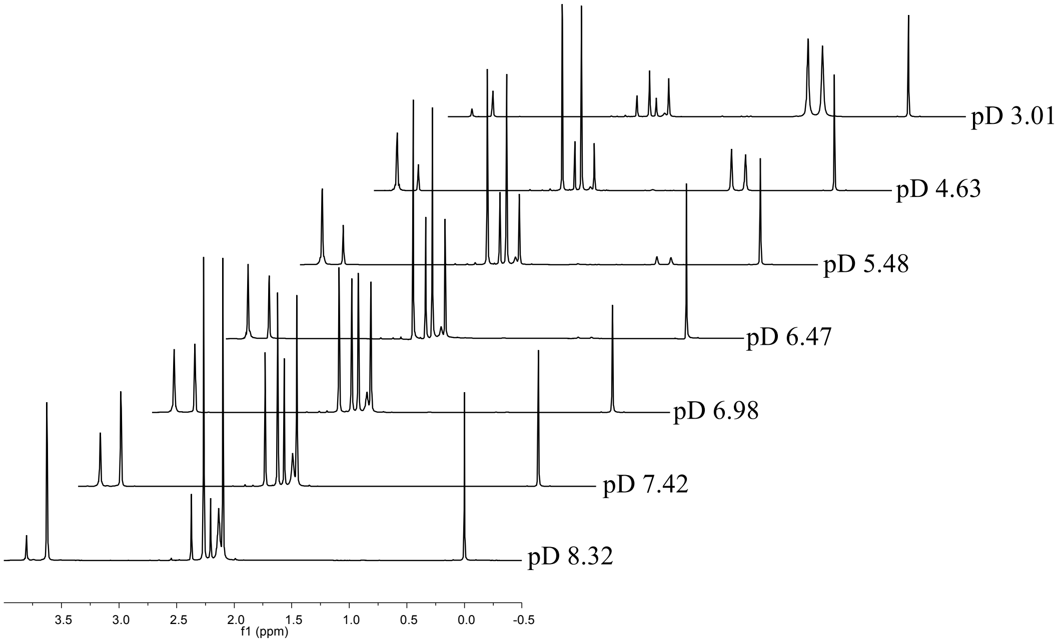
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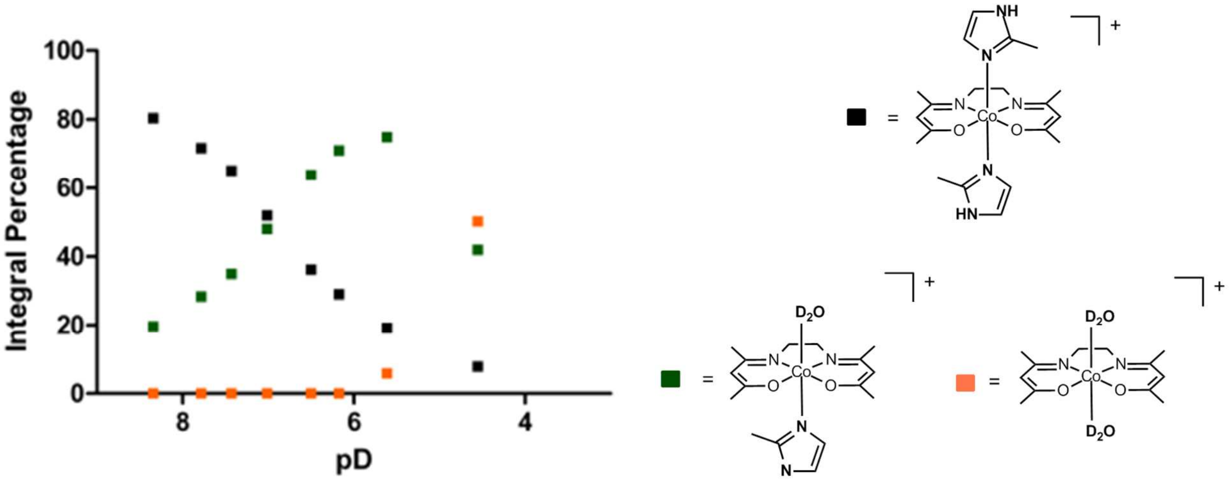
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

PART 2C. DCl titration of Co(III) Schiff base complexes, DCl titration of [Co(acacen)(2MeIm)$_2$]Br

(A) Integral percentage of each Co(III) Schiff base complex in solution as a function of pD: **(B)** complete NMR spectrum, **(C)** alkyl NMR region **(D)** aromatic NMR region.

(A)



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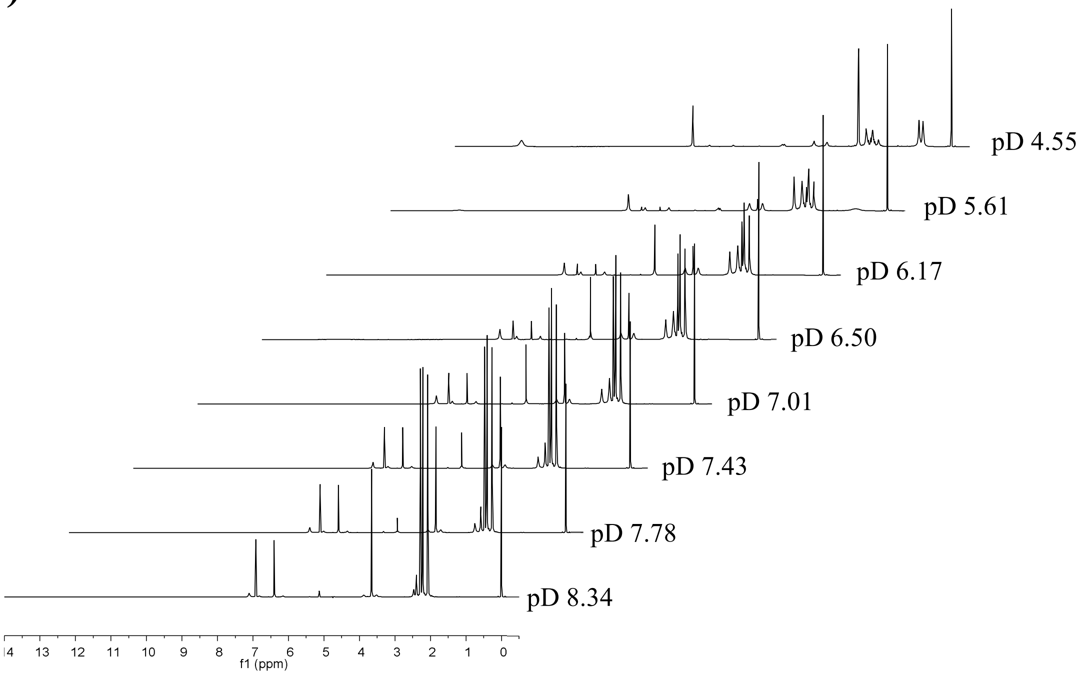

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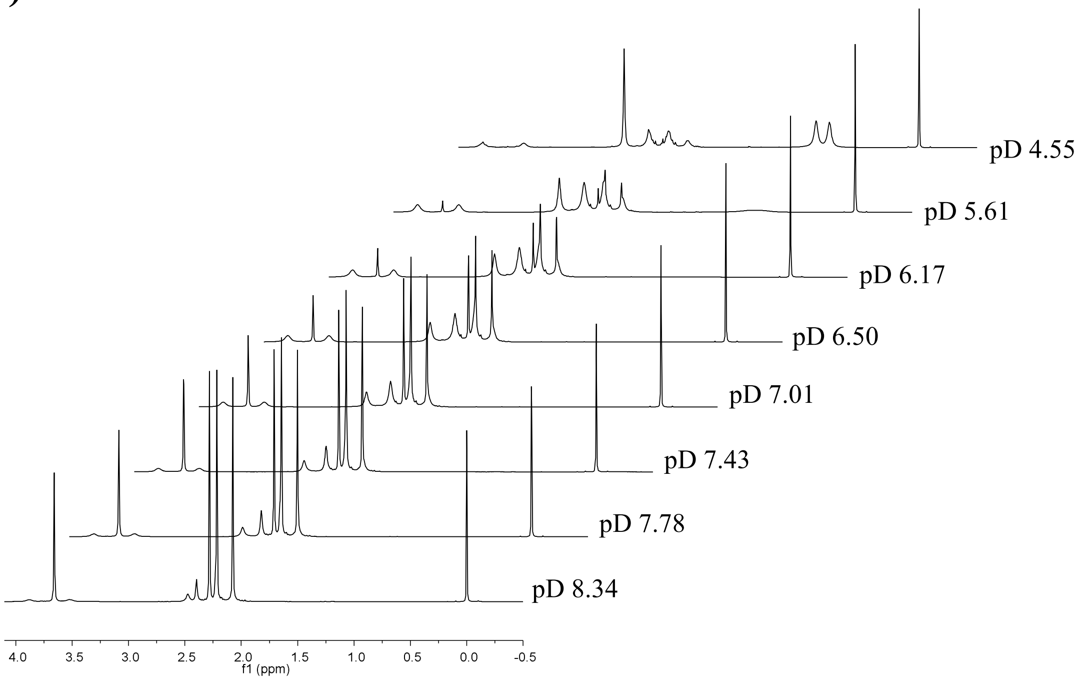
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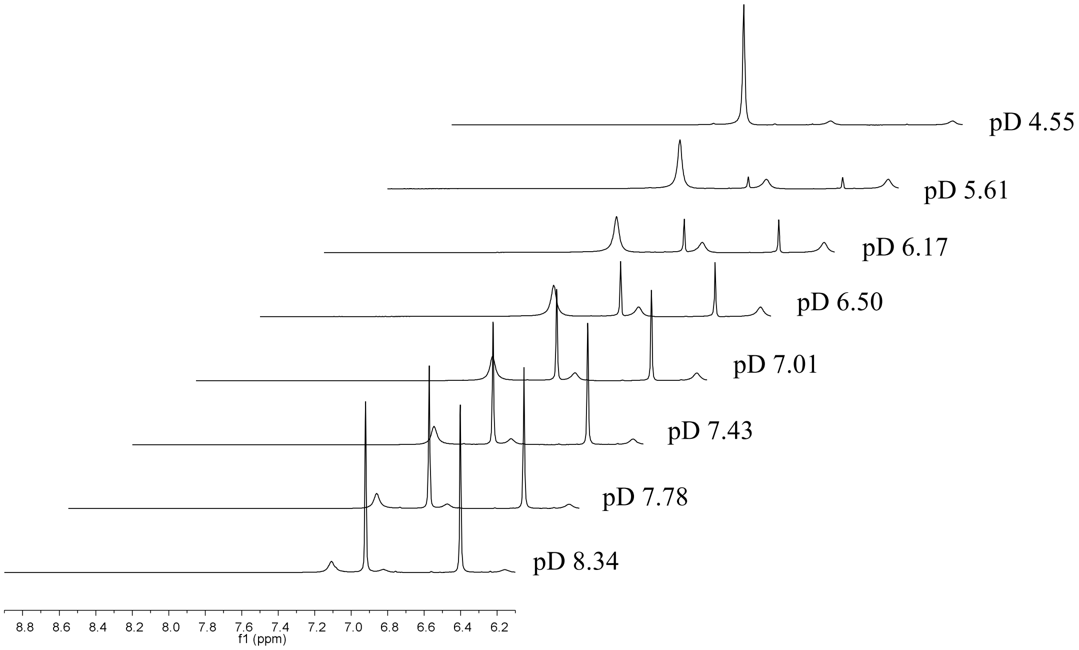
(D)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6.8
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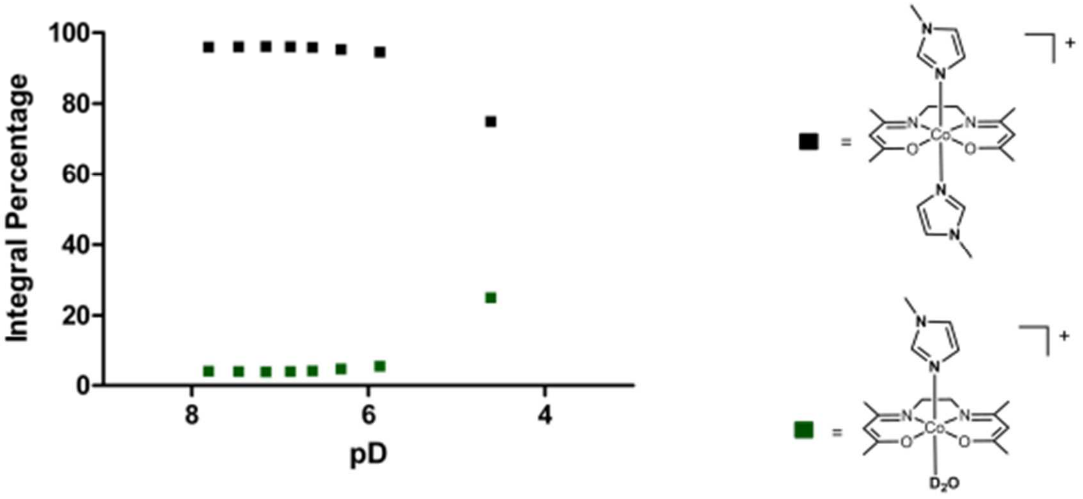
6.4
6.2
f1 (ppm)

PART 2D. DCl titration of Co(III) Schiff base complexes, DCl titration of [Co(acacen)(NMeIm)$_2$]Br

(A) Integral percentage of each Co(III) Schiff base complex in solution as a function of pD: **(B)** complete NMR spectrum, **(C)** alkyl NMR region **(D)** aromatic NMR region.

(A)



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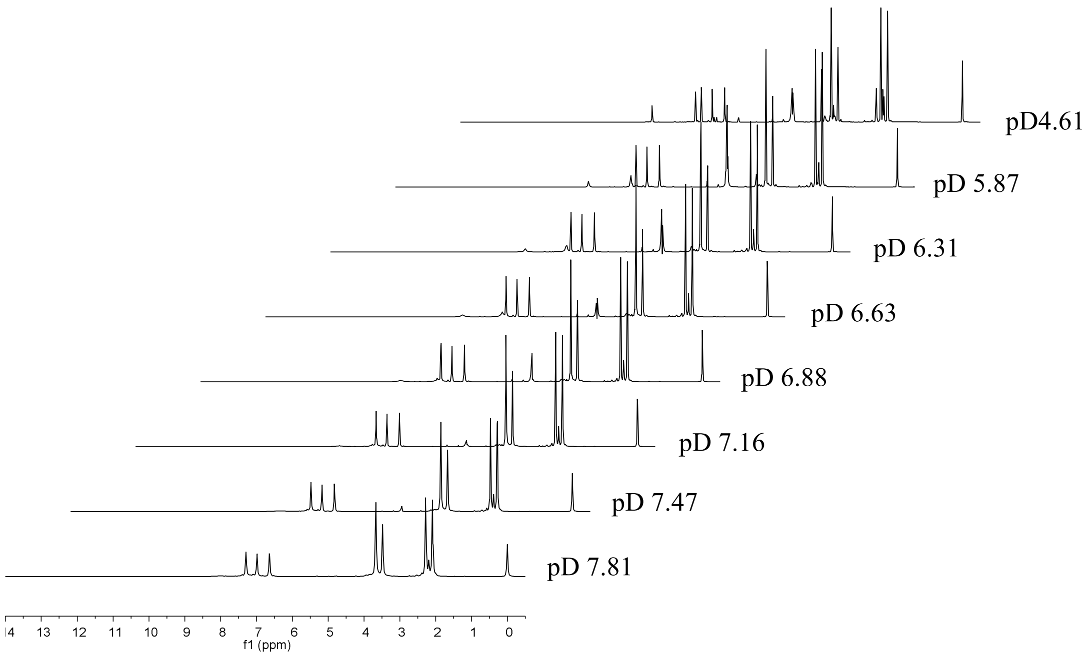

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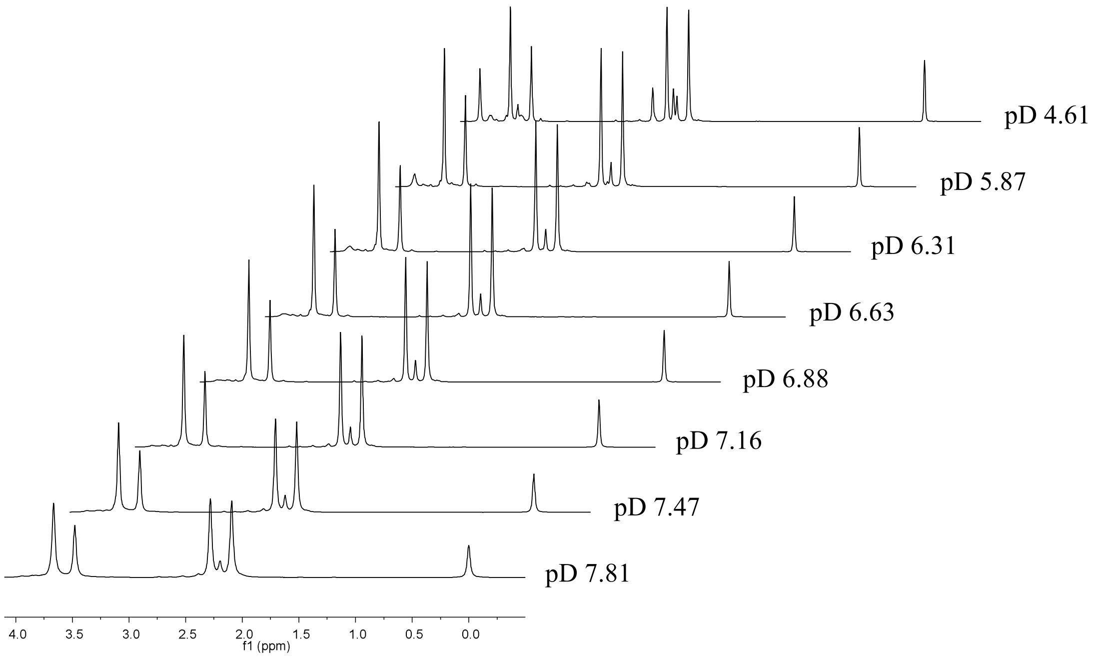
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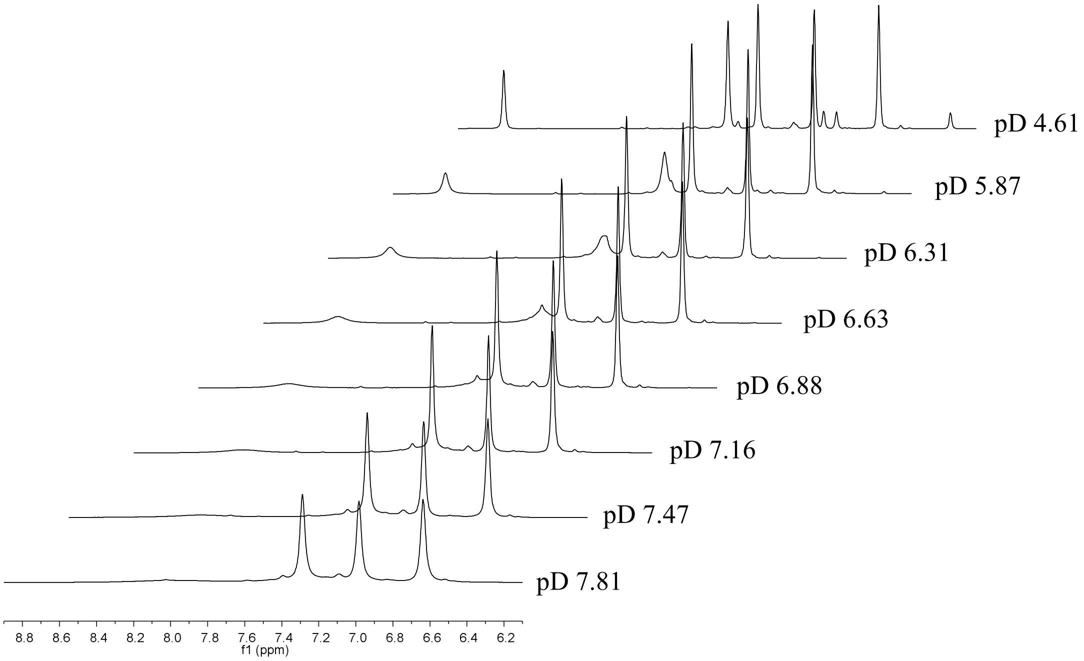
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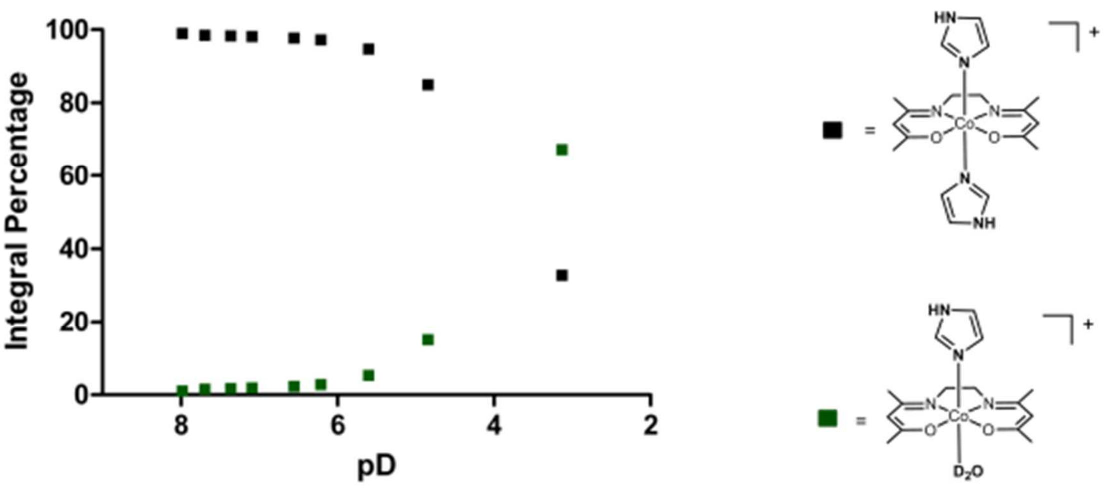
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
f1 (ppm)

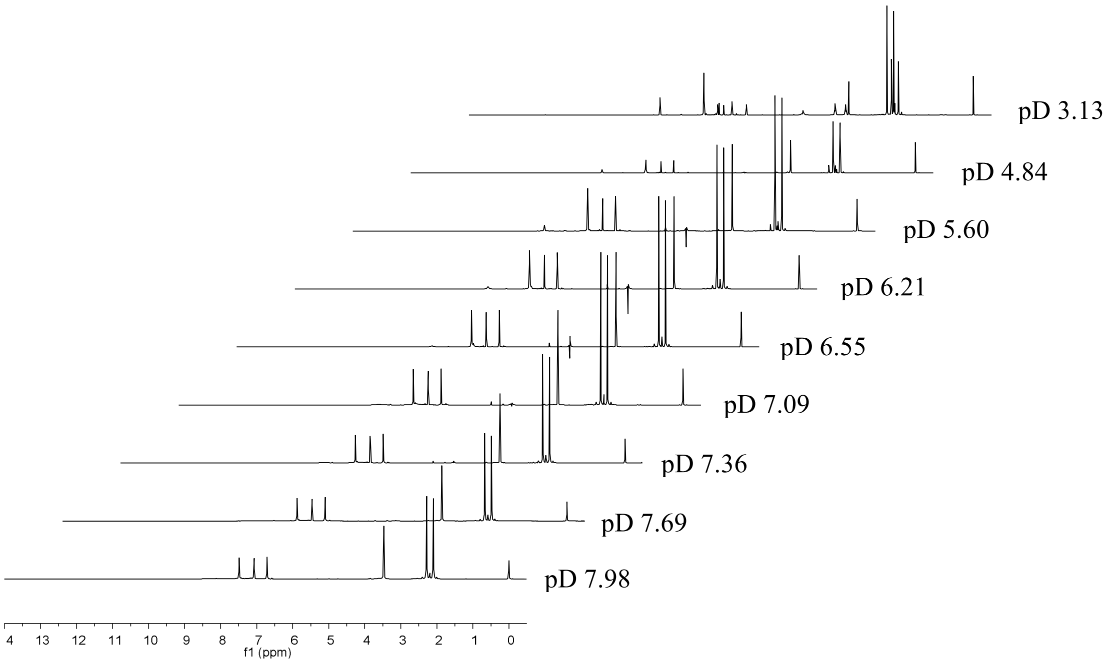
PART 2E. DCl titration of Co(III) Schiff base complexes, DCl titration of [Co(acacen)(Im)$_2$]Br

(A) Integral percentage of each Co(III) Schiff base complex in solution as a function of pD: **(B)** complete NMR spectrum, **(C)** alkyl NMR region **(D)** aromatic NMR region.

