Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Material

Acetate as a model for aspartate-based CXCR4 chemokine receptor binding of cobalt and nickel complexes of cross-bridged tetraazamacrocycles

Amy N. Cain,[a] TaRynn N. Carder Freeman,[a] Kimberly D. Roewe,[a] David L. Cockriel,[c] Travis R. Hasley,[a] Randall D. Maples,[a] Elisabeth M. A. Allbritton,[a] Thomas D'Huys,[d] Tom van Loy,[d] Benjamin P. Burke,[b] Timothy J. Prior,[b] Dominique Schols,[d] Stephen J. Archibald[b*] and Timothy J. Hubin[a*]

Contents

1. Crystallography

Table S1. Crystal Data and Structural Refinement Details for Cobalt Complexes.

Complex	[Co(**1**)Cl_2] sja15_04	[Co(**2**)(OAc)]$(PF_6)_2$ sja21_12	[Co(**6**)(OAc)]$(PF_6)_2$ sja32_08	[Co(**5**)(OAc)(H_2O)](PF_6) sja26_08
CCDC number	1566342	1567495	1567486	1567487
formula	C26 H38 Cl2 Co N4	C26 H37 Co F12 N4 O2 P2	C14 H29 Co F12 N4 O2 P2	C16 H35 Co F6 N4 O3 P
formual wt.	536.43	786.46	634.28	535.38
space group	C 2/c	C 2/c	P $2_12_12_1$	R 3 c
a(Å)	9.149(2)	16.0338(18)	9.2044(11)	25.992(3)
b(Å)	13.467(2)	11.4266(14)	12.7702(17)	25.992(3)
c(Å)	20.060(6)	17.658(2)	19.650(3)	17.3325(15)
α(deg)	90	90	90	90
ß(deg)	96.18(2)	104.712(9)	90	90
γ(deg)	90	90	90	120
V($Å^3$)	2457.1(10)	3129.1(6)	2309.7(5)	10141(2)
Z	4	4	4	18
ρ_{calc}(g/cm^3)	1.450	1.669	1.824	1.578
temp(K)	150(2)	150(2)	150(2)	150(2)
wavelength(Å)	0.71073	0.71073	0.71073	0.71073
abs. coeff.(mm^{-1})	0.939	0.756	0.999	0.907
R1(F_o^2) =	0.0953	0.0469	0.0376	0.0370
wR2(F_o^2) =	0.2144	0.0924	0.0509	0.0563

[a][I > 2σ(I)] [b]wR1 = $\Sigma||F_o| - |F_c||/|F_o|$ [c]wR2 = $\{\Sigma w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{½}$ w = $1/[s^2(F_o^2) + (aP)^2 + bP]$ where P = $(F_o^2 + 2F_c^2)/3$

Table S2. Crytal Data and Structural Refinement Details for Nickel Complexes

Complex	[Ni(**1**)Cl_2] sja4_04	[Ni(**2**)Cl_2] sja65_06	[Ni(**2**)(OAc)(H_2O)]PF_6 sja309	[Ni(**4**)(OAc)]PF_6 sja2_08	[Ni(**6**)(OAc)]PF_6 sja24_08
CCDC number	1566343	1566346	1566345	1567488	1567489
formula	C26 H38 Cl2 N4 Ni	C24 H34 Cl2 N4 Ni	C27 H43 F6 N4 Ni O4 P	C20 H33 F6 N4 Ni O2 P	C15 H31 Cl2 F6 N4 Ni O2 P
formual wt.	536.21	508.16	691.33	565.18	574.02
space group	C 222_1	C 2/c	P 2_1/c	P -1	P 2_1/n
a(Å)	9.0137(16)	8.8352(17)	18.1480(18)	7.6252(10)	12.0210(16)
b(Å)	13.3814(17)	13.1417(17)	9.4592(8)	11.0029(14)	16.226(3)
c(Å)	20.352(3)	19.920(3)	20.795(2)	14.884(2)	12.4026(16)
α(deg)	90	90	90	71.316(10)	90
ß(deg)	90	91.985(16)	119.919(7)	81.906(11)	103.909(10)
γ(deg)	90	90	90	87.281(11)	90
V($Å^3$)	2454.8(6)	2311.5(6)	3094.0(5)	1171.2(3)	2348.3(6)
Z	4	4	4	2	4
ρ_{calc}(g/cm^3)	1.451	1.460	1.484	1.603	1.624
temp(K)	150(2)	150(2)	150(2)	150(2)	150(2)
wavelength(Å)	0.71073	0.71073	0.71073	0.71073	0.71073
abs. coeff.(mm^{-1})	1.031	1.090	0.754	0.970	1.189
R1(F_o^2) =	0.0311	0.0258	0.0352	0.0478	0.0678
wR2(F_o^2) =	0.0603	0.0670	0.0775	0.1669	0.1275

[a]$I > 2\sigma(I)$ [b]$wR1 = \Sigma||F_o| - |F_c||/|F_o|$ [c]$wR2 = \{\Sigma w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{½}$ $w = 1/[s^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$

Table S3. Selected bond lengths [Å] and angles [º]:

[Co(**1**)Cl_2]

Co(1)-N(1)#1	2.185(8)	Co(1)-N(2)	2.294(8)
Co(1)-N(1)	2.185(8)	Co(1)-Cl(1)	2.426(3)
Co(1)-N(2)#1	2.294(8)	Co(1)-Cl(1)#1	2.426(3)
N(1)#1-Co(1)-N(1)	82.5(4)	N(2)-Co(1)-Cl(1)#1	89.2(2)
N(1)#1-Co(1)-N(2)#1	89.2(3)	Cl(1)-Co(1)-Cl(1)#1	93.27(13)
N(1)-Co(1)-N(2)#1	81.6(3)	N(2)#1-Co(1)-N(2)	167.7(4)
N(1)#1-Co(1)-N(2)	81.6(3)	N(1)#1-Co(1)-Cl(1)	92.8(2)
N(1)-Co(1)-N(2)	89.2(3)	N(1)-Co(1)-Cl(1)	169.7(2)
N(1)#1-Co(1)-Cl(1)#1	169.7(2)	N(2)#1-Co(1)-Cl(1)	89.2(2)
N(1)-Co(1)-Cl(1)#1	92.8(2)	N(2)-Co(1)-Cl(1)	99.25(19)
N(2)#1-Co(1)-Cl(1)#1	99.25(19)		

[Co(**2**)(OAc)]$(PF_6)_2$

Co(1)-N(1)	1.898(3)	Co(1)-O(1)	1.939(3)
Co(1)-N(1)#1	1.898(3)	Co(1)-N(2)#1	2.033(3)
Co(1)-O(1)#1	1.939(3)	Co(1)-N(2)	2.033(3)
N(1)-Co(1)-N(1)#1	90.42(17)	O(1)#1-Co(1)-N(2)#1	95.35(12)
N(1)-Co(1