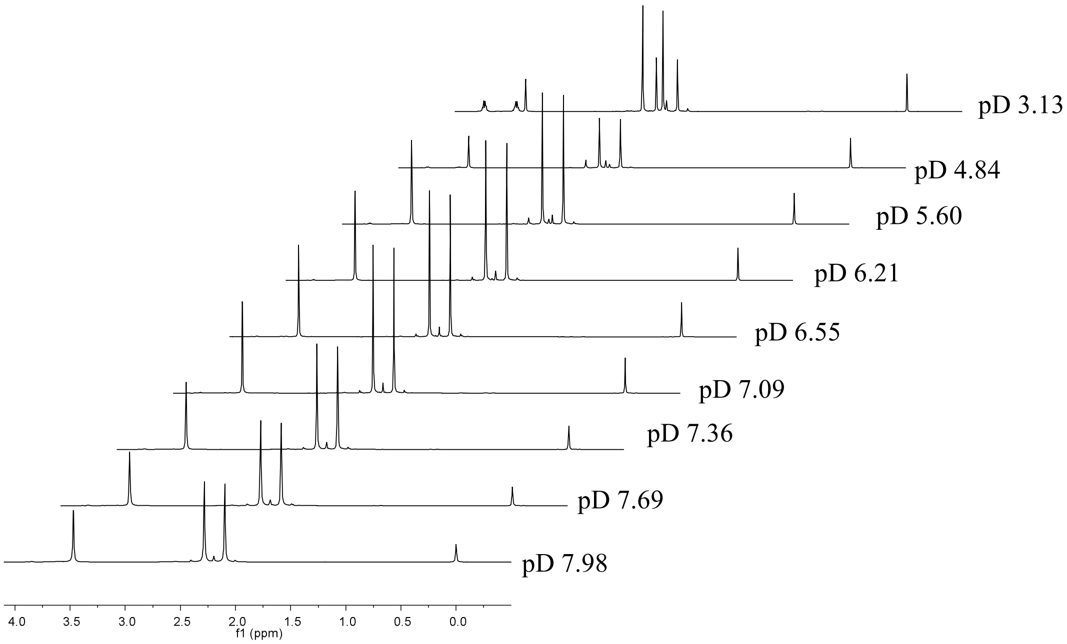
(A)



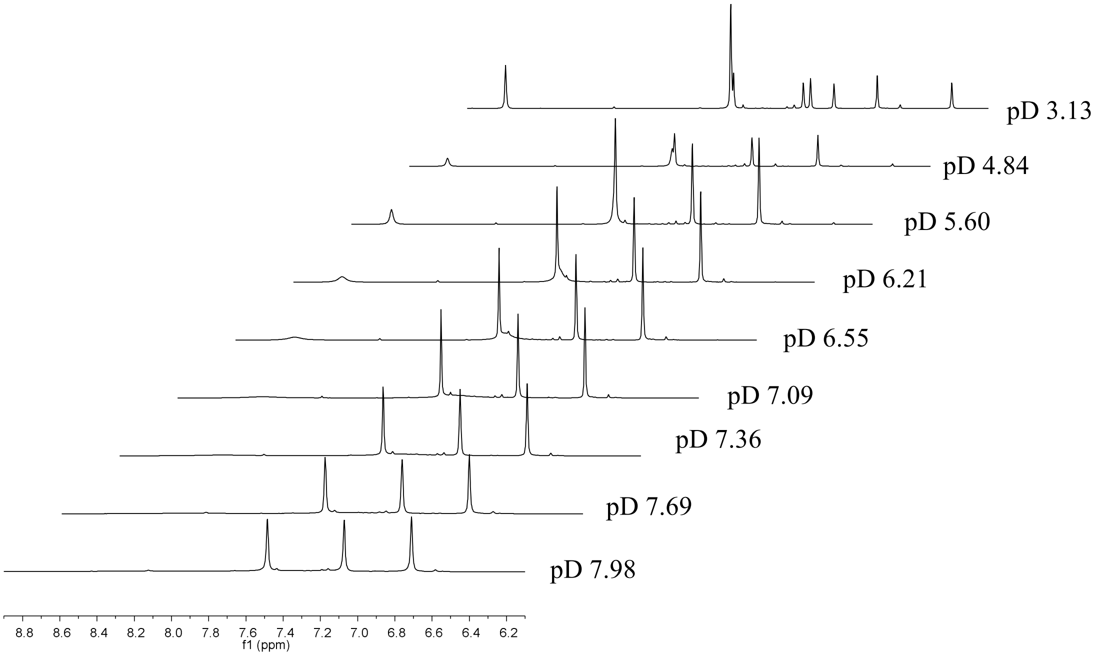
(B)



(C)


pD 3.13
pD 4.84
pD 5.60
pD 6.21
pD 6.55
pD 7.09
pD 7.36
pD 7.69
pD 7.98
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

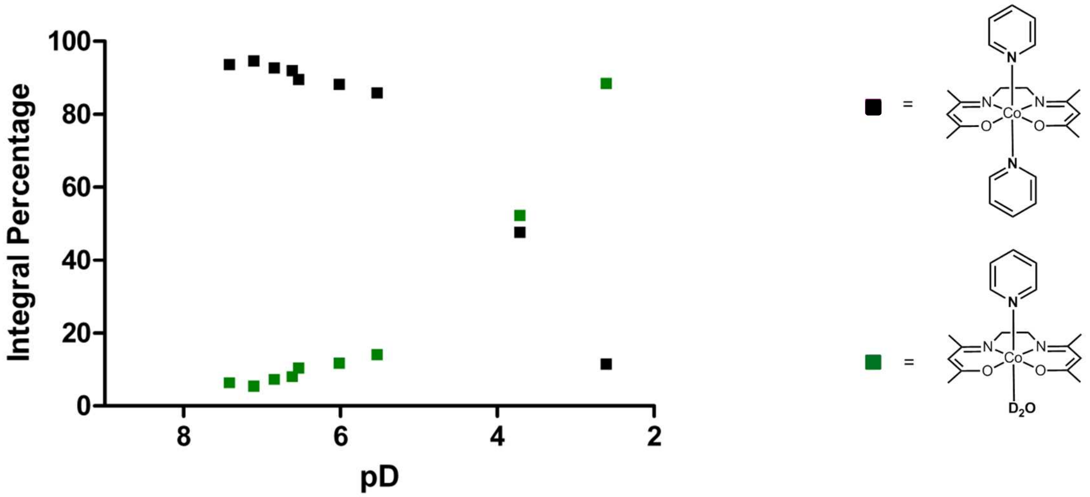
(D)


pD 3.13
pD 4.84
pD 5.60
pD 6.21
pD 6.55
pD 7.09
pD 7.36
pD 7.69
pD 7.98
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
f1 (ppm)

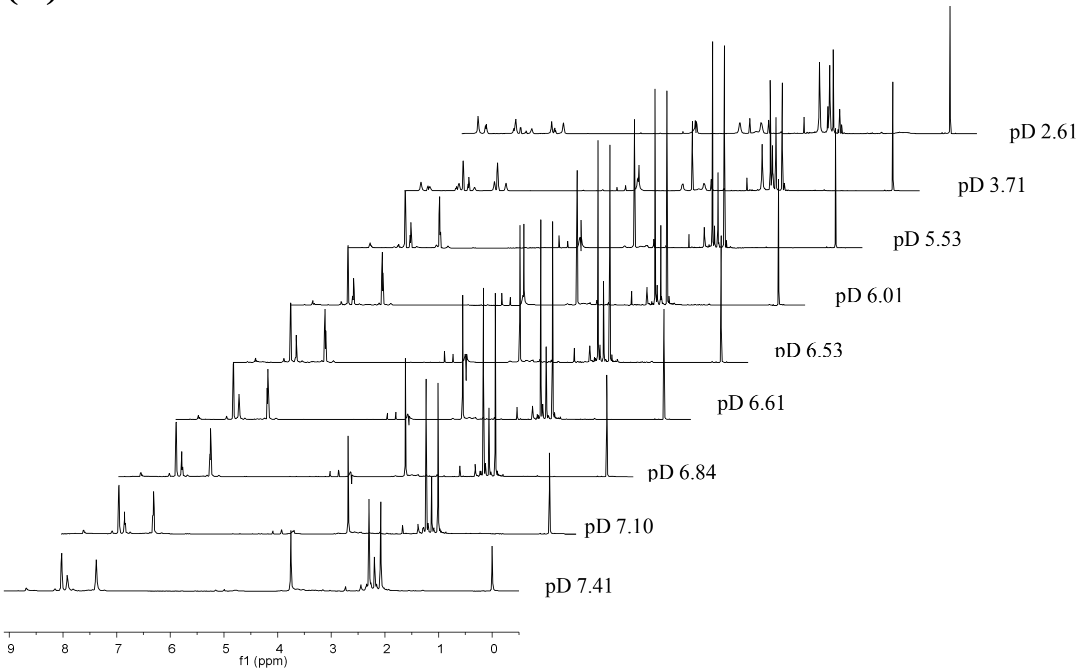
PART 2F. DCl titration of Co(III) Schiff base complexes, DCl titration of [Co(acacen)(Py)$_2$]Br

(A) Integral percentage of each Co(III) Schiff base complex in solution as a function of pD: **(B)** complete NMR spectrum, **(C)** alkyl NMR region **(D)** aromatic NMR region.

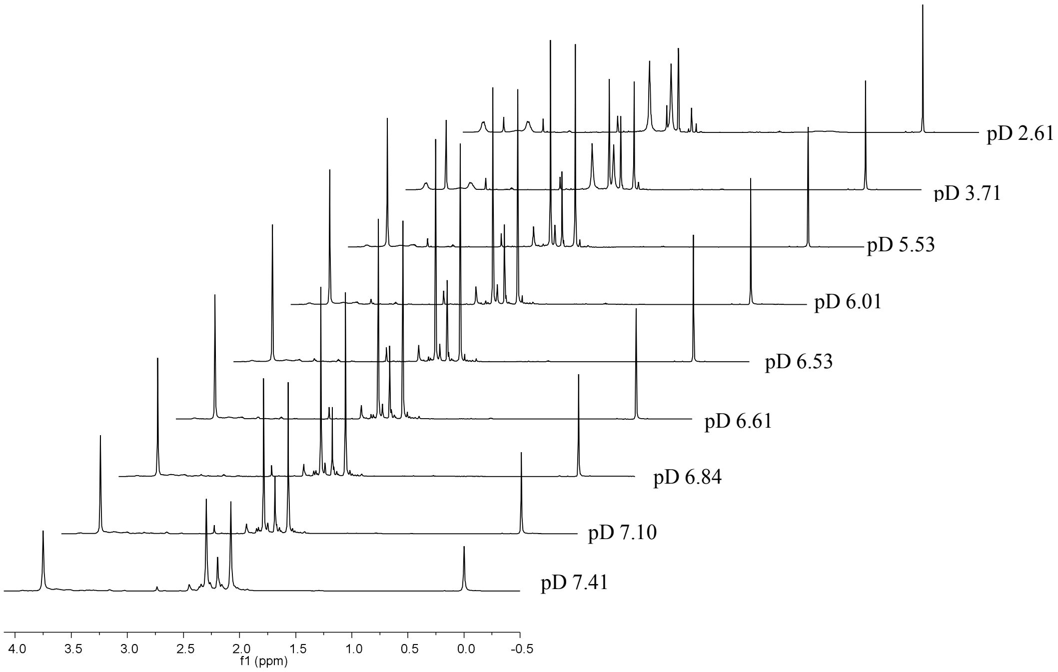
(A)



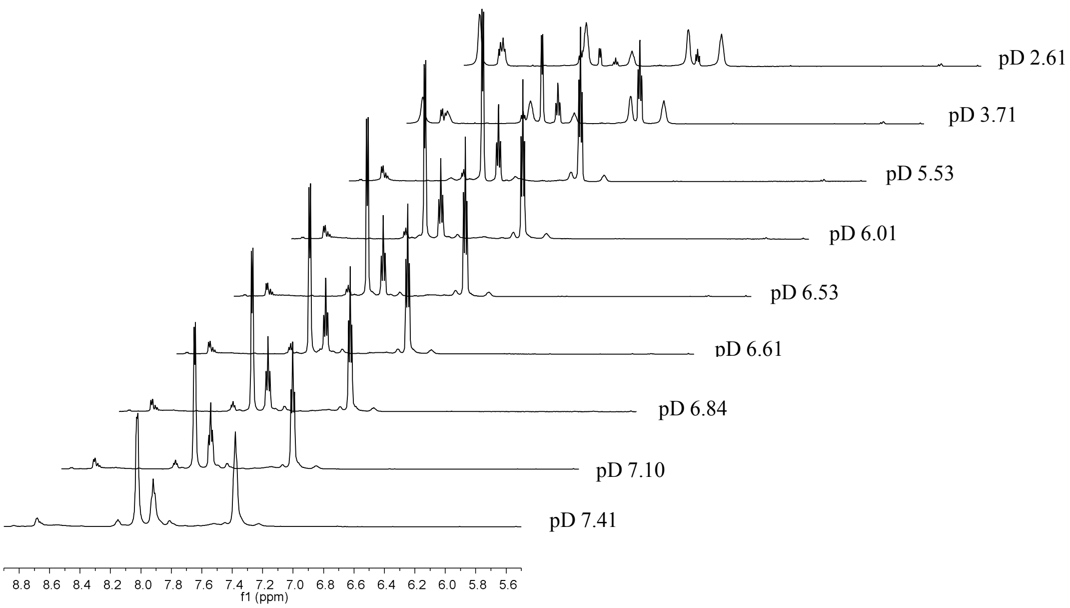
(B)



(C)


pD 2.61
pD 3.71
pD 5.53
pD 6.01
pD 6.53
pD 6.61
pD 6.84
pD 7.10
pD 7.41
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

(D)


pD 2.61
pD 3.71
pD 5.53
pD 6.01
pD 6.53
pD 6.61
pD 6.84
pD 7.10
pD 7.41
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
f1 (ppm)

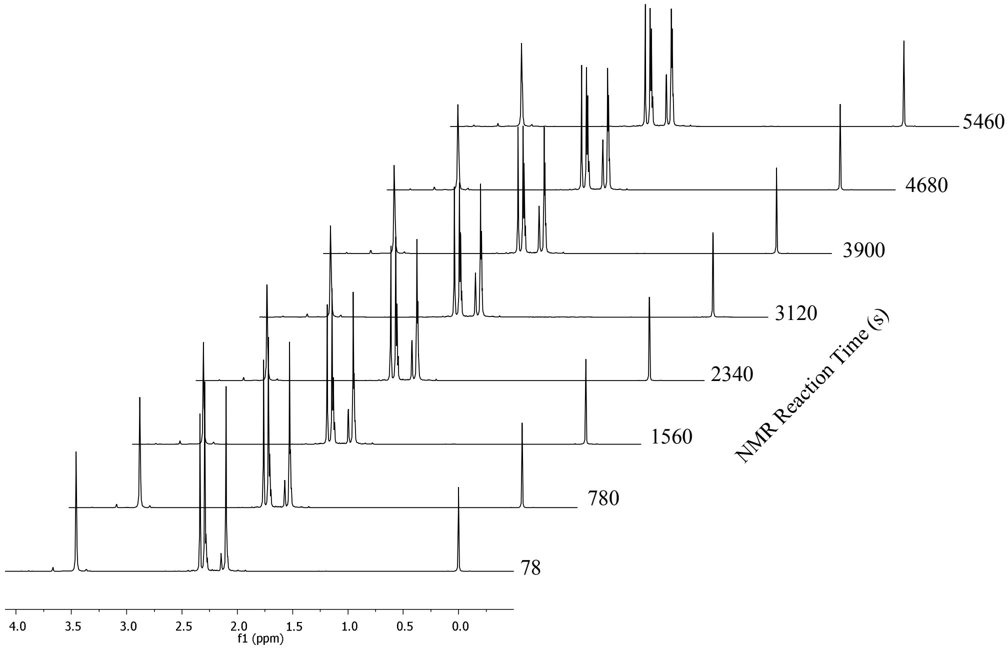
PART 3a. pH/Temperature dependence of 4MeIm Exchange, [Co(acacen)(Im)$_2$]Br

Equilibrium integral percentages of the resultant species in the reaction of **5** (1 eq) with 4MeIm (2 eq) as a function of temperature and pD. (**A**) **5**, (**B**) [Co(acacen)(Im)(4MeIm)]$^+$, (**C**) **1**. * Species are not in equilibrium.

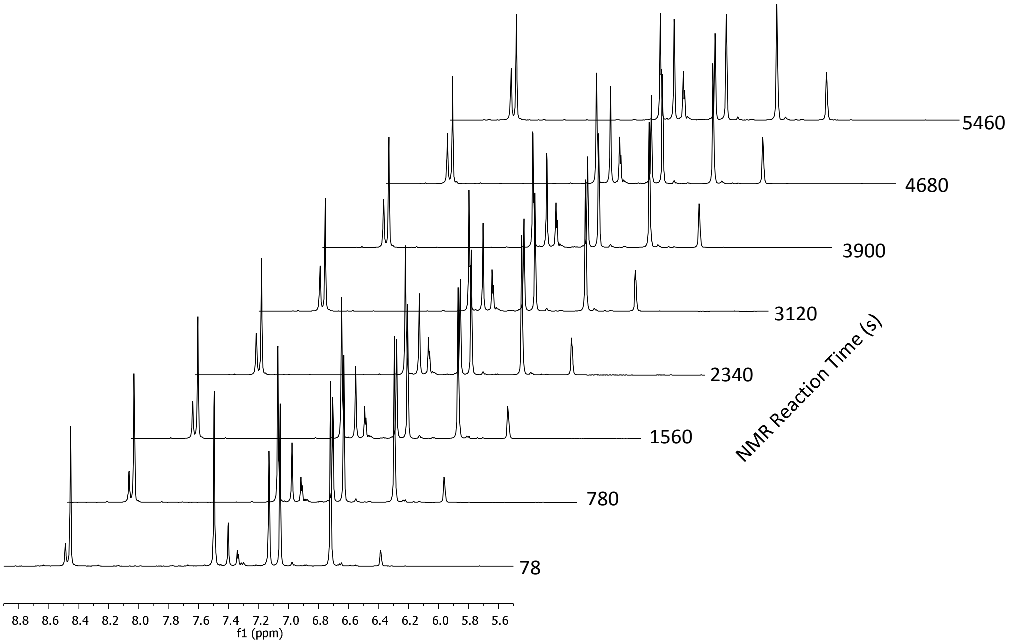
T (ºC)	pD 7.20 – 7.00			pD 6.30 – 6.10			pD 5.60 – 5.40		
	A	B	C	A	B	C	A	B	C
18*	50.3	37.7	12.0	47.9	36.9	15.2	44.0	40.9	15.1
25	39.3	46.0	14.7	37.8	46.2	16.0	44.9	42.8	12.3
30	40.4	45.6	14.0	36.8	45.3	17.9	42.1	43.7	14.2
37	40.6	45.7	13.7	44.4	42.0	13.6	44.5	43.3	12.2

Representative NMR time course profile of the reaction of [Co(acacen)(Im)$_2$]Br (1eq) with 4MeIm (2 eq) [pH 7.80-7.50, 18 °C]: **(A)** alkyl NMR region, and **(B)** aromatic NMR region.

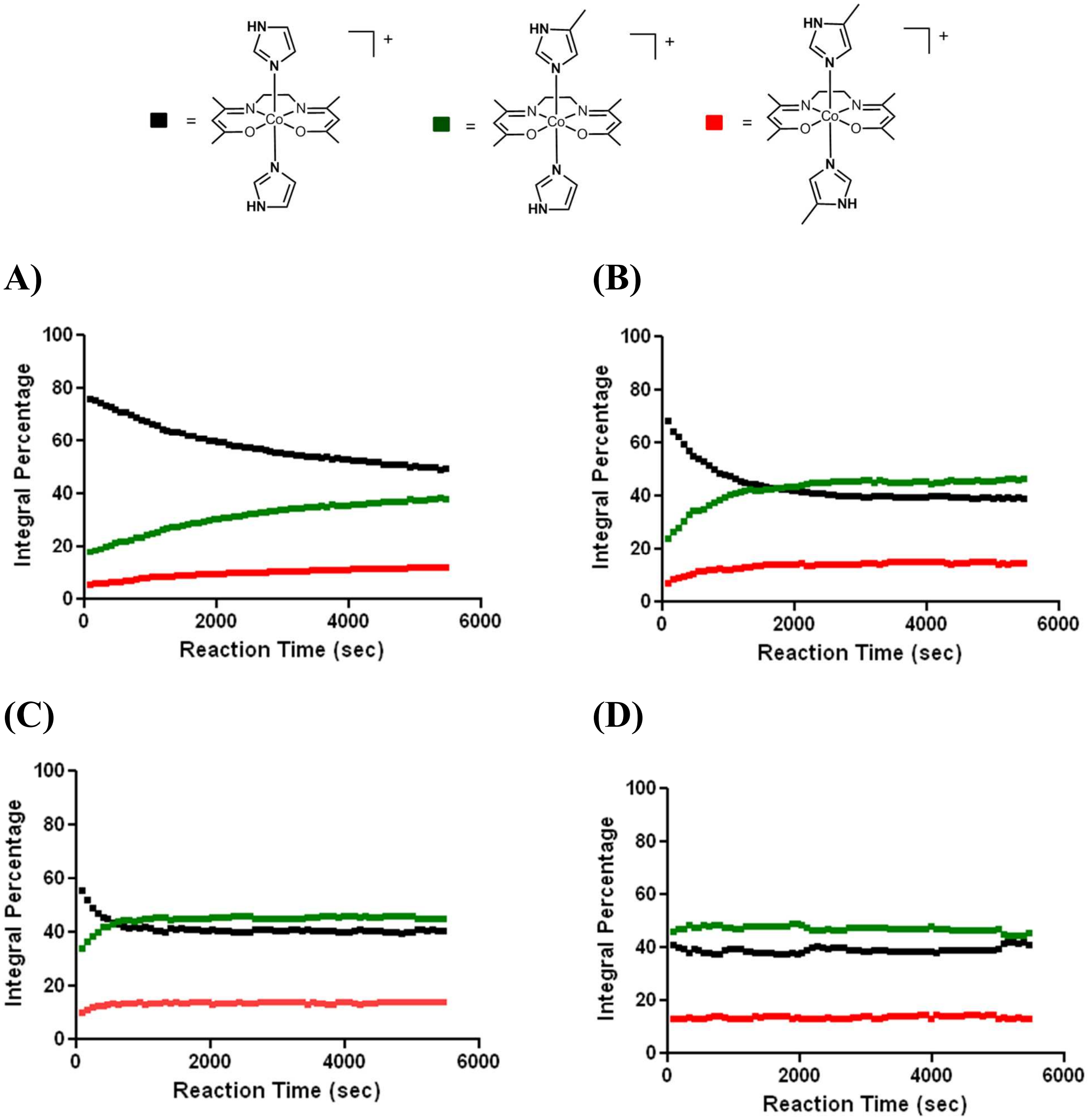
(A)



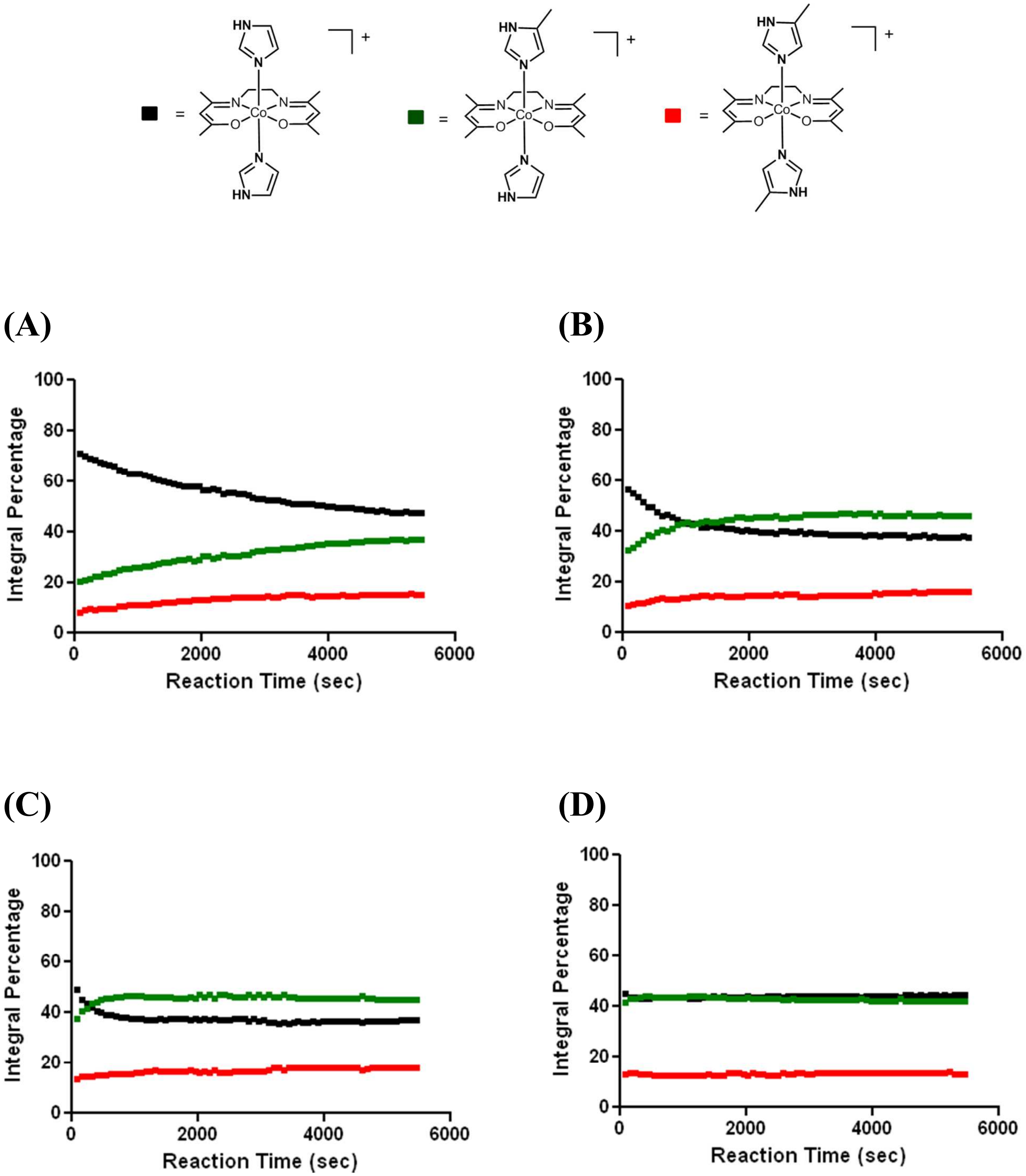
(B)


5460
4680
3900
3120
2340
1560
780
78
NMR Reaction Time (s)
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
f1 (ppm)

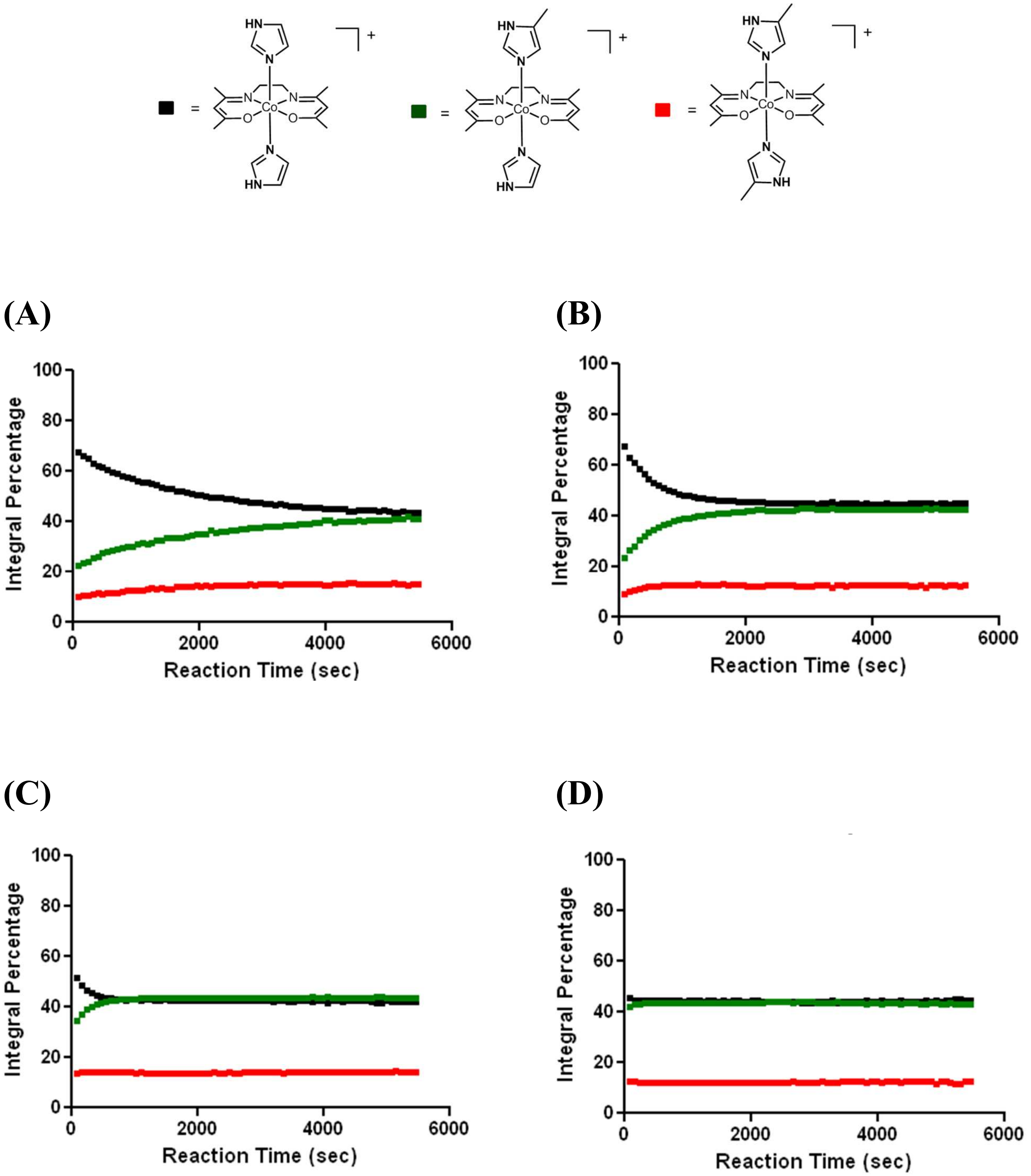
Temperature-dependent time course plots of the reaction of [Co(acacen)(Im)$_2$]Br (1eq) with 4MeIm (2eq) at pD 7.20 – 7.00. The integral percentage of each Co(III) Schiff base in solution is shown with respect to an internal standard as a function of reaction time. **(A)** 18 °C, **(B)** 25 °C, **(C)** 30 °C, and **(D)** 37 °C.



Temperature-dependent time course plots of the reaction of [Co(acacen)(Im)$_2$]Br (1eq) with 4MeIm (2eq) at pD 6.30 – 6.10. The integral percentage of each Co(III) Schiff base in solution is shown with respect to an internal standard as a function of reaction time. **(A)** 18 °C, **(B)** 25 °C, **(C)** 30 °C, and **(D)** 37 °C.



Temperature-dependent time course plots of the reaction of [Co(acacen)(Im)$_2$]Br (1eq) with 4MeIm (2eq) at pD 5.60 – 5.40. The integral percentage of each Co(III) Schiff base in solution is shown with respect to an internal standard as a function of reaction time. **(A)** 18 °C, **(B)** 25 °C, **(C)** 30 °C, and **(D)** 37 °C.


HN
N
N
Co
O
+
=
NH
(A)
(B)
(C)
(D)
Integral Percentage
Reaction Time (sec)
0
20
40
60
80
100
2000
4000
6000

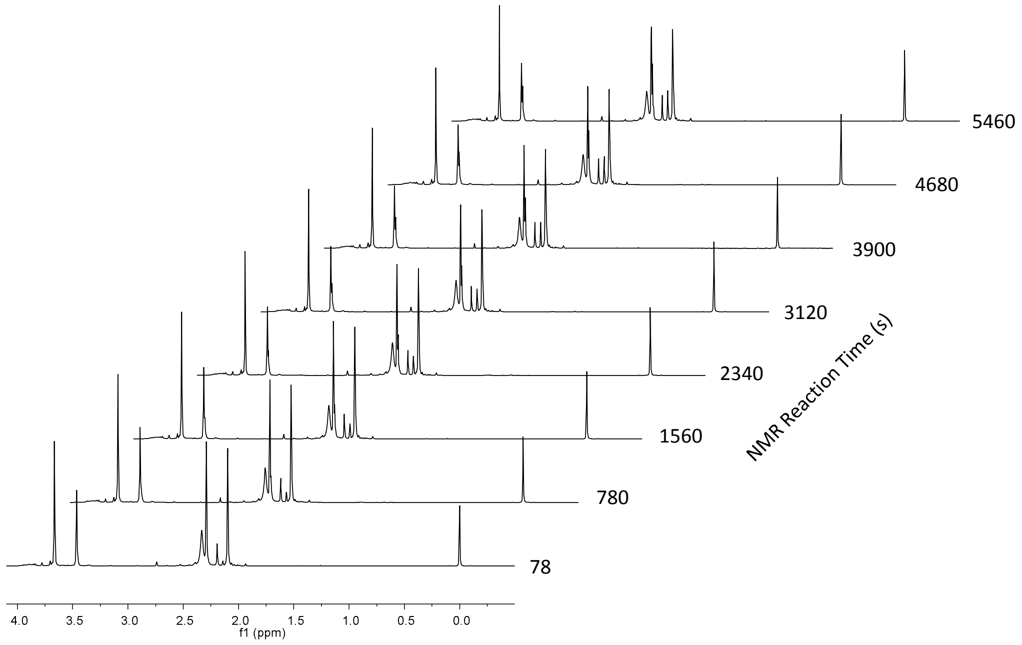
PART 3b. pH/Temperature dependence of 4MeIm Exchange, [Co(acacen)(NMeIm)$_2$]Br

Equilibrium integral percentages of the resultant species in the reaction of **4** (1 eq) with 4MeIm (2 eq) as a function of temperature and pD. (**A**) **4**, (**B**) [Co(acacen)(NMeIm)(4MeIm)]$^+$, (**C**) **1**. * Species are not in equilibrium

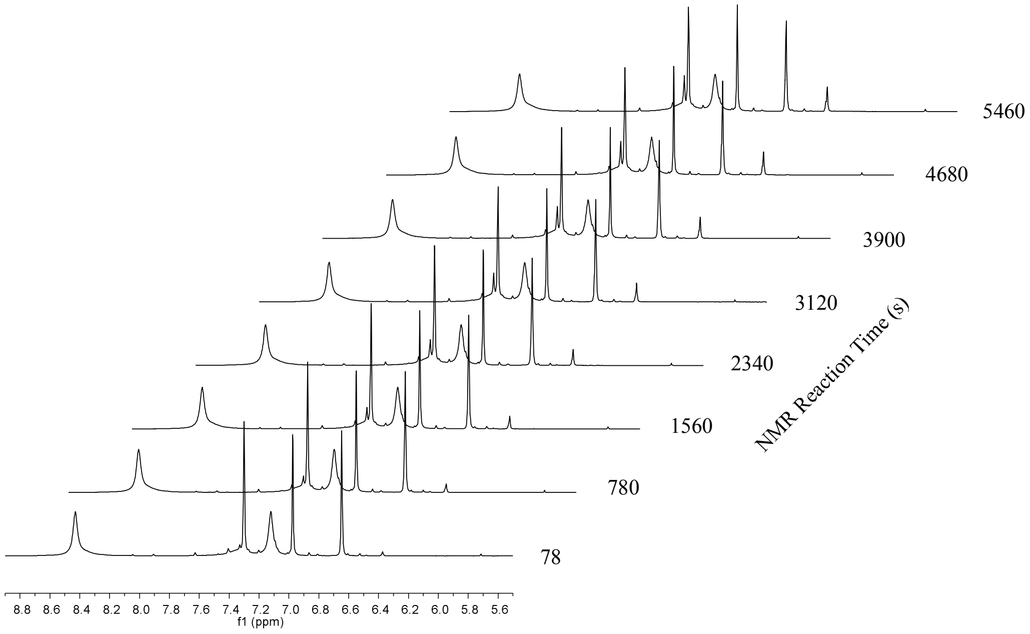
T (ºC)	pD 7.20 – 7.00			pD 6.30 – 6.10			pD 5.60 – 5.40		
	A	B	C	A	B	C	A	B	C
18*	59.5	31.6	8.9	55.7	34.6	9.7	52.5	37.2	10.3
25	42.4	43.3	14.3	47.4	41.7	10.9	47.6	41.7	10.8
30	41.0	44.5	14.6	48.9	39.8	11.2	46.6	41.2	12.2
37	42.6	43.8	13.5	46.3	42.6	11.0	44.1	40.7	15.3

Representative NMR time course profile of the reaction of [Co(acacen)(NMeIm)$_2$]Br (1eq) with 4MeIm (2 eq) [pH 7.80-7.50, 18 °C]: **(A)** alkyl NMR region, and **(B)** aromatic NMR region.

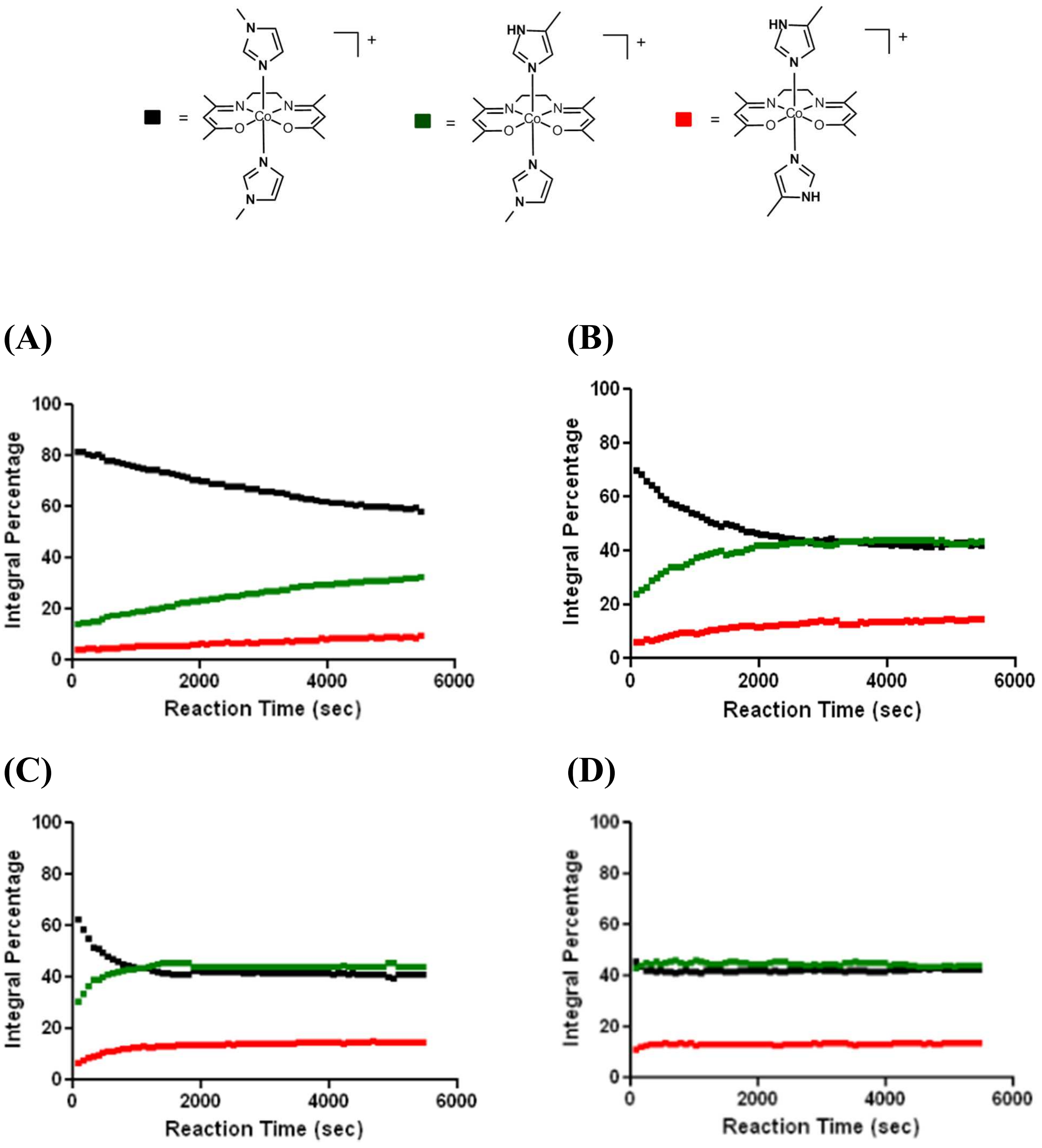
(A)



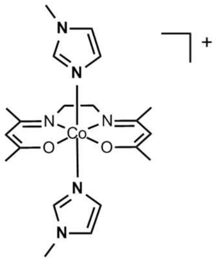
(B)

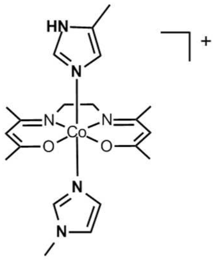

5460
4680
3900
3120
2340
1560
780
78
NMR Reaction Time (s)
8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6
f1 (ppm)

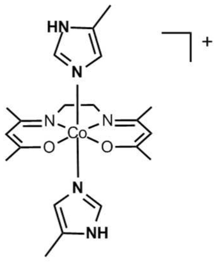
Temperature-dependent time course plots of the reaction of [Co(acacen)(NMeIm)$_2$]Br (1eq) with 4MeIm (2eq) at pD 7.20 – 7.00. The integral percentage of each Co(III) Schiff base in solution is shown with respect to an internal standard as a function of reaction time. **(A)** 18 °C, **(B)** 25 °C, **(C)** 30 °C, and **(D)** 37 °C.

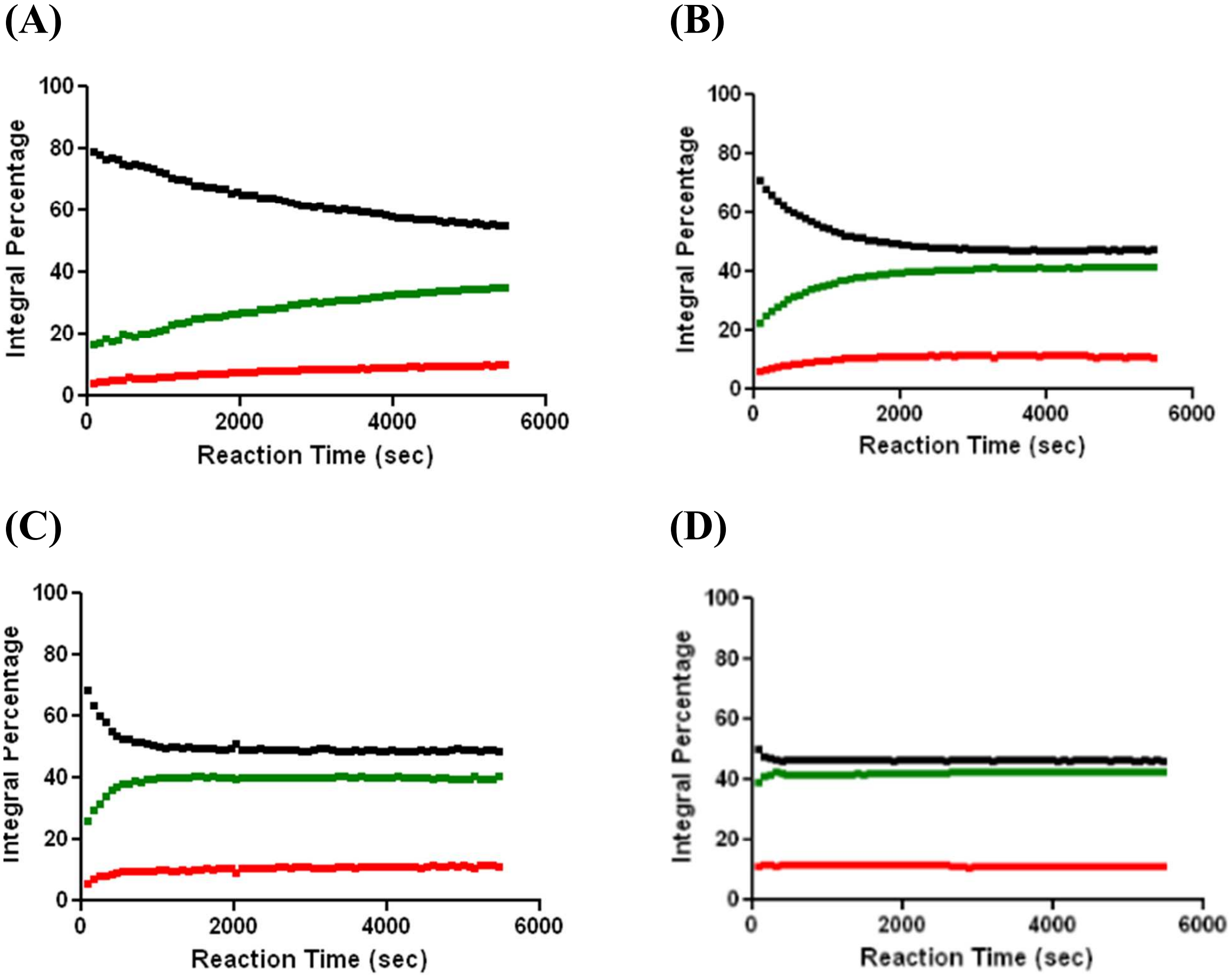


Temperature-dependent time course plots of the reaction of [Co(acacen)(NMeIm)$_2$]Br (1eq) with 4MeIm (2eq) at pD 6.30 – 6.10. The integral percentage of each Co(III) Schiff base in solution is shown with respect to an internal standard as a function of reaction time. (A) 18 °C, (B) 25 °C, (C) 30 °C, and (D) 37 °C.

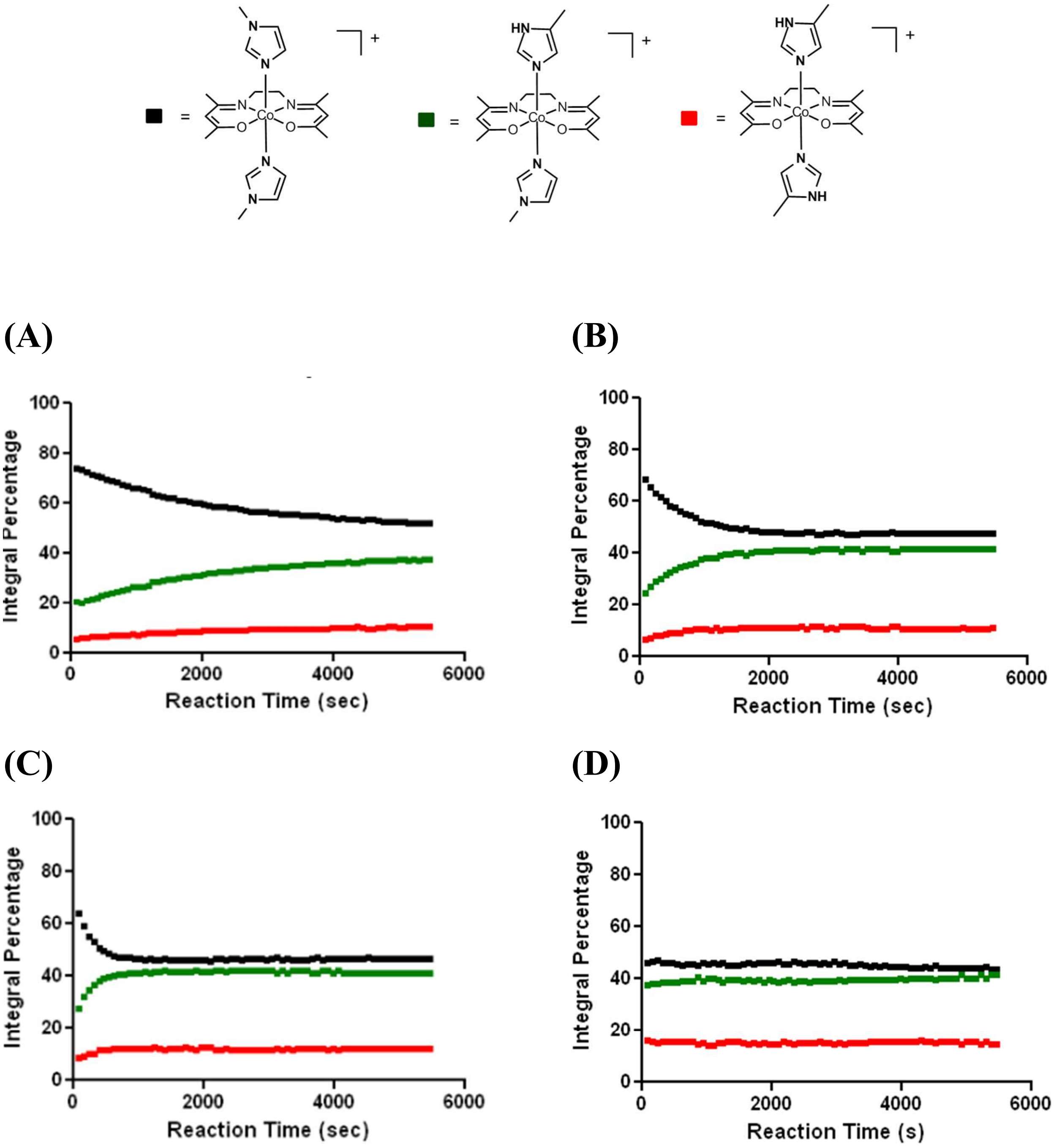
⬛ =


🟩 =


🟥 =




Temperature-dependent time course plots of the reaction of $[Co(acacen)(NMeIm)_2]Br$ (1eq) with 4MeIm (2eq) at pD 5.60 – 5.40. The integral percentage of each Co(III) Schiff base in solution is shown with respect to an internal standard as a function of reaction time. **(A)** 18 °C, **(B)** 25 °C, **(C)** 30 °C, and **(D)** 37 °C.



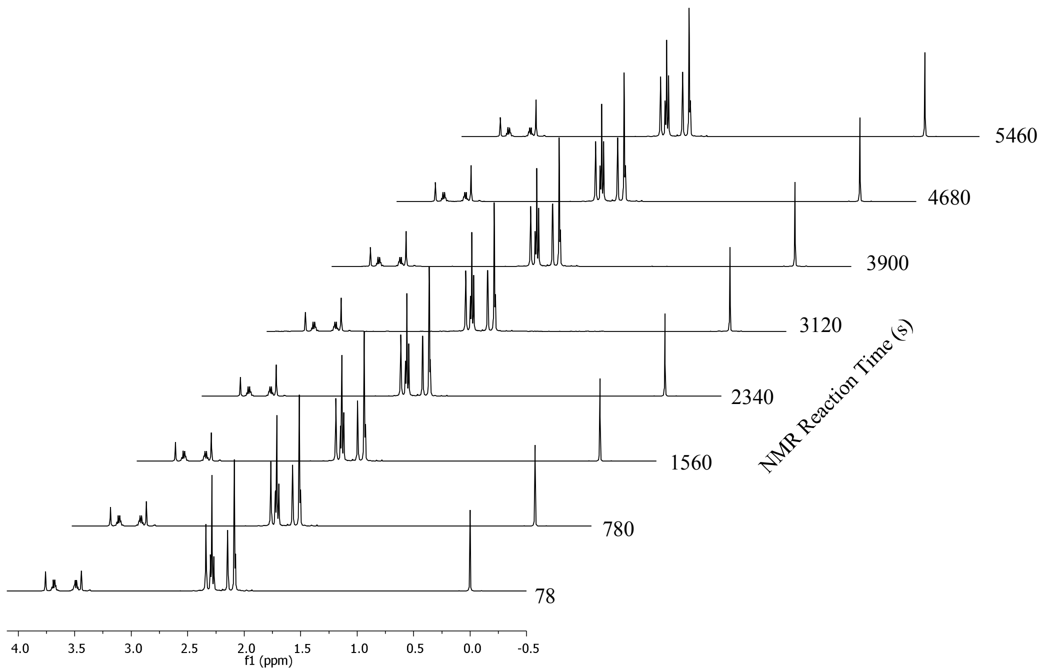
PART 3c. pH/Temperature dependence of 4MeIm Exchange, [Co(acacen)(Py)$_2$]Br

Equilibrium integral percentages of the resultant species in the reaction of **6** (1 eq) with 4MeIm (2 eq) as a function of temperature and pD. (**A**) **6**, (**B**) [Co(acacen)(Py)(4MeIm)]$^+$, (**C**) **1**.

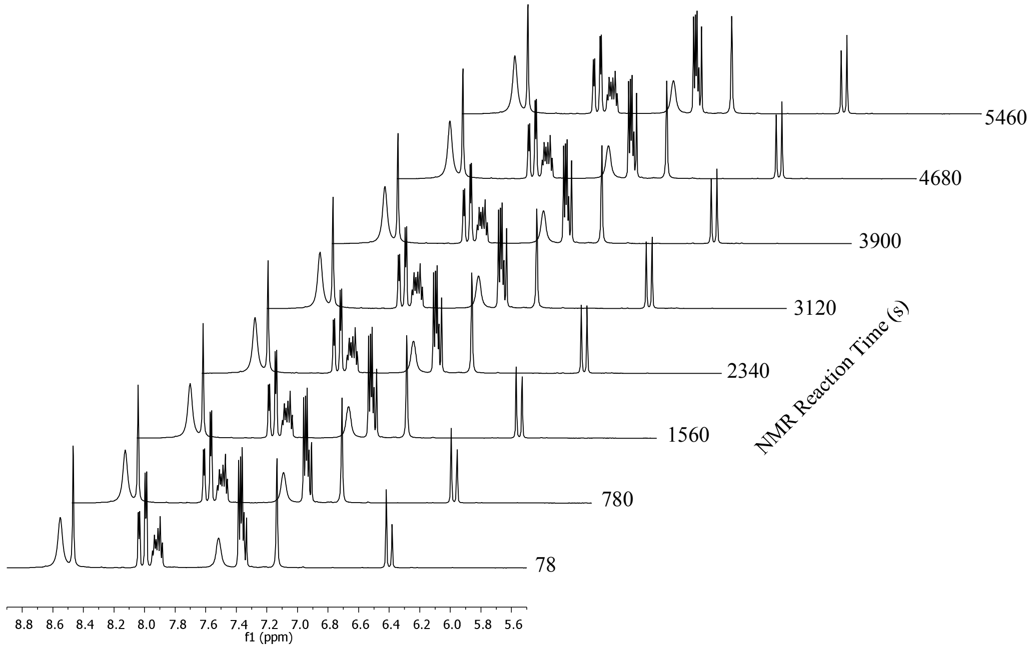
T (ºC)	**pD 7.20 – 7.00**			**pD 6.30 – 6.10**			**pD 5.60 – 5.40**		
	A	B	C	A	B	C	A	B	C
18	16.8	51.3	31.9	42.3	47.5	10.2	40.3	50.9	8.8
25	17.6	51.3	31.1	39.4	48.5	12.1	37.9	50.0	12.1
30	15.8	50.1	34.0	38.2	48.1	13.7	31.9	52.4	15.7
37	13.5	48.7	37.7	31.5	53.0	15.7	31.8	53.2	15.1

Representative NMR time course profile of the reaction of [Co(acacen)(Py)$_2$]Br (1eq) with 4MeIm (2 eq) [pH 7.80-7.50, 18 °C]: **(A)** alkyl NMR region, and **(B)** aromatic NMR region.

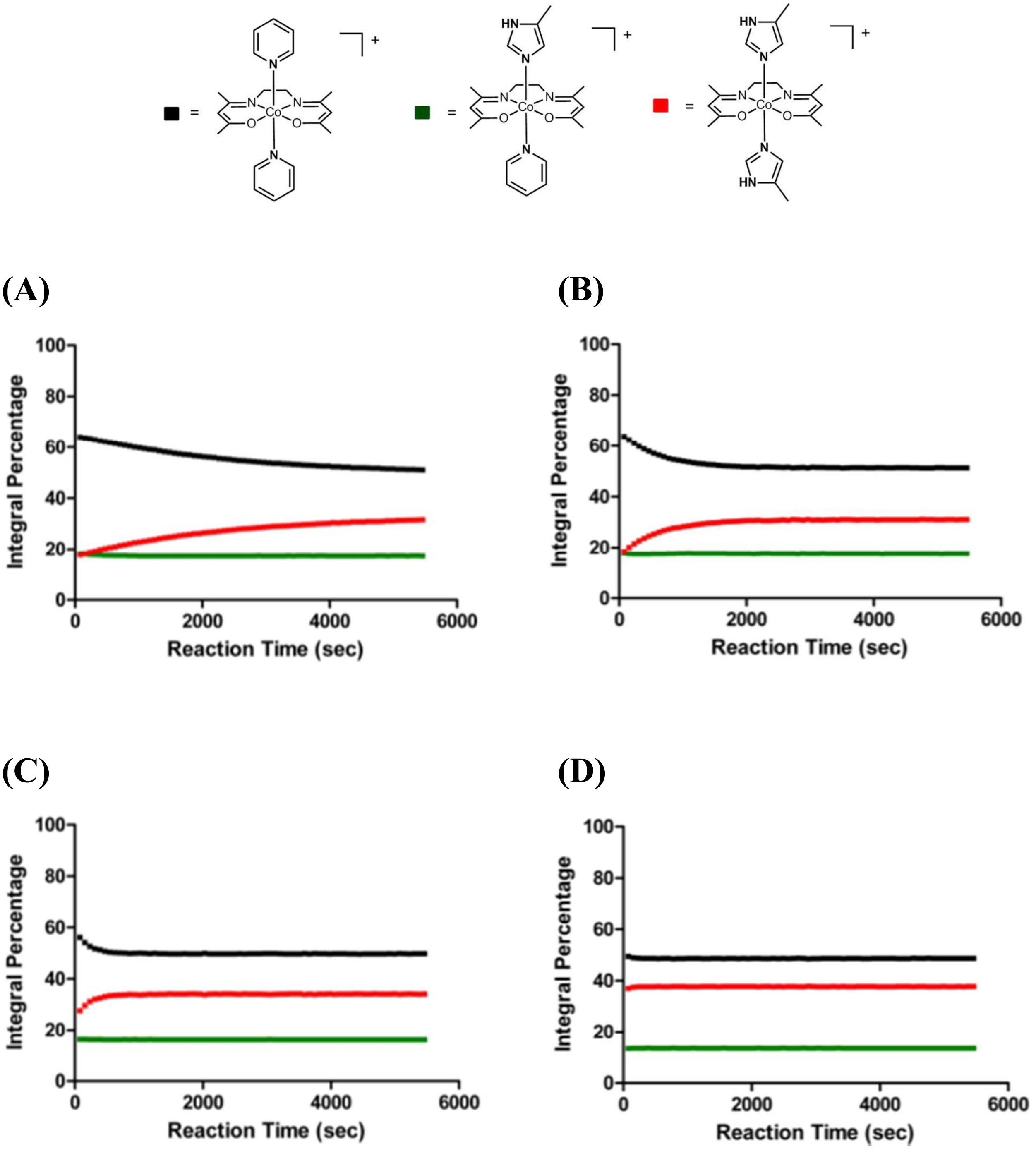
(A)



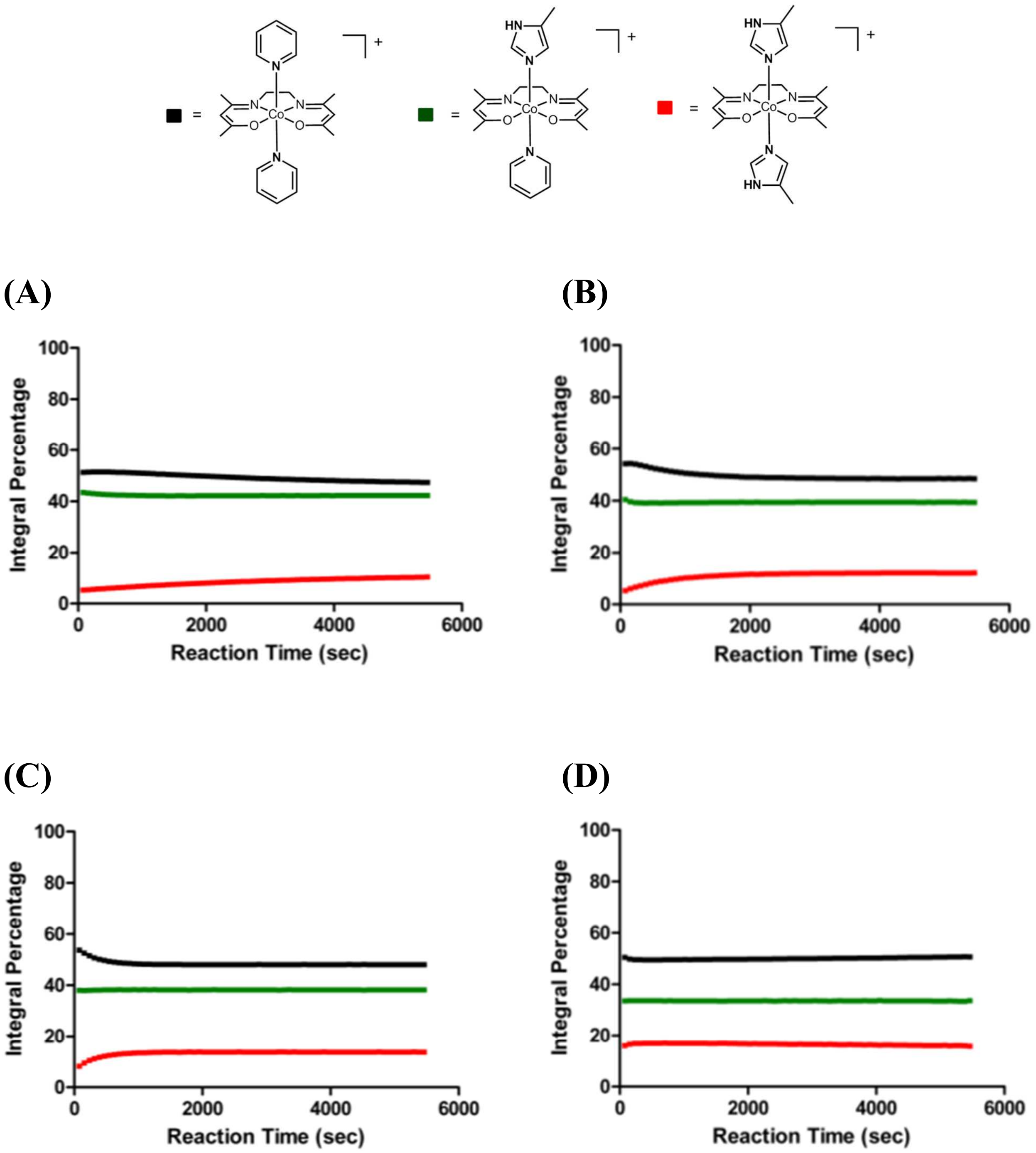
(B)


5460
4680
3900
3120
2340
1560
780
78
NMR Reaction Time (s)
8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6
f1 (ppm)

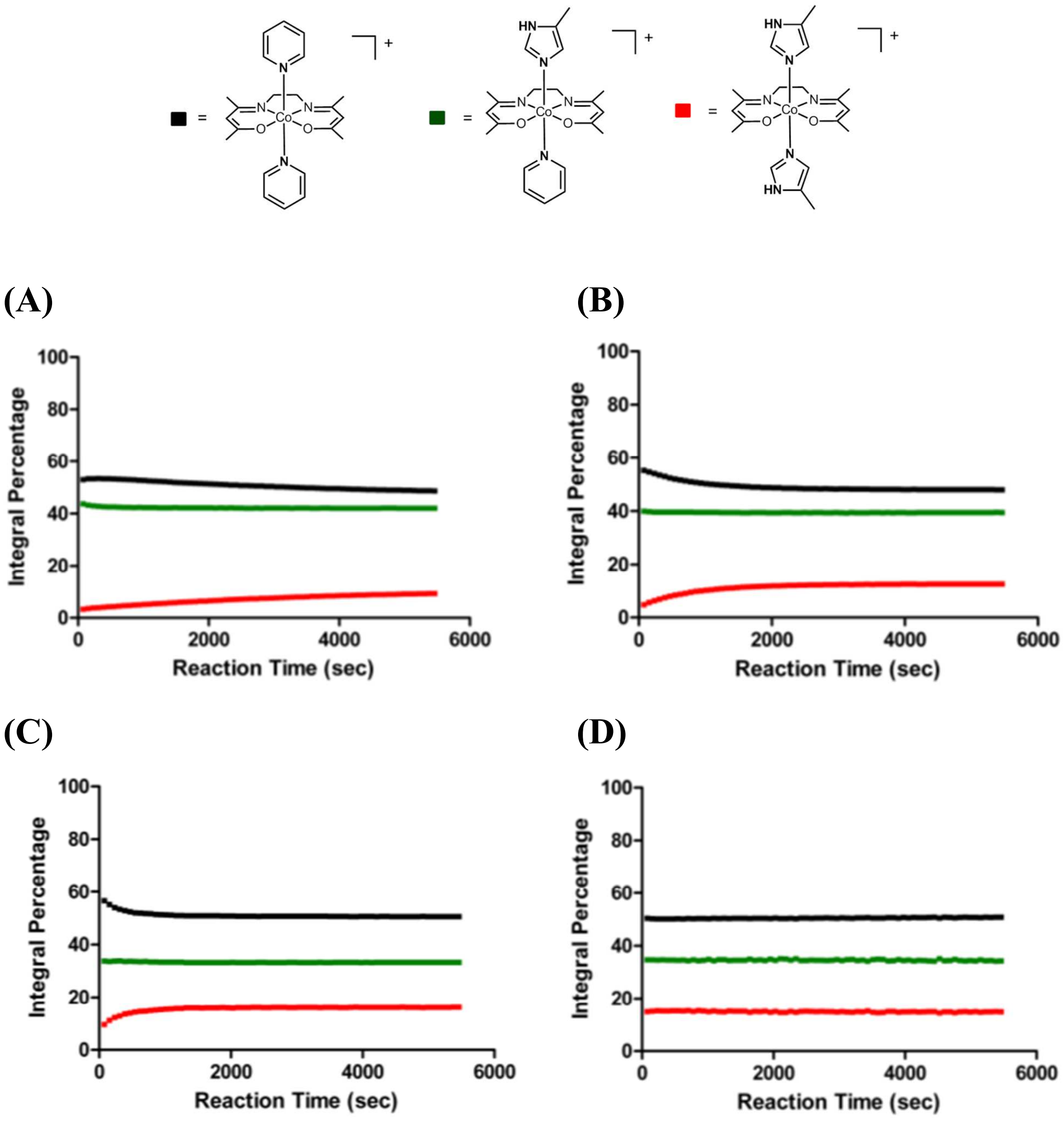
Temperature-dependent time course plots of the reaction of [Co(acacen)(Py)$_2$]Br (1eq) with 4MeIm (2eq) at pD 7.20 – 7.00. The integral percentage of each Co(III) Schiff base in solution is shown with respect to an internal standard as a function of reaction time. **(A)** 18 °C, **(B)** 25 °C, **(C)** 30 °C, and **(D)** 37 °C.



Temperature-dependent time course plots of the reaction of [Co(acacen)(Py)$_2$]Br (1eq) with 4MeIm (2eq) at pD 6.30 – 6.10. The integral percentage of each Co(III) Schiff base in solution is shown with respect to an internal standard as a function of reaction time. **(A)** 18 °C, **(B)** 25 °C, **(C)** 30 °C, and **(D)** 37 °C.



Temperature-dependent time course plots of the reaction of [Co(acacen)(Py)$_2$]Br (1eq) with 4MeIm (2eq) at pD 5.60 – 5.40. The integral percentage of each Co(III) Schiff base in solution is shown with respect to an internal standard as a function of reaction time. **(A)** 18 °C, **(B)** 25 °C, **(C)** 30 °C, and **(D)** 37 °C.



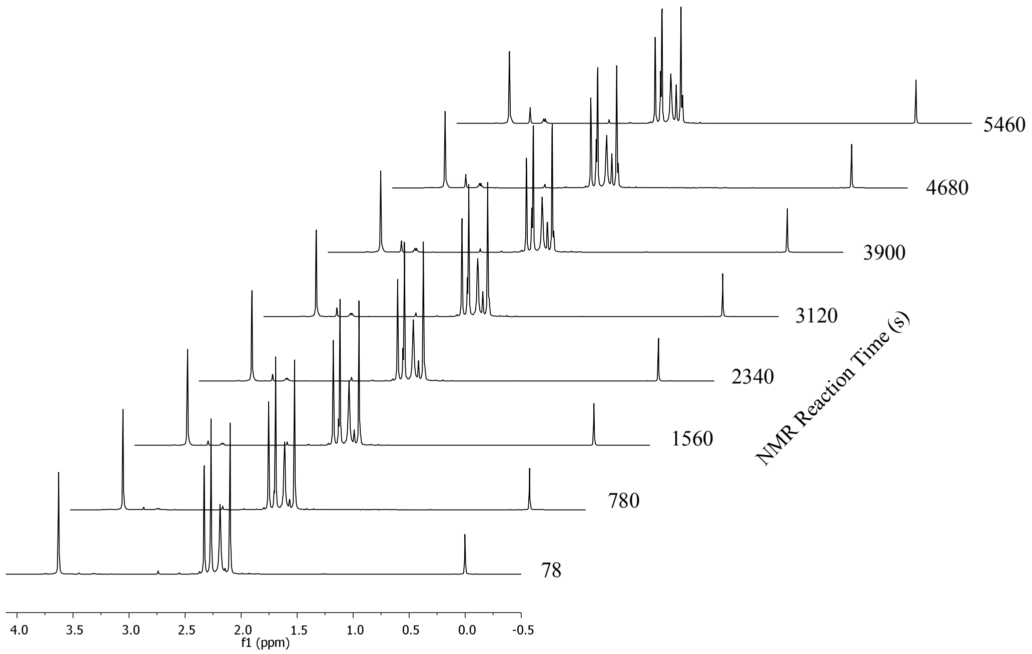
PART 3d. pH/Temperature dependence of 4MeIm Exchange, [Co(acacen)(NH_3)$_2$]Cl

Equilibrium integral percentages of the resultant species in the reaction of **2** (1 eq) with 4MeIm (2 eq) as a function of temperature and pD. (**A**) **2**, (**B**) [Co(acacen)(NH_3)(4MeIm)]$^+$, (**C**) [Co(acacen)(H_2O)(4MeIm)]$^+$, (**D**) **1**. * Species are not in equilibrium.

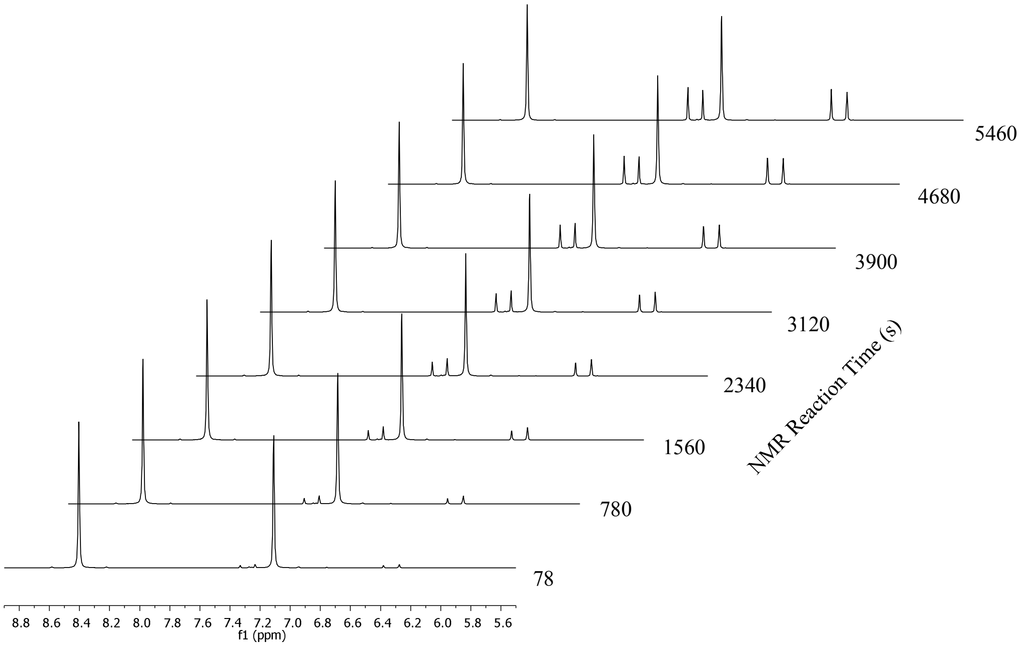
T (ºC)	**pD 7.20 – 7.00**				**pD 6.30 – 6.10**				**pD 5.60 – 5.40**			
	A	B	C	D	A	B	C	D	A	B	C	D
18*	13.2	24.9	0.0	61.9	63.6	4.3	1.5	30.5	54.5	2.8	7.6	35.2
25*	15.7	20.4	0.0	63.9	17.7	5.8	5.7	70.8	15.8	2.1	20.1	62.1
30	1.4	19.3	0.0	79.3	1.0	11.4	10.0	77.6	1.7	3.2	13.9	81.2
37	0.2	20.5	0.0	79.3	0.6	20.8	15.4	63.2	2.1	14.5	32.7	50.8

Representative NMR time course profile of the reaction of [Co(acacen)(NH_3)$_2$]Cl (1eq) with 4MeIm (2 eq) [pH 7.80-7.50, 18 °C]: **(A)** alkyl NMR region, and **(B)** aromatic NMR region.

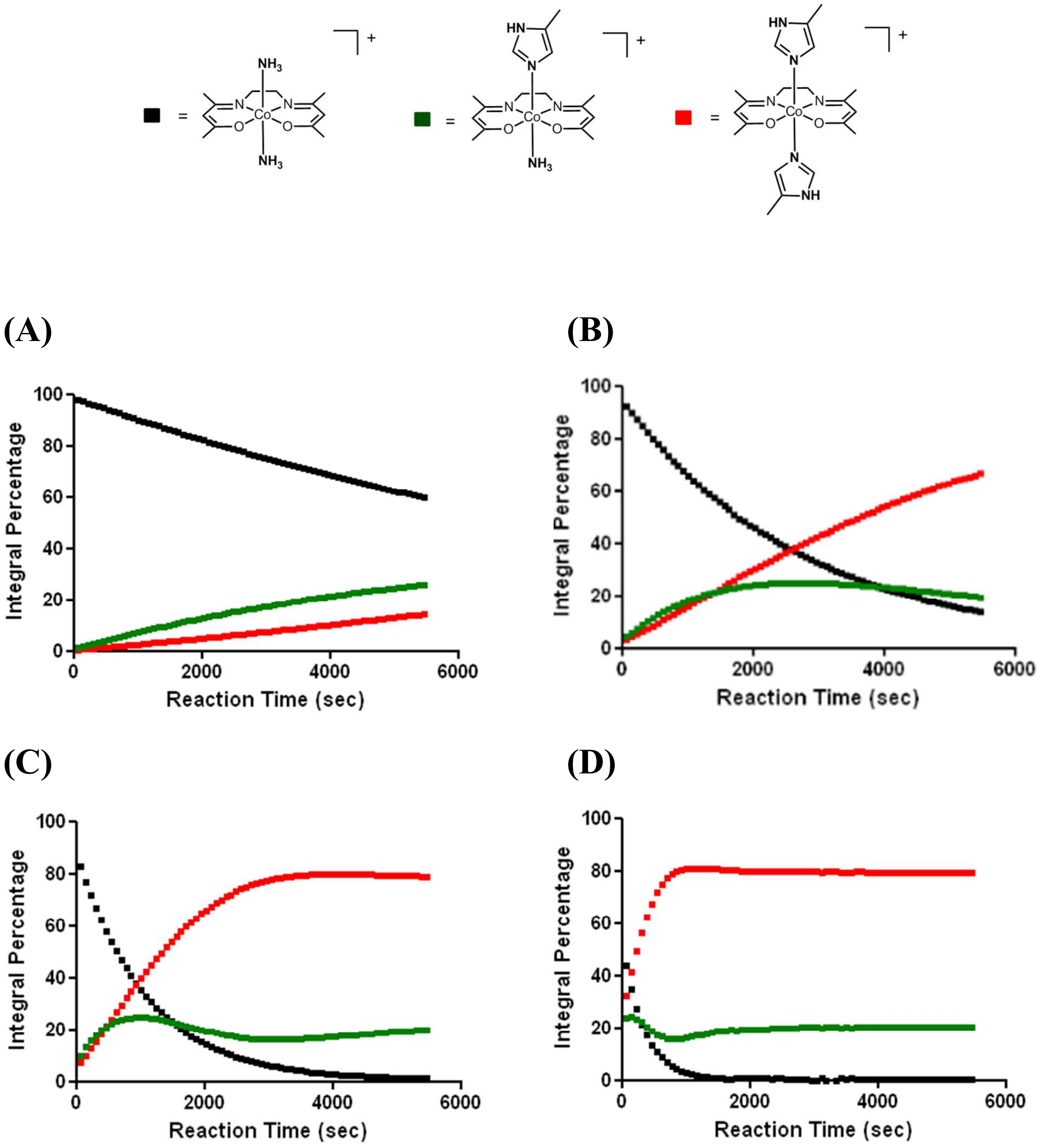
(A)



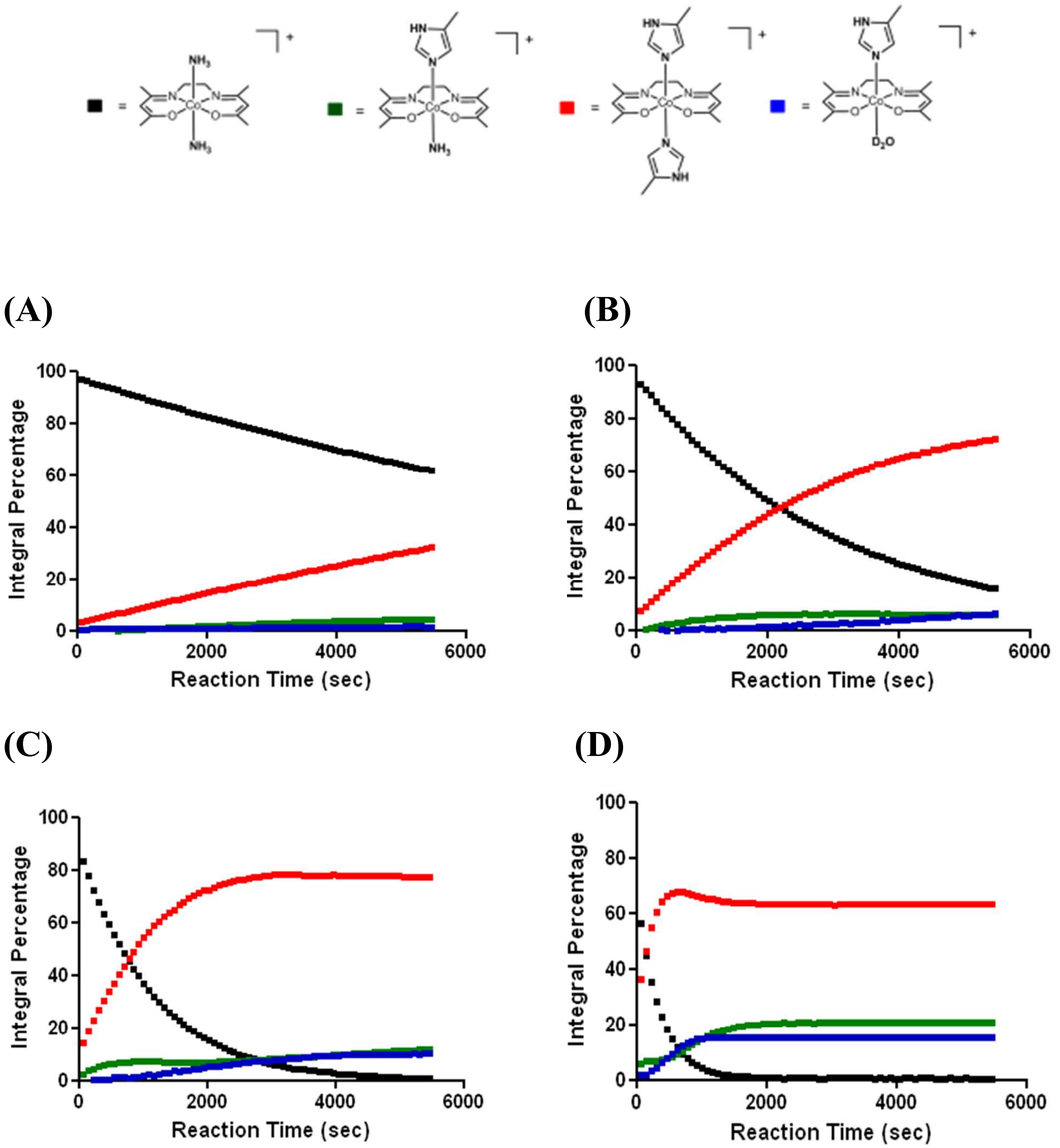
(B)


5460
4680
3900
3120
2340
1560
780
78
NMR Reaction Time (s)
8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6
f1 (ppm)

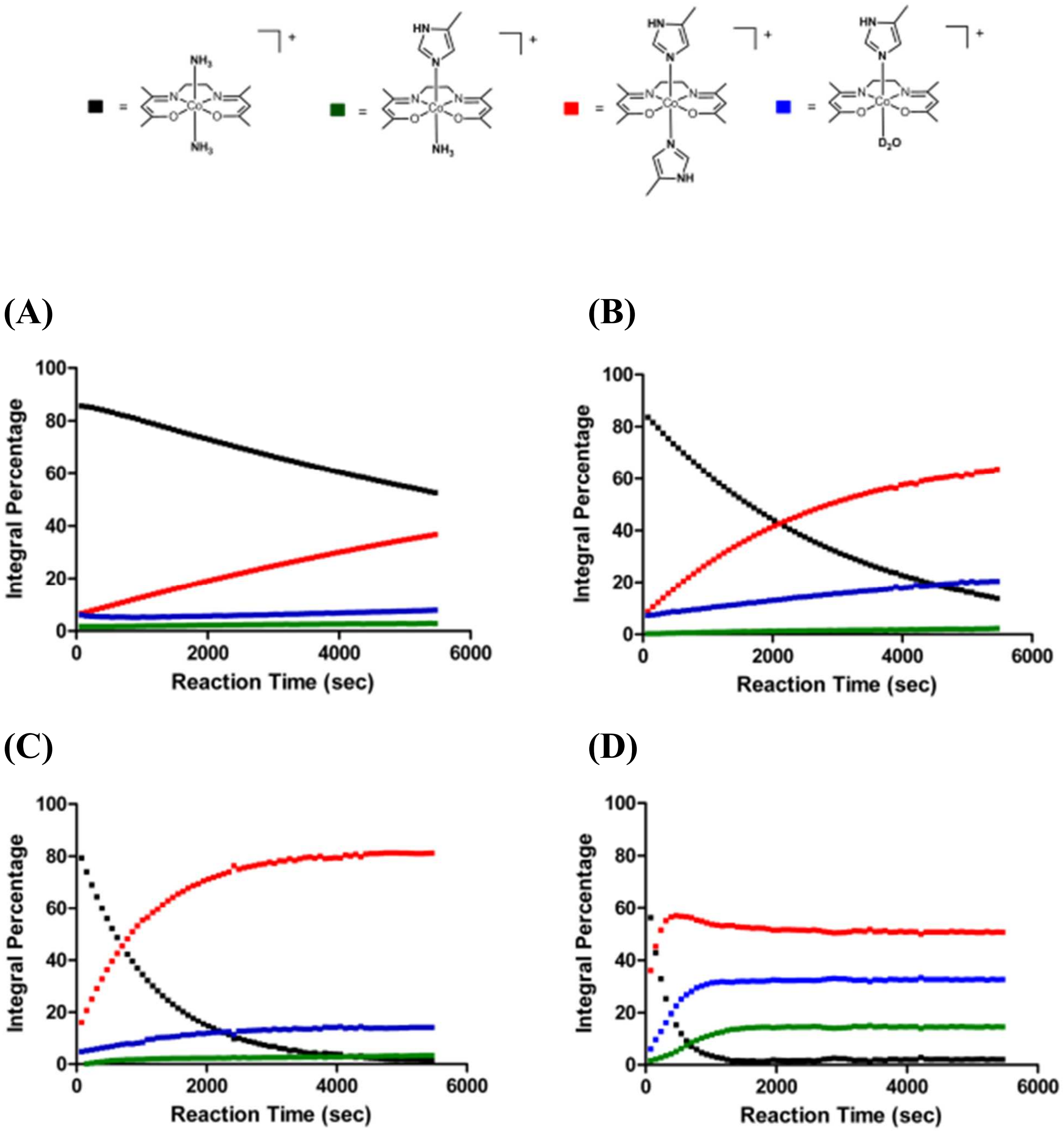
Temperature-dependent time course plots of the reaction of [Co(acacen)(NH$_3$)$_2$]Cl (1eq) with 4MeIm (2eq) at pD 7.80 – 7.50. The integral percentage of each Co(III) Schiff base in solution is shown with respect to an internal standard as a function of reaction time. **(A)** 18 °C, **(B)** 25 °C, **(C)** 30 °C, and **(D)** 37 °C.



Temperature-dependent time course plots of the reaction of [Co(acacen)$(NH_3)_2$]Cl (1eq) with 4MeIm (2eq) at pD 6.30 – 6.10. The integral percentage of each Co(III) Schiff base in solution is shown with respect to an internal standard as a function of reaction time. **(A)** 18 °C, **(B)** 25 °C, **(C)** 30 °C, and **(D)** 37 °C.



Temperature-dependent time course plots of the reaction of $[Co(acacen)(NH_3)_2]Cl$ (1eq) with 4MeIm (2eq) at pD 5.60 – 5.40. The integral percentage of each Co(III) Schiff base in solution is shown with respect to an internal standard as a function of reaction time. **(A)** 18 °C, **(B)** 25 °C, **(C)** 30 °C, and **(D)** 37 °C.



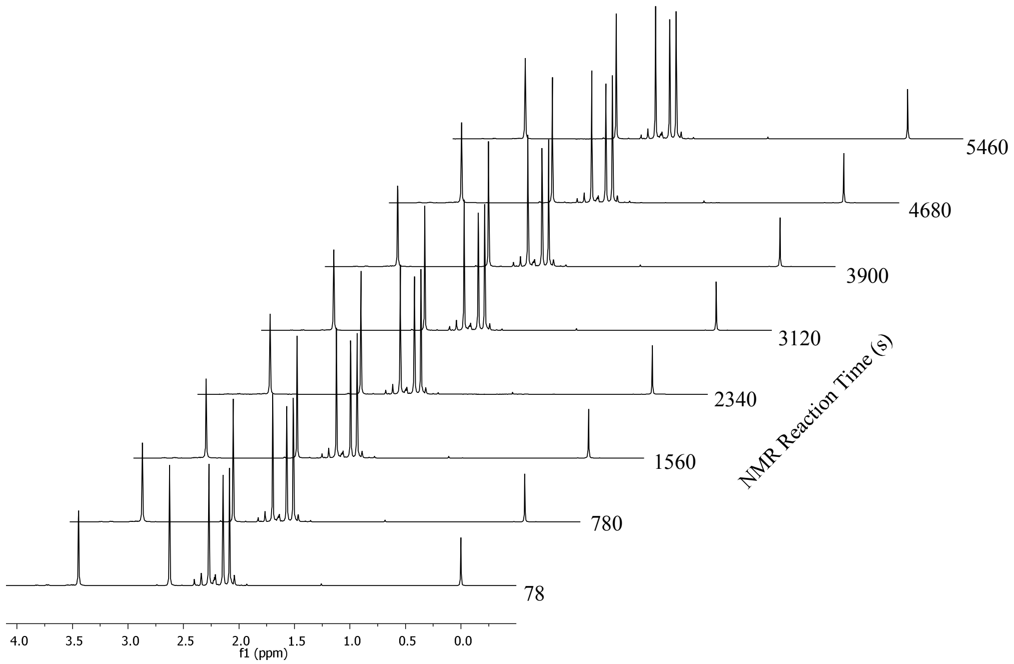
PART 3e. pH/Temperature dependence of 4MeIm Exchange, [Co(acacen)(2MeIm)$_2$]Br

Equilibrium integral percentages of the resultant species in the reaction of **3** (1 eq) with 4MeIm (2 eq) as a function of temperature and pD. (**A**) [Co(acacen)(H$_2$O)(4MeIm)]$^+$, (**B**) [Co(acacen)(2MeIm)(4MeIm)]$^+$, (**C**) **1**.

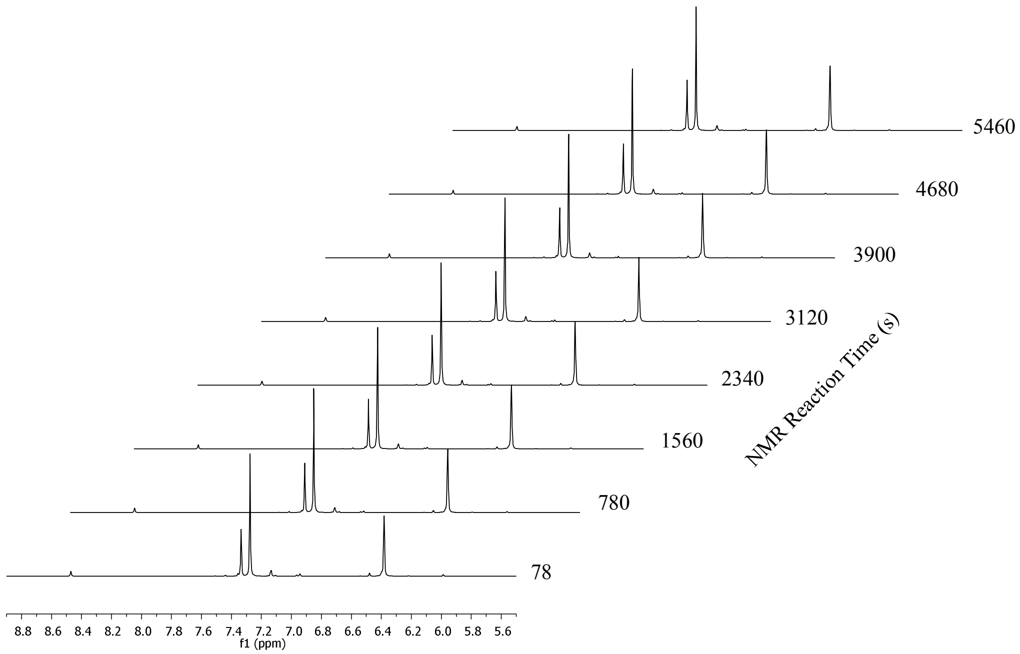
T (ºC)	pD 7.20 – 7.00			pD 6.30 – 6.10			pD 5.60 – 5.40		
	A	B	C	A	B	C	A	B	C
18	1.3	2.9	95.8	10.9	1.5	87.6	29.8	1.1	69.1
25	0.0	0.8	99.2	14.0	3.7	82.3	25.9	2.5	71.6
30	7.2	2.1	90.8	11.5	3.6	84.9	21.6	2.6	75.8
37	7.6	1.5	90.9	12.8	6.4	80.8	24.1	3.9	72.0

Representative NMR time course profile of the reaction of [Co(acacen)(2MeIm)$_2$]Br (1eq) with 4MeIm (2 eq) [pH 7.80-7.50, 18 °C]: **(A)** alkyl NMR region, and **(B)** aromatic NMR region.

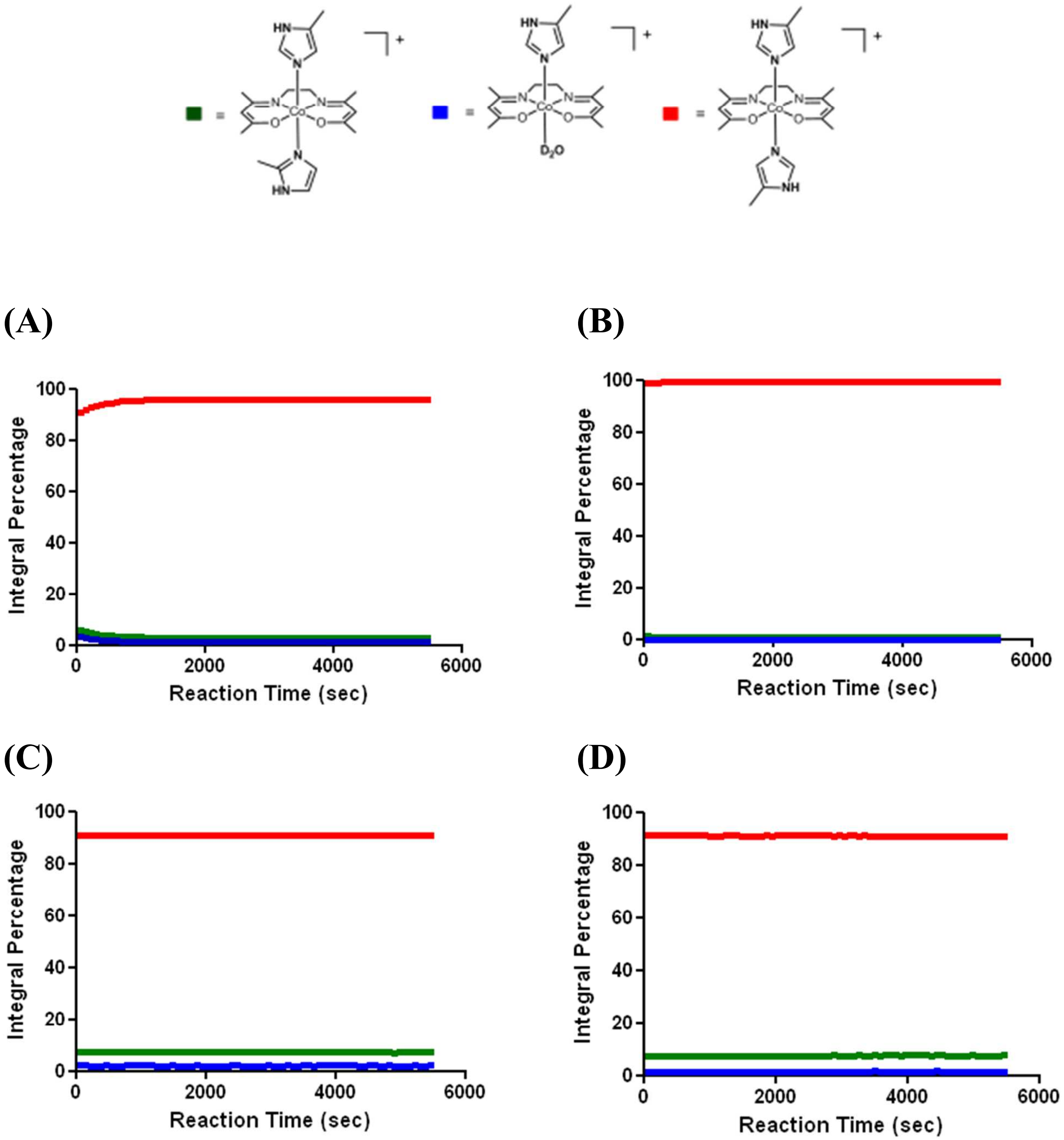
(A)



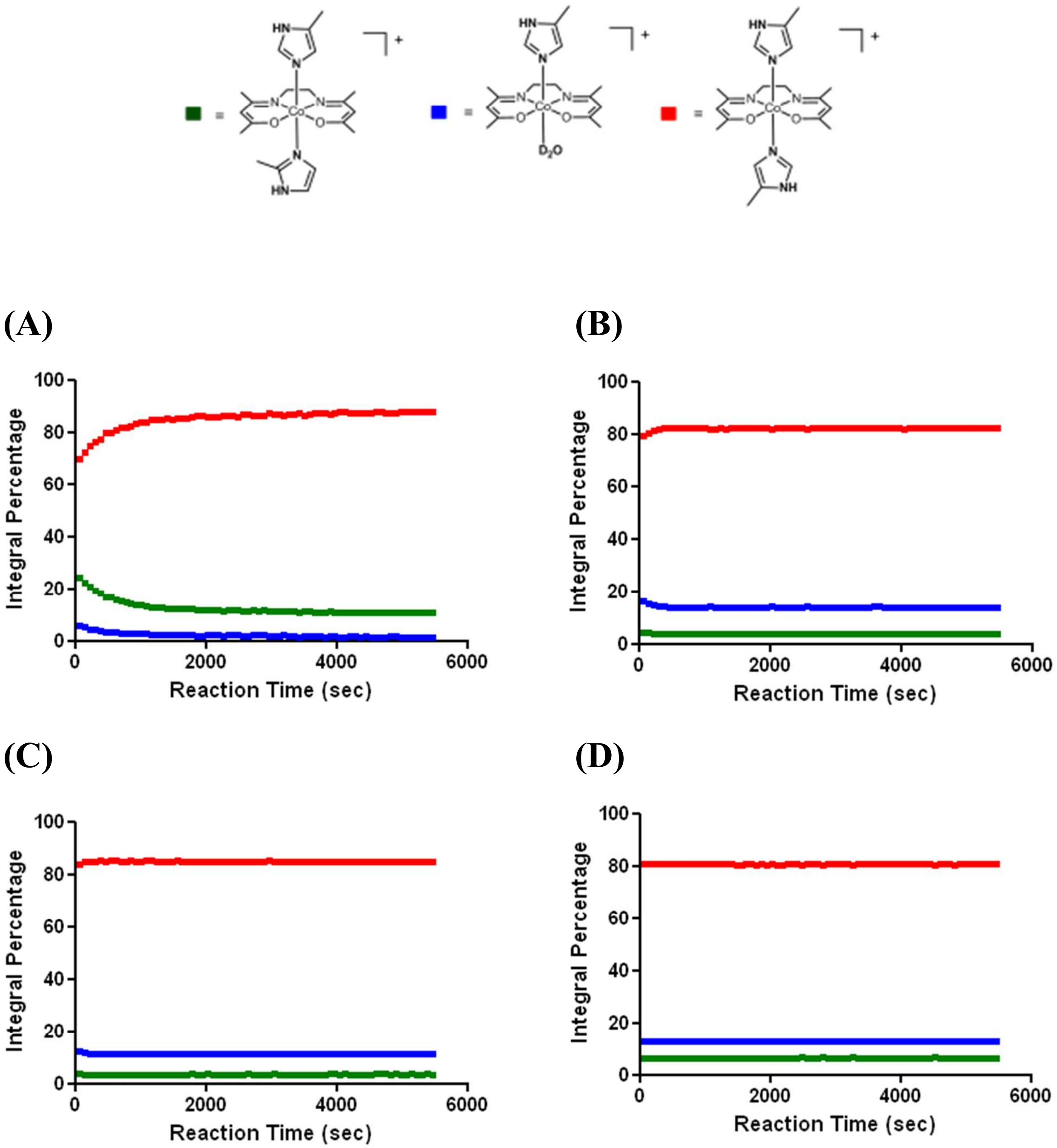
(B)


5460
4680
3900
3120
2340
1560
780
78
NMR Reaction Time (s)
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
f1 (ppm)

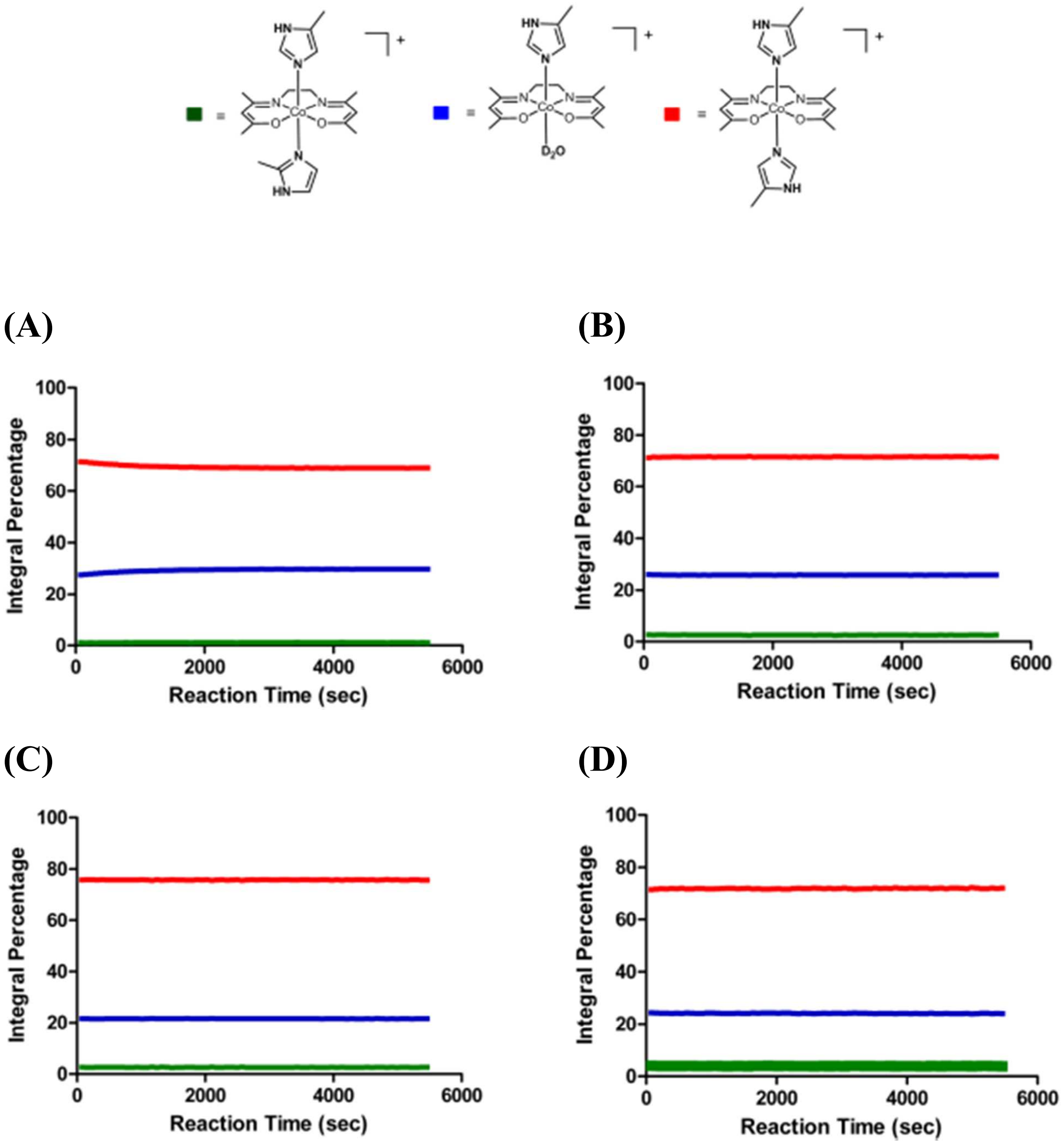
Temperature-dependent time course plots of the reaction of [Co(acacen)(2MeIm)$_2$]Br (1eq) with 4MeIm (2eq) at pD 7.20 – 7.00. The integral percentage of each Co(III) Schiff base in solution is shown with respect to an internal standard as a function of reaction time. **(A)** 18 °C, **(B)** 25 °C, **(C)** 30 °C, and **(D)** 37 °C.



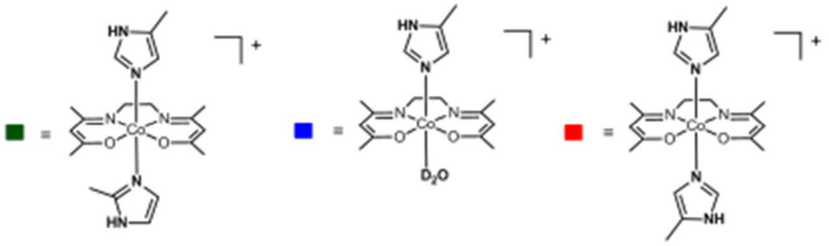
Temperature-dependent time course plots of the reaction of $[Co(acacen)(2MeIm)_2]Br$ (1eq) with 4MeIm (2eq) at pD 6.30 – 6.10. The integral percentage of each Co(III) Schiff base in solution is shown with respect to an internal standard as a function of reaction time. **(A)** 18 °C, **(B)** 25 °C, **(C)** 30 °C, and **(D)** 37 °C.



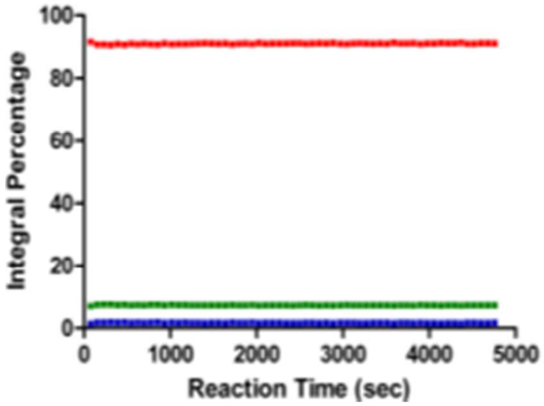
Temperature-dependent time course plots of the reaction of [Co(acacen)(2MeIm)$_2$]Br (1eq) with 4MeIm (2eq) at pD 5.60 – 5.40. The integral percentage of each Co(III) Schiff base in solution is shown with respect to an internal standard as a function of reaction time. **(A)** 18 °C, **(B)** 25 °C, **(C)** 30 °C, and **(D)** 37 °C.



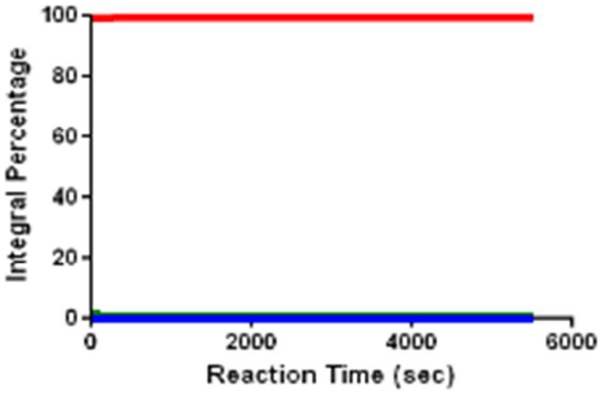
PART 4A. Reversibility of 4MeIm Exchange, [Co(acacen)(4MeIm)$_2$]Br and 2MeIm



(A) Reaction of [Co(acacen)(2MeIm)$_2$]Br (1eq) with 4MeIm (2eq) at pD 7.20 – 7.00. The integral percentage of each Co(III) Schiff base in solution is shown with respect to an internal standard as a function of reaction time.

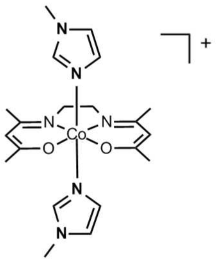


(B) Reaction of [Co(acacen)(4MeIm)$_2$]Br (1eq) with 2MeIm (2eq) at pD 7.20 – 7.00. The integral percentage of each Co(III) Schiff base in solution is shown with respect to an internal standard as a function of reaction time.

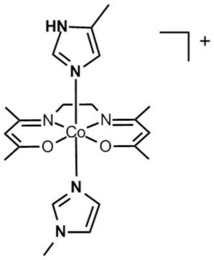


PART 4B. Reversibility of 4MeIm Exchange, [Co(acacen)(4MeIm)$_2$]Br and NMeIm

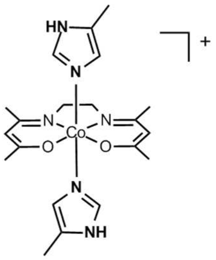
■ =



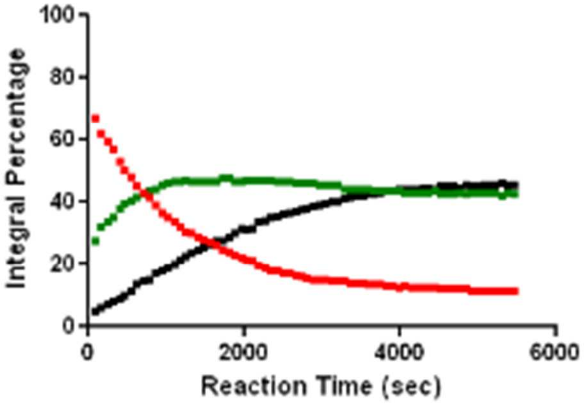
🟩 =



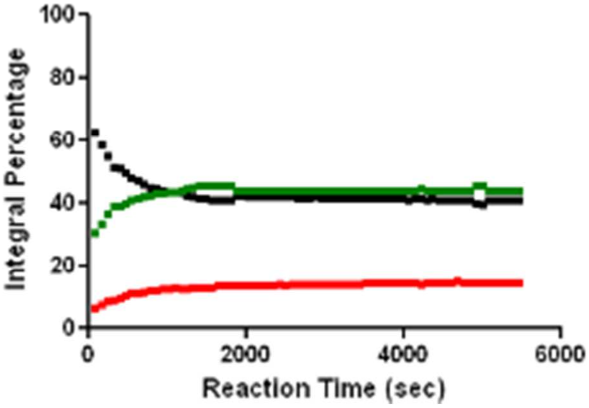
🟥 =



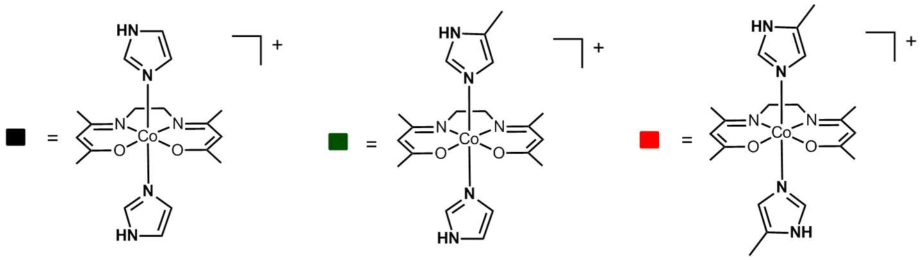
(A) Reaction of [Co(acacen)(NMeIm)$_2$]Br (1eq) with 4MeIm (2eq) at pD 7.20 – 7.00. The integral percentage of each Co(III) Schiff base in solution is shown with respect to an internal standard as a function of reaction time.



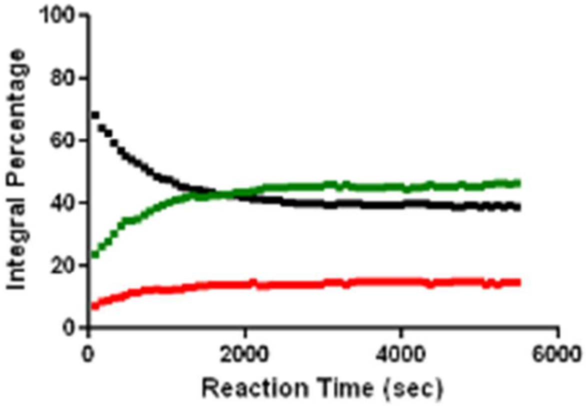
(B) Reaction of [Co(acacen)(4MeIm)$_2$]Br (1eq) with NMeIm (2eq) at pD 7.20 – 7.00. The integral percentage of each Co(III) Schiff base in solution is shown with respect to an internal standard as a function of reaction time.



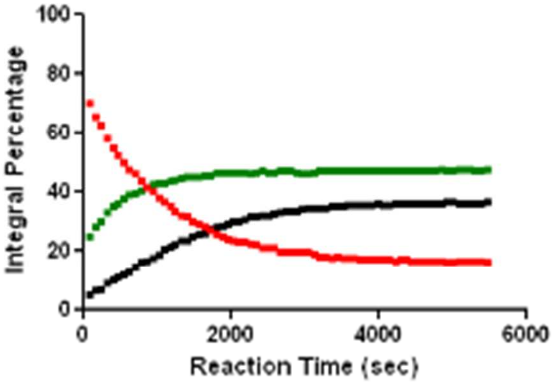
PART 4C. Reversibility of 4MeIm Exchange, [Co(acacen)(4MeIm)$_2$]Br and Im



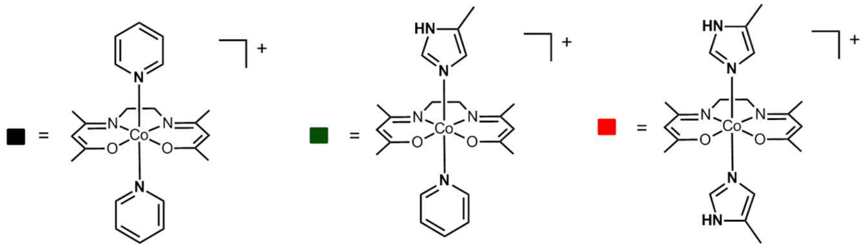
(A) Reaction of [Co(acacen)(Im)$_2$]Br (1eq) with 4MeIm (2eq) at pD 7.20 – 7.00. The integral percentage of each Co(III) Schiff base in solution is shown with respect to an internal standard as a function of reaction time.



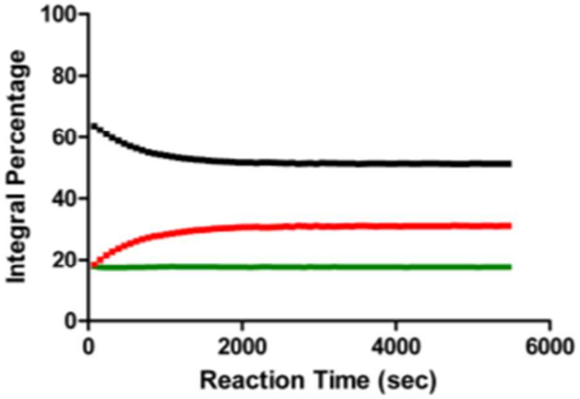
(B) Reaction of [Co(acacen)(4MeIm)$_2$]Br (1eq) with Im (2eq) at pD 7.20 – 7.00. The integral percentage of each Co(III) Schiff base in solution is shown with respect to an internal standard as a function of reaction time.



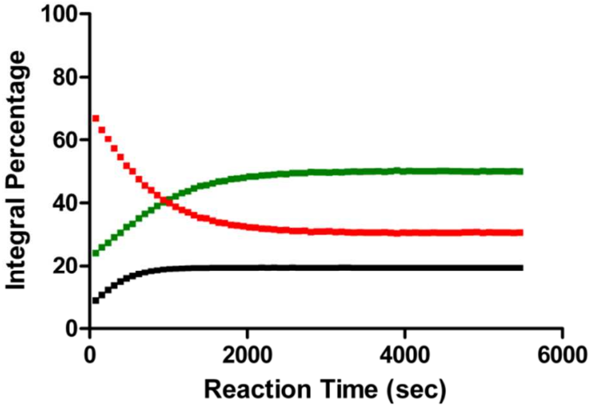
PART 4D. Reversibility of 4MeIm Exchange, [Co(acacen)(4MeIm)$_2$]Br and Py



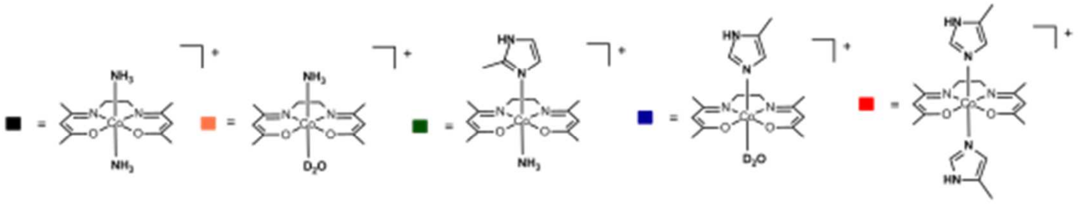
(A) Reaction of [Co(acacen)(Py)$_2$]Br (1eq) with 4MeIm (2eq) at pD 7.20 – 7.00. The integral percentage of each Co(III) Schiff base in solution is shown with respect to an internal standard as a function of reaction time.



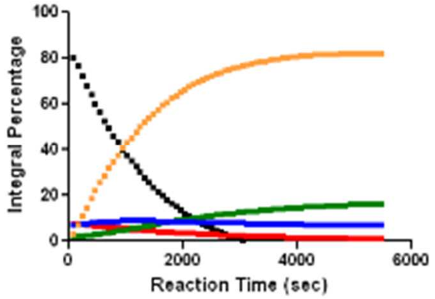
(B) Reaction of [Co(acacen)(4MeIm)$_2$]Br (1eq) with Py (2eq) at pD 7.20 – 7.00. The integral percentage of each Co(III) Schiff base in solution is shown with respect to an internal standard as a function of reaction time.



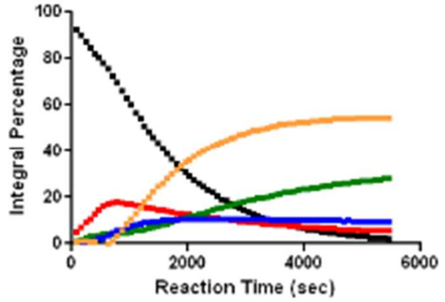
PART 5A. Chemical Equilibrium - Variation in 4MeIm Equivalents, [Co(acacen)$(NH_3)_2$]Cl



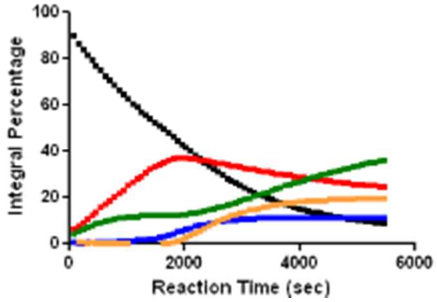
0.25 eq 4MeIm



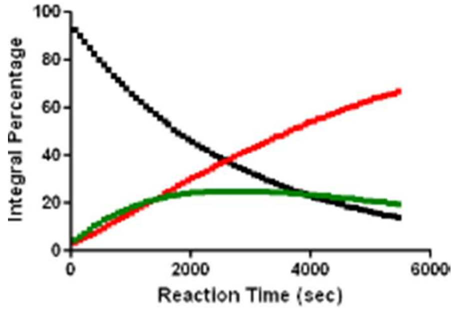
0.5 eq 4MeIm



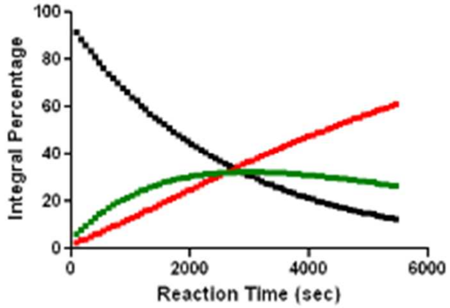
1 eq 4MeIm



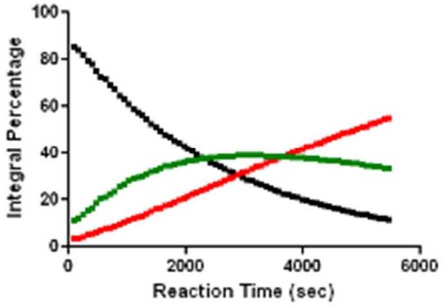
2 eq 4MeIm



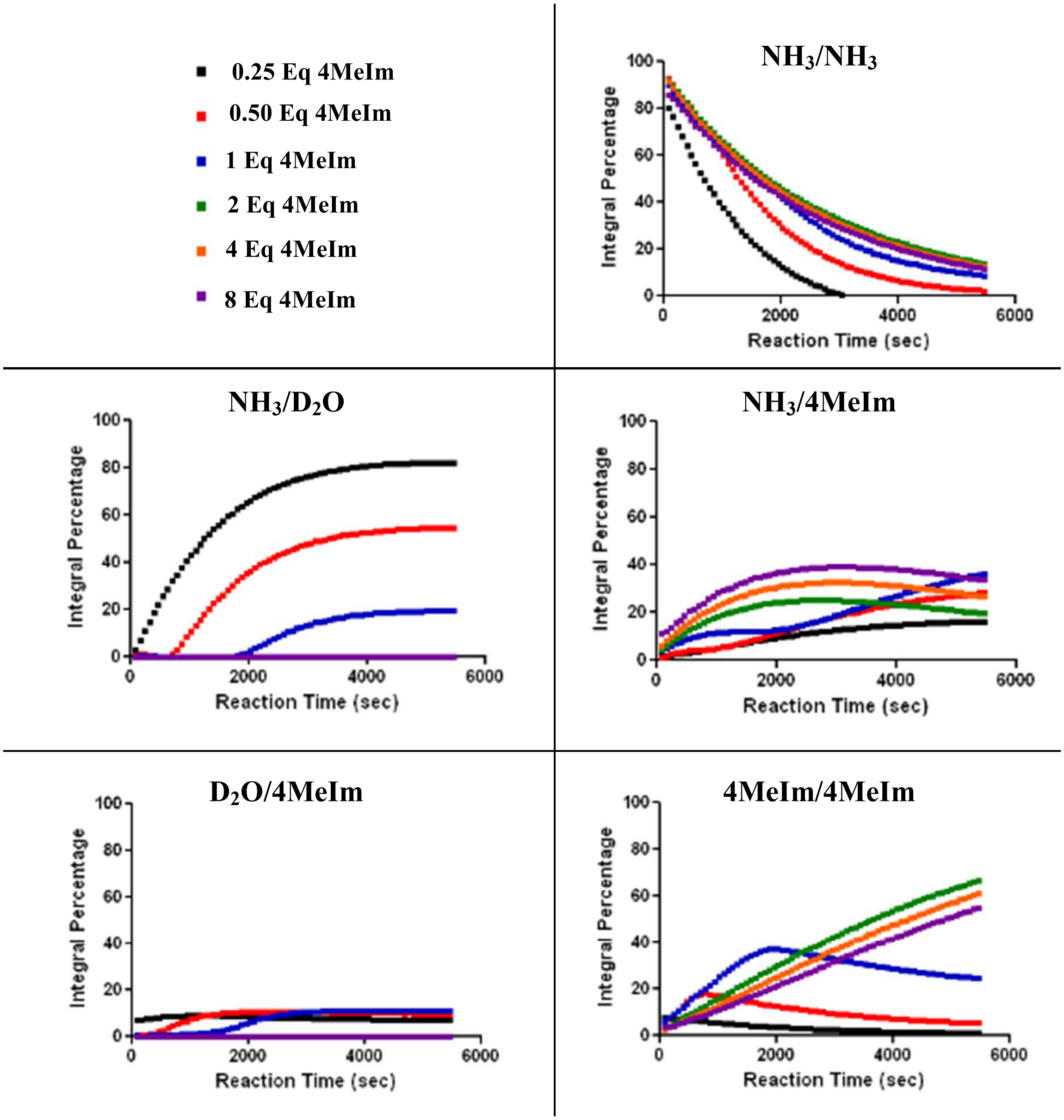
4 eq 4MeIm



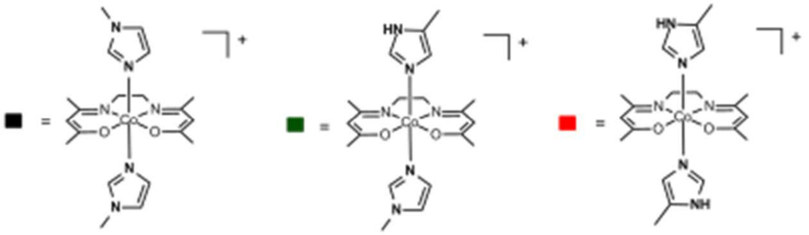
8 eq 4MeIm



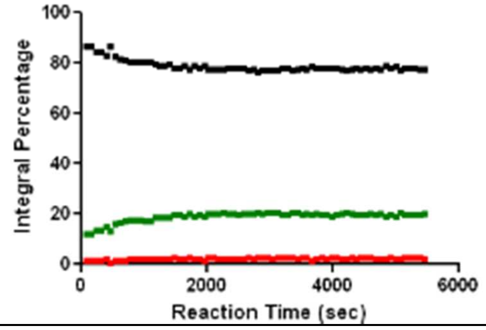
Plots of the integral percentage of each $[Co(acacen)(X_1/X_2)]^+$ derivative in solution as a function of the reagent equivalents of a 4MeIm in reaction with $[Co(acacen)(NH_3)_2]^+$.



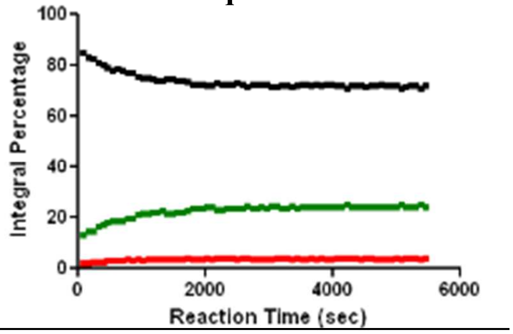
PART 5B. Chemical Equilibrium - Variation in 4MeIm Equivalents, [Co(acacen)(NMeIm)$_2$]Br



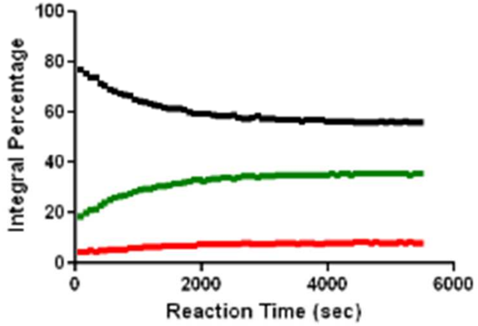
0.25 eq 4MeIm



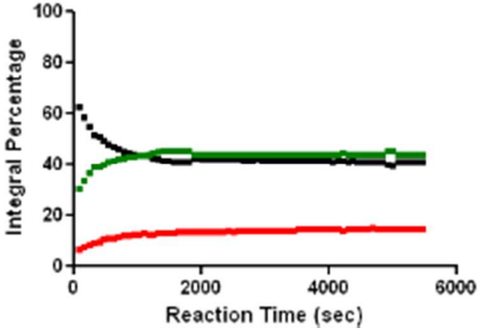
0.5 eq 4MeIm



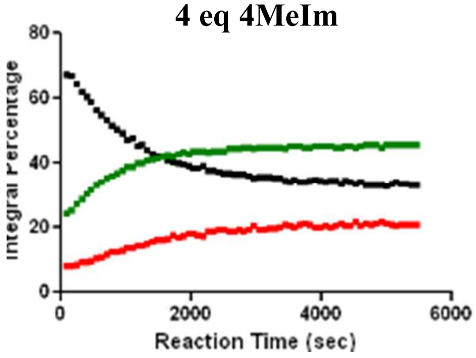
1 eq 4MeIm



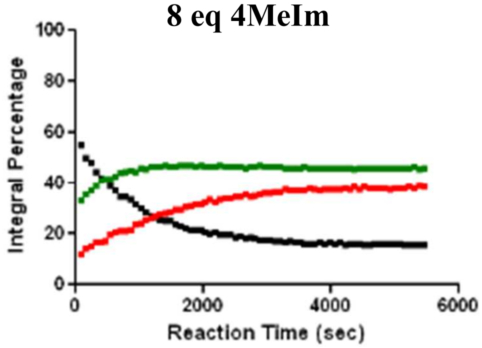
2 eq 4MeIm



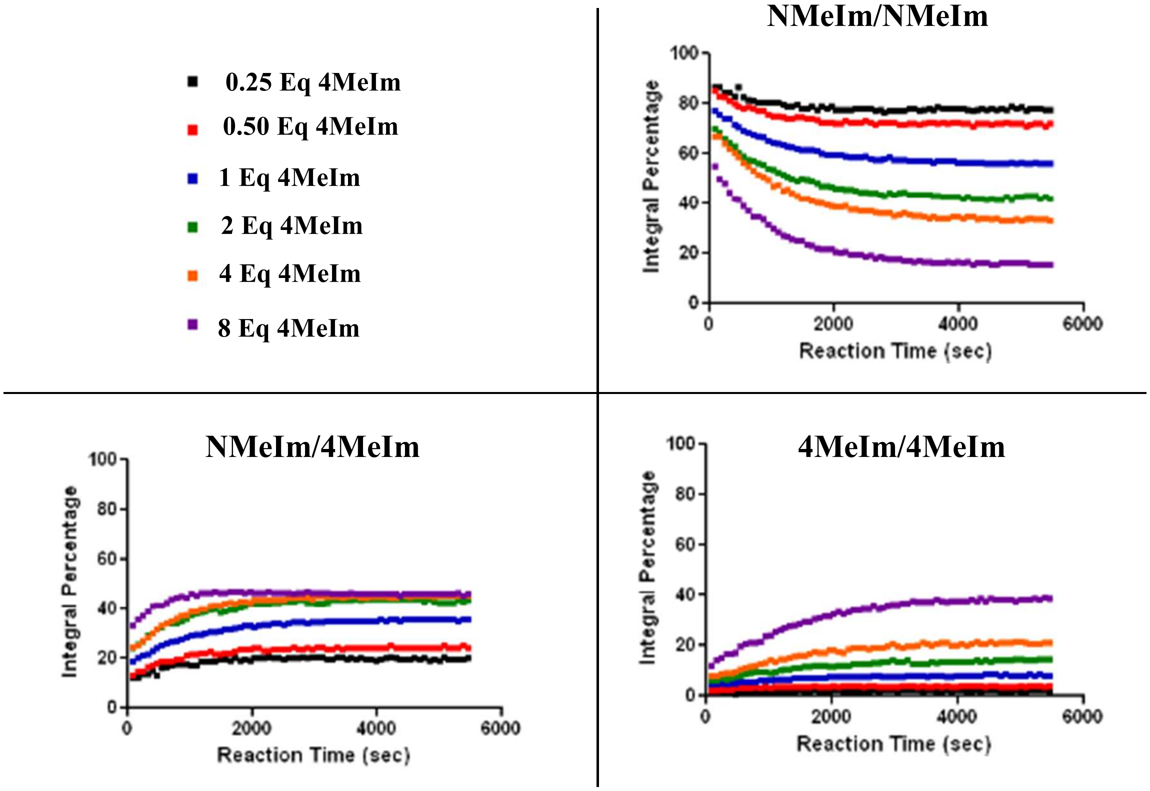
4 eq 4MeIm



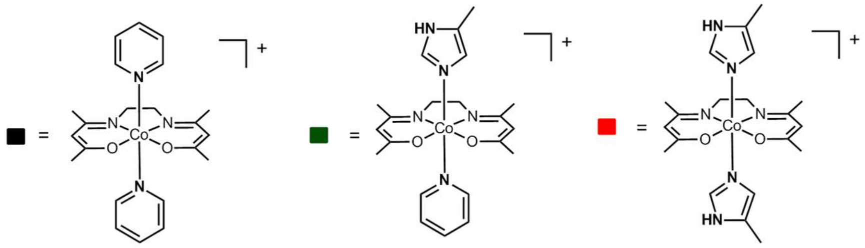
8 eq 4MeIm

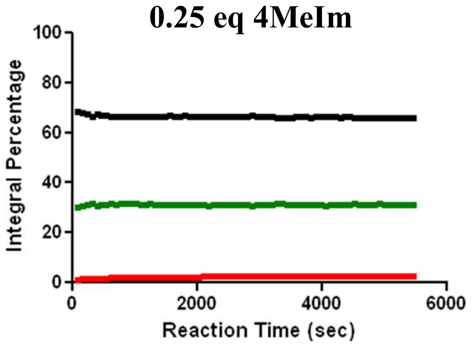


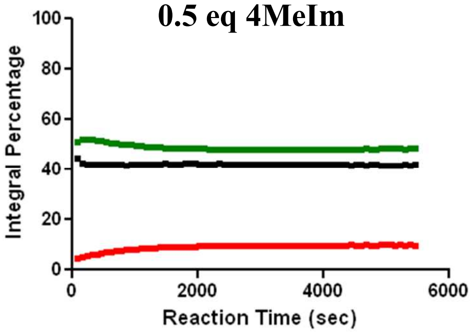
Plots of the integral percentage of each [Co(acacen)(X$_1$/X$_2$)]$^+$ derivative in solution as a function of the reagent equivalents of a 4MeIm in reaction with [Co(acacen)(NMeIm)$_2$]$^+$.

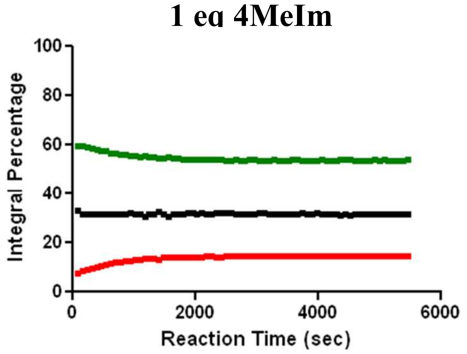


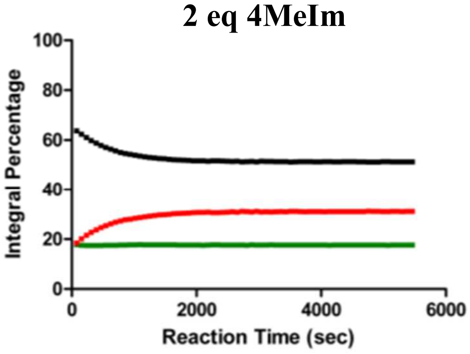
PART 5D. Chemical Equilibrium - Variation in 4MeIm Equivalents, [Co(acacen)(Py)$_2$]Br

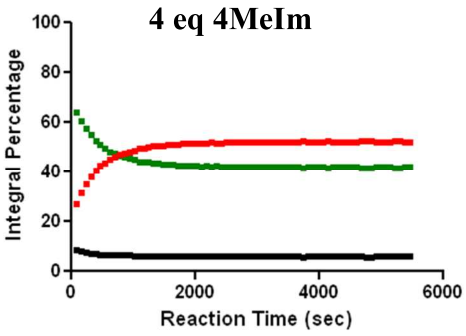


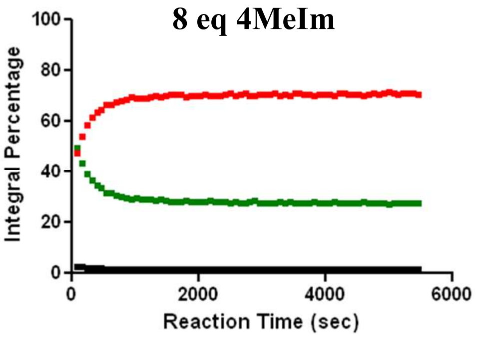

0.25 eq 4MeIm


0.5 eq 4MeIm

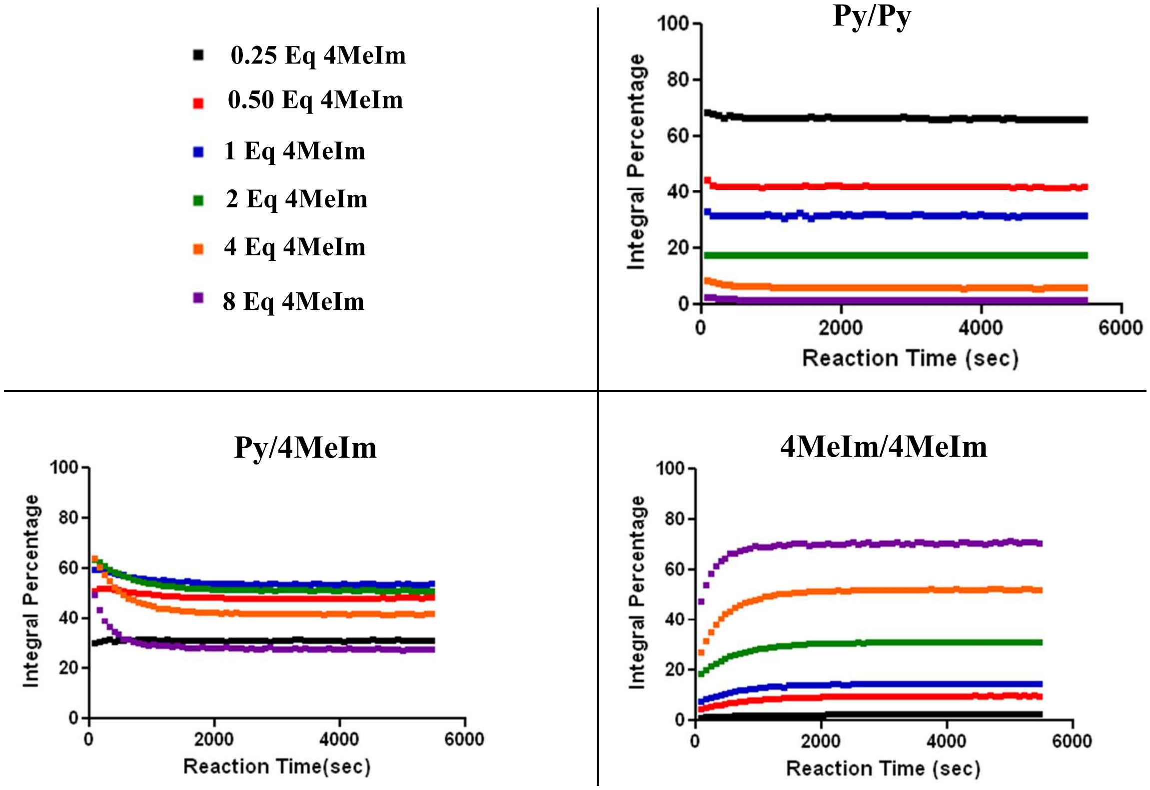

1 eq 4MeIm

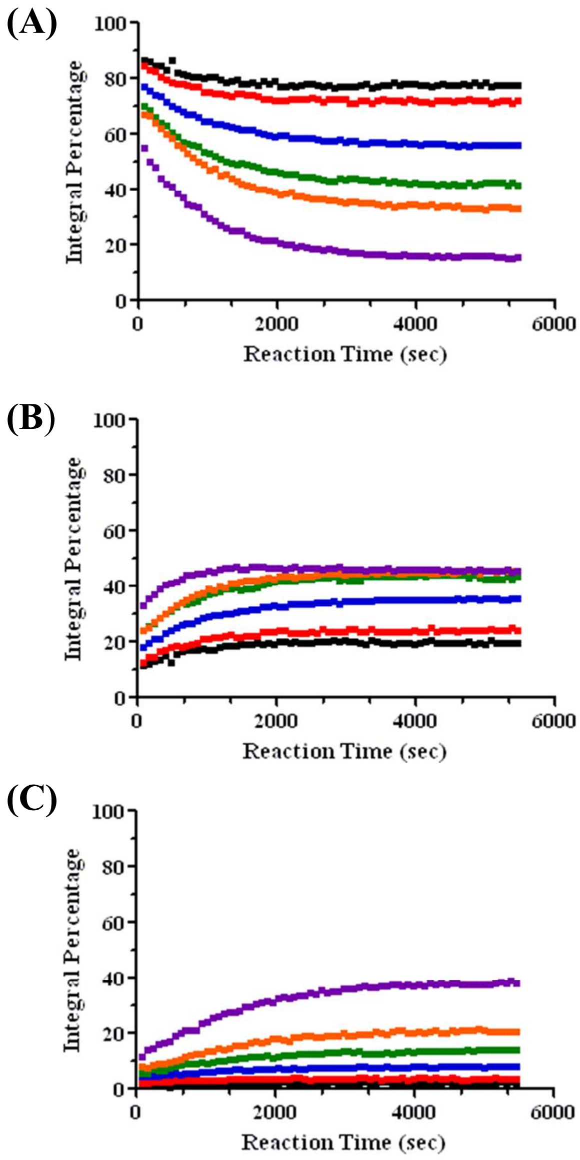

2 eq 4MeIm


4 eq 4MeIm


8 eq 4MeIm

Plots of the integral percentage of each $[Co(acacen)(X_1/X_2)]^+$ derivative in solution as a function of the reagent equivalents of a 4MeIm in reaction with $[Co(acacen)(Py)_2]^+$.





Supp. Part 5c. Reaction of **4** with varying equivalents of 4MeIm shows a clear dependence of the equilibrium ratios of each independent [Co(III)(acacen)] species. **(A) 4**, **(B)** [Co(acacen)(NMeIm)(4MeIm)]$^+$, **(C) 1**. ⬛ 0.25 eq 4MeIm, 🟥 0.50 eq 4MeIm, 🟦 1 eq 4MeIm, 🟩 2 eq 4MeIm, 🟧 4eq 4MeIm, and 🟪 8 4MeIm.

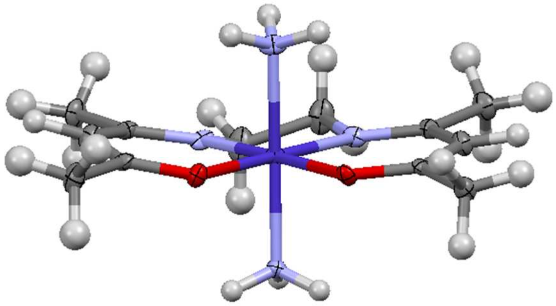
PART 6. Mass spectroscopy studies of cobalt(III) Schiff base complexes

Mass spectrometry studies of $[Co(acacen)(X)_2]^+$ with 4MeIm confirmed the identity of the NMR reaction species and showed evidence of the mixed species.

$[Co(acacen)(X/X)_2]^+$	Reagent Ligand	(*m*/*z*)	Resultant Species $[Co(acacen)(X_1/X_2)]^+$
NH_3/ NH_3	4MeIm	281.1	-/-
		363.1	4MeIm/-
		380.2	4MeIm/NH3
		445.2	4MeIm/4MeIm
2MeIm/2MeIm	4MeIm	363.0	4MeIm/-, 2MeIm/-
		445.1	4MeIm/4MeIm, 4MeIm/2MeIm, 2MeIm/2MeIm
4MeIm/4MeIm	2MeIm	363.0	4MeIm/-, 2MeIm/-
		445.1	4MeIm/4MeIm, 4MeIm/2MeIm, 2MeIm/2MeIm
2MeIm/2MeIm	Im	349.0	Im/-
		417.1	Im/Im
Im/Im	2MeIm	349.0	Im/-
		417.1	Im/Im
2MeIm/2MeIm	2MeIm	281.1	-/-
		363.1	2MeIm/-
		445.2	2MeIm/2MeIm
Im/Im	4MeIm	349.1	Im/-
		363.1	4MeIm/-
		417.1	Im/Im
		431.1	4MeIm/Im
		445.1	4MeIm/4MeIm
4MeIm/4MeIm	Im	349.1	Im/-
		363.1	4MeIm/-
		417.1	Im/Im
		431.1	4MeIm/Im
		445.1	4MeIm/4MeIm
NMeIm/NMeIm	4MeIm	363.0	NMeIm/-, 4MeIm/-
		445.1	NMeIm/NMeIm, NMeIm/4MeIm, 4MeIm/4MeIm
4MeIm/4MeIm	NMeIm	363.0	NMeIm/-, 4MeIm/-
		445.1	NMeIm/NMeIm, NMeIm/4MeIm, 4MeIm/4MeIm
NMeIm/NMeIm	Im	349.1	Im/-
		363.1	NMeIm/-
		417.1	Im/Im
		431.1	NMeIm/Im
		445.1	NMeIm/4MeIm, NMeIm/NMeIm, 4MeIm/4MeIm

Im/Im	NMeIm	349.1	Im/-
		363.1	NMeIm/-
		417.1	Im/Im
		431.1	NMeIm/Im
		445.1	NMeIm/4MeIm, NMeIm/NMeIm, 4MeIm/4MeIm
Py/Py	4MeIm	445.2	4MeIm/4MeIm
		363.1	4MeIm/-
4MeIm/4MeIm	Py	445.1	4MeIm/4MeIm
		363.1	4MeIm/-
Py/Py	Im	417.1	Im/Im
		349.1	Im/-
		341.0	MeOH/MeOH
Im/Im	Py	417.1	Im/Im
		349.1	Im/-
Py/Py	Py	439.1	Py/Py
		360.0	Py/-
		281.0	-/-

PART 7A. X-ray Crystallography studies of Co(III) Schiff base Complexes, [Co(acacen)(NH_3)$_2$]BPh_4, plot with 30% probability ellipsoids.



Data Collection

Single orange crystals of $C_{36}H_{44}BCoN_4O_2$ having approximate dimensions of 0.27 × 0.21 × 0.05 mm mounted using oil (Infineum V8512) on a glass fiber. All measurements were made on a Bruker Apex CCD detector diffractometer with moncrhomated MoKα radiation.

Cell constants and an orientation matrix for data collection corresponded to a Monoclinic cell with dimensions:

$a = 12.4323(5)$ Å $\alpha = 90^{\circ}$
$b = 17.3432(7)$ Å $\beta = 93.308^{\circ}$
$c = 15.4529(6)$ Å $\gamma = 90^{\circ}$
$V = 3326.3(2)$ Å^3

For Z = 4 and F.W. = 634.49, the calculated density is 1.276 g/cm^3. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

Cc

The data were collected at a temperature of 99.97 K with a theta range for data collection of 4.04 to 52.74°. Data were collected in 0.5° oscillations with 40 second exposures. The crystal-to-detector distance was 60.00 mm.

Data Reduction

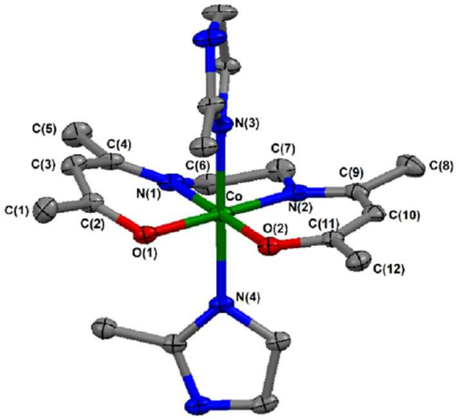
Of the 27717 reflections which were collected, 6248 were unique (R_{int} = 0.0513). Data were collected using Bruker APEX2 detector and processed using SAINTPLUS from Bruker.

The linear absorption coefficient, mu, for MoKα radiation is 0.855 mm^{-1}. The data were corrected for Lorentz and polarization effects.

Empirical formula	$C_{36}H_{44}BCoN_4O_2$
Formula weight	634.49

Temperature	99.97
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, Cc
Unit cell dimensions	a = 12.4323(5) Å α = 90° b = 17.3432(7) Å β = 93.308° c = 15.4529(6) Å γ = 90°
Volume	3326.3(2) $Å^3$
Z, Calculated density	4, 1.267 mg/mm^3
Absorption coefficient	0.553 m/mm^{-1}
F(000)	1344.0
Crystal size	0.27 x 0.21 x 0.05
Theta range for data collection	4.04° to 52.74°
Limiting indices	$-15 \le h \le 15$, $-21 \le k \le 21$, $-19 \le l \le 19$
Reflections collected / unique	27717/6248[R(int) = 0.0513]
Absorption correction	Numerical
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	6248/128/403
Goodness-of-fit on F^2	0.809
Final R indices [I>2sigma(I)]	$R_1 = 0.0426$, $wR_2 = 0.1107$
R indices (all data)	$R_1 = 0.0636$, $wR_2 = 0.1250$
Largest diff. peak and hole	0.28/-0.38 e $Å^{-3}$

PART 7B. X-ray Crystallography studies of Co(III) Schiff base Complexes, [Co(acacen)(2MeIm)$_2$]Cl



Data Collection

An orange plate crystal of $C_{41.20}H_{63.10}Cl_2Co_2N_{12}O_{6.35}$ having approximate dimensions of 0.44 x 0.14 x 0.04 mm was mounted using oil (Infineum V8512) on a glass fiber. All measurements were made on a Bruker APEX-II C with graphite monochromated MoKα radiation.

Cell constants and an orientation matrix for data collection corresponded to a Monoclinic cell with dimensions:

a = 24.8162(9) Å α = 90°
b = 11.6873(4) Å β = 100.328(2)°
c = 16.9470(6) Å γ = 90°
V = 4835.6(3) $Å^3$

For Z = 4 and F.W. = 1016.90, the calculated density is 1.397 g/cm^3. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

P2(1)/c

The data were collected at a temperature of 100(2)K with a theta range for data collection of 0.83 to 27.58°. Data were collected in 0.5° oscillations with 40 second exposures. The crystal-to-detector distance was 60.00 mm.

Data Reduction

Of the 41559 reflections which were collected, 10981 were unique (R_{int} = 0.1431). Data were collected using Bruker APEX2 detector and processed using SAINTPLUS from Bruker.

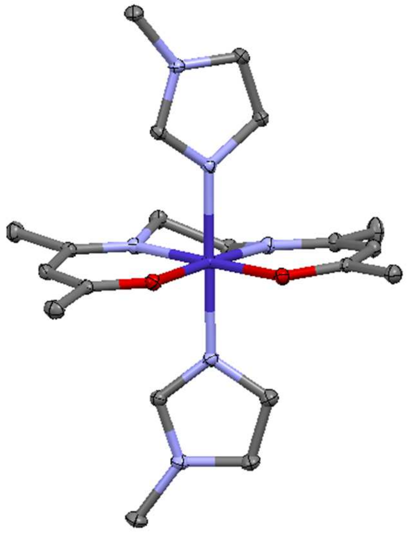
The linear absorption coefficient, mu, for MoKα radiation is 0.855 mm^{-1}. The data were corrected for Lorentz and polarization effects.

There are several disordered solvent molecules and anions in the lattice. The two independent chloride anions are disordered over 2 and 3 unique positions. Additionally, there are three partially occupied water molecules and one partially occupied ethanol molecule in the lattice. Hydrogen atoms for the water molecules could not be found from residual electron density and were not included in the refinement.

Empirical formula	$C_{41.20} H_{63.10} Cl_2 Co_2 N_{12} O_{6.35}$
Formula weight	1016.90
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 24.8162(9) Å α= 90 °
	b = 11.6873(4) Å β = 100.328(2) °
	c = 16.9470(6) Å γ= 90 °
Volume	4835.6(3) $Å^3$
Z, Calculated density	4, 1.397 Mg/m^3
Absorption coefficient	0.855 mm^{-1}
F(000)	2132
Crystal size	0.44 x 0.14 x 0.04 mm
Theta range for data collection	0.83 to 27.58 °
Limiting indices	-29<=h<=32, -15<=k<=15, -21<=l<=21
Reflections collected / unique	41559 / 10981 [R(int) = 0.1431]

Completeness to theta = 27.58	98.1 %
Absorption correction	Numerical
Max. and min. transmission	0.9699 and 0.7070
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	10981 / 0 / 645
Goodness-of-fit on F^2	0.914
Final R indices [I>2sigma(I)]	R1 = 0.0540, wR2 = 0.1255
R indices (all data)	R1 = 0.1219, wR2 = 0.1585
Largest diff. peak and hole	0.809 and -0.398 e-/Å-3

PART 7C. X-ray Crystallography studies of Co(III) Schiff base Complexes, [Co(acacen)(NMeIm)$_2$]BPH$_4$, plot with 30% probability ellipsoids.



Data Collection

A orange tabular crystal of $C_{48}H_{62}$ $BCoN_6O_4$ having approximate dimensions of 0.39 x 0.28 x 0.13 mm was mounted using oil (Infineum V8512) on a glass fiber. All measurements were made on a Bruker APEX-II CCD detector with graphite monochromated MoK\α radiation.

Cell constants and an orientation matrix for data collection corresponded to a Monoclinic cell with dimensions:

a = 13.9254(5) Å
b = 18.0542(6) Å β = 97.6470(18)°
c = 17.8151(6) Å
V = 4439.1(3) Å^3

For Z = 4 and F.W. = 856.78, the calculated density is 1.282 g/cm^3. Based on systematic absences, and the successful solution and refinement of the structure, the space group was determined to be:

P2(1)/c

The data were collected at a temperature of 100(2)K with a theta range for data collection of 1.48 to 30.03º. Data were collected in 0.5º oscillations with 15 second exposures. The crystal-to-detector distance was 60.00 mm.

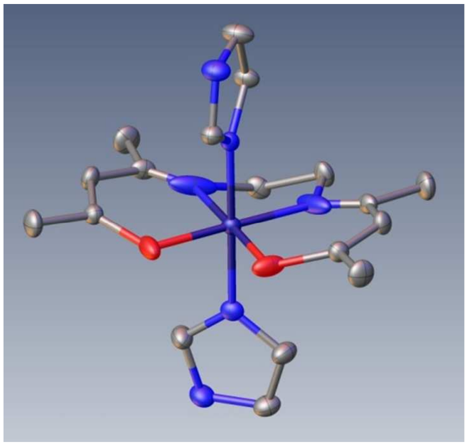
Data Reduction

Of the 76376 reflections which were collected, 12872 were unique (R_{int} = 0.0504). Data were collected using Bruker APEX2 detector and processed using SAINTPLUS from Bruker.

The linear absorption coefficient, mu, for MoK\a radiation is 0.437 mm^{-1}. A numerical absorption correction was applied. Minimum and maximum transmission factors were: 0.8904 and 0.9631, respectively. The data were corrected for Lorentz and polarization effects.

Empirical formula	$C_{48}H_{62}BCoN_6O_4$
Formula weight	856.78
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, *P*2$_1$/*c*
Unit cell dimensions	a = 13.9254(5) Å α = 90° b = 18.0542(6) Å β = 97.6470(18)º c = 17.8151(6) Å γ = 90°
Volume	4439.1(3) $Å^3$
Z, Calculated density	4, 1.282 Mg/m^3
Absorption coefficient	0.437 mm^{-1}
F(000)	1824
Crystal size	0.39 x 0.28 x 0.13 mm
Theta range for data collection	1.48 to 30.03 º
Limiting indices	-19<=h<=19, -24<=k<=25, -23<=l<=25
Reflections collected / unique	76376 / 12872 [R(int) = 0.0504]
Completeness to theta = 30.03	99.1 %
Absorption correction	Numerical
Max. and min. transmission	0.9631 and 0.8904
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	12872 / 75 / 581
Goodness-of-fit on F^2	1.302
Final R indices [I>2sigma(I)]	R1 = 0.0479, wR2 = 0.1297
R indices (all data)	R1 = 0.0749, wR2 = 0.1437
Largest diff. peak and hole	1.032 and -0.634 e-/$Å^{-3}$

PART 7D. X-ray Crystallography studies of Co(III) Schiff base Complexes, [Co(acacen)(Im)$_2$]Cl



Data Collection

A red tabular crystal of $C_{44}H_{51}BCoN_6O_3$ having approximate dimensions of 0.369 x 0.252 x 0.03 mm was mounted using oil (Infineum V8512) on a glass fiber. All measurements were made on a Bruker APEX-II CCD detector with graphite monochromated MoK\α radiation.

Cell constants and an orientation matrix for data collection corresponded to a Monoclinic cell with dimensions:

a = 9.6818(5) Å α = 90°
b = 14.5560(8) Å β = 97.6470(18)º
c = 14.3710(8) Å γ = 90°
V = 2004.20(19) $Å^3$

For Z = 2 and F.W. = 781.65, the calculated density is 1.295 g/cm^3. Based on systematic absences, and the successful solution and refinement of the structure, the space group was determined to be:

P2(1)/m

The data were collected at a temperature of 100.09 K with a theta range for data collection of 4 to 60.14º. Data were collected in 0.5º oscillations with 15 second exposures. The crystal-to-detector distance was 60.00 mm.

Data Reduction

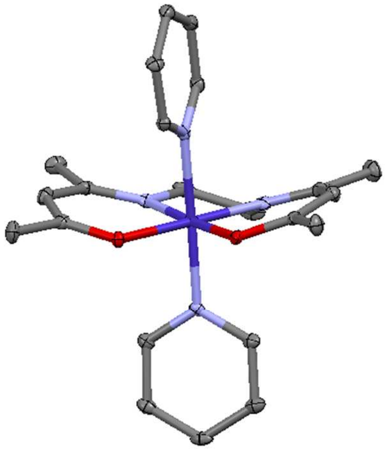
Of the 6066 reflections which were collected, 6066 were unique (R_{int} = 0.0000). Data were collected using Bruker APEX2 detector and processed using SAINTPLUS from Bruker.

The linear absorption coefficient, mu, for MoK\a radiation is 0.476 mm^{-1}. A numerical absorption correction was applied. Minimum and maximum transmission factors were: 0.8904 and 0.9631, respectively. The data were corrected for Lorentz and polarization effects.

The structure is characterized by disorder in the equatorial plane of the cobalt(III) center. The wagging of the acacen ligand between two conformations is likely driven by the flipping of the ethylene backbone. The O and N atoms of the acacen are slightly disordered due to this wagging however their disorder was not modeled. There is a mirror plane that dissects the molecule. One of the imidazole ligands lies in the mirror plane while the other one is perpendicular to it. Therefore, N5 and C12 occupy the same symmetry generated position. Finally, a disordered molecule of ethanol occupying two positions was included in the solution.

Empirical formula	$C_{44}H_{51}BCoN_6O_3$
Formula weight	781.65
Temperature	100.09 K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, $P2_1/m$
Unit cell dimensions	a = 9.6818(5) Å $\alpha = 90°$
	b = 14.5560(8) Å $\beta = 98.273°$
	c = 14.3710(8) Å $\gamma = 90°$
Volume	2004.20(19) $Å^3$
Z, Calculated density	2, 1.295 mg/m^3
Absorption coefficient	0.476 mm^{-1}
F(000)	826.0
Crystal size	0.369 x 0.252 x 0.03
Theta range for data collection	4° to 60.14°
Limiting indices	$-13 \leq h \leq 13$, $0 \leq k \leq 20$, $0 \leq l \leq 20$
Reflections collected / unique	6066/6066[R(int) = 0.0000]
Absorption correction	Numerical
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	6066/0/339
Goodness-of-fit on F^2	1.013
Final R indices [I>2sigma(I)]	$R_1 = 0.0459$, $wR_2 = 0.1190$
R indices (all data)	$R_1 = 0.0597$, $wR_2 = 0.1278$
Largest diff. peak and hole	0.77/-0.74 e/$Å^{-3}$

PART 7E. X-ray Crystallography studies of Co(III) Schiff base Complexes, $[Co(acacen)(Py)_2]Br$



Data Collection

A red tabular crystal of $C_{24}H_{36}BrCoN_4O_4$ having approximate dimensions of 0.3 x 0.245x 0.188 mm was mounted using oil (Infineum V8512) on a glass fiber. All measurements were made on a Bruker APEX-II CCD detector with graphite monochromated MoK\α radiation.

Cell constants and an orientation matrix for data collection corresponded to a Orthorhombic cell with dimensions:

$a =$ 23.538(5) Å $\alpha = 90°$
$b =$ 14.3729(3) Å $\beta = 90°$
$c =$ 15.616(3) Å $\gamma = 90°$
$V =$ 5282.6(18) $Å^3$

For Z = 8 and F.W. = 583.41, the calculated density is 1.295 g/cm^3. Based on systematic absences, and the successful solution and refinement of the structure, the space group was determined to be:

$Pna2_1$

The data were collected at a temperature of 100.14 K with a theta range for data collection of 3.32 to 55.12°. Data were collected in 0.5° oscillations with 15 second exposures. The crystal-to-detector distance was 60.00 mm.

Data Reduction

Of the 6300 reflections which were collected, 6300 were unique ($R_{int} = 0.0000$). Data were collected using Bruker APEX2 detector and processed using SAINTPLUS from Bruker.

The linear absorption coefficient, mu, for MoK\a radiation is 2.198 mm^{-1}. A numerical absorption correction was applied. Minimum and maximum transmission factors were: 0.8904 and 0.9631, respectively. The data were corrected for Lorentz and polarization effects

Empirical formula	$C_{24}H_{36}BrCoN_4O_4$
Formula weight	583.41
Temperature	100.14 K
Wavelength	0.71073 Å
Crystal system, space group	*P*na2$_1$
Unit cell dimensions	a = 23.538(5) Å $\alpha = 90°$
	b = 14.372(3) Å $\beta = 90°$
	c = 15.616(3) Å $\gamma = 90°$
Volume	5282.6(18) Å^3
Z, Calculated density	8, 1.467 Mg/m^3
Absorption coefficient	2.198 mm^{-1}
F(000)	2416
Crystal size	0.3 × 0.245 × 0.188
Theta range for data collection	3.32 to 55.12°
Limiting indices	$0 \leq h \leq 30$, $0 \leq k \leq 18$, $0 \leq l \leq 20$
Reflections collected / unique	6300/6300[R(int) = 0.0000]
Absorption correction	Numerical
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	6300/1/629
Goodness-of-fit on F^2	1.156
Final R indices [I>2sigma(I)]	$R_1 = 0.0362$, $wR_2 = 0.0867$
R indices (all data)	$R_1 = 0.0371$, $wR_2 = 0.0871$
Largest diff. peak and hole	1.265/-0.596 e-/Å^{-3}

Structure Solution and Refinement

The structure was solved by direct methods and expanded using Fourier techniques3. Rigid bond restraints (esd 0.01) were imposed on the displacement parameters as well as restraints on similar amplitudes (esd 0.05) separated by less than 1.7 Å on the disordered ethanol solvent molecule. Chemically equivalent, but not symmetry equivalent disordered ethanol molecules atoms were restrained so that bond distances and angles were similar to the non-disordered ethanol. The remaining non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealized positions, but not refined. The final cycle of full-matrix least-squares refinemene4 on F2 was based on 12872 reflections and 581 variable parameters and converged (largest parameter shift was 0.009 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma| |F_o|-|F_c| |/\Sigma|F_o| = 0.0479$$

$$wR^2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2} = 0.1297$$

The weighting scheme was calc.
calc $w=1/[\sigma^2(F_o^2)+(0.0660P)^2 + 0.0000P]$ where $P=(F_o^2+2F_c^2)/3$

The standard deviation of an observation of unit weight[5] was 1.321. The weighting scheme was based on counting statistics and included a factor to downweight the intense reflections. Plots of $\Sigma\ w\ (|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, sin θ/λ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.032 and -0.634 e-/Å^3, respectively.

Neutral atom scattering factors were taken from Cromer and Waber.[6] Anomalous dispersion effects were included in Fcalc[7]; the values for Df' and Df" were those of Creagh and McAuley.[8] The values for the mass attenuation coefficients are those of Creagh and Hubbell.[9] All calculations were performed using the Bruker SHELXTL3 crystallographic software package.

Structure Solution and Refinement

Using Olex2[1], the structure was solved with the XS[2] structure solution program using Direct Methods and refined with the XL[3] refinement package using Least Squares minimization.

1. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program. J. Appl. Cryst. (2009). 42, 339-341.
2. SHELXS-97 (Sheldrick, 1990)
3. XL, G.M. Sheldrick, Acta Cryst. (2008). A64, 112-122

References

(1) APEX2 V2.1-4 Bruker Analytical X-ray Instruments, Inc.: Madison, WI, 2007

(2) APEX2 V2.1-4 Bruker Analytical X-ray Instruments, Inc.: Madison, WI, 2007

(3) Sheldrick, G.M. SHELXTL Version 6.14; Bruker Analytical X-ray Instruments, Inc.: Madison, WI, 2003

(4) Full-Matrix Least-Squares refinement on F^2:

$$wR^2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$$

(5) GooF = S = $\{\Sigma[w(F_o^2-F_c^2)^2]/(n-p)\}^{1/2}$ n = number of reflections; p = total number of reflections refined

(6) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

(7) Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).

(8) Creagh, D. C. & McAuley, W.J .; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(9) Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

Supp. Part 7c Displacement (Å) from the N_2O_2 plane for select atoms on of the [Co(III)(acacen)] derivatives. The N_2O_2 plane refers to the acacen nitrogen and oxygen atoms coordinating the Co(III) center [N(1), N(2), O(1), O(2)]. Carbons are as indicated in **Figure 2**. Positive values designate deviations above the N_2O_2 plane; negative values indicate deviations below the N_2O_2 plane.

[a] Crystal structure of **1-Br** reported in *Inorg. Chem.* **1997,** *36*, 2498-2504.

	1[a]	**2**	**3**	**4**	**5**	**6**
Co	-0.003	+0.013	+0.005	-0.005	-0.003	-0.017
C(3)	+0.098	+0.409	+0.785	-0.096	+0.360	-0.569
C(6)	+0.130	-0.397	-0.527	+0.227	-0.002	+0.439
C(1)	-0.107	+0.256	+0.845	-0.253	+0.165	-0.560
C(5)	+0.272	+0.235	+0.391	+0.117	+0.533	-0.452
C(10)	+0.234	+0.215	+0.323	+0.219	+0.360	-0.503
C(7)	-0.410	+0.064	-0.133	-0.374	-0.563	+0.331
C(12)	+0.347	-0.021	+0.342	+0.296	+0.165	-0.505
C(8)	-0.105	+0.284	+0.342	-0.054	+0.533	-0.259

Supp. Part 7d Dihedral angles (deg) between each planar face of the acacen ligand and the N_2O_2 plane. The N_2O_2 plane refers to the acacen nitrogen and oxygen atoms coordinating the Co(III) center [N(1), N(2), O(1), O(2)]. Plane_1 refers to a plane draw between N(1), O(1), C(2), C(4). Plane_2 refers to a plane draw between N(2), O(2), C(9), and C(11).

[a] Crystal structure of **1-BPH$_4$** reported in *Inorg. Chem.* **1997,** *36*, 2498-2504.

	1[a]	**2**	**3**	**4**	**5**	**6**
N_2O_2-Plane_1	6.34	9.98	18.57	3.11	11.12	13.05
N_2O_2-Plane_2	3.15	5.70	13.32	5.51	11.12	13.05
Plane_1-Plane_2	9.35	15.63	31.87	5.16	22.20	28.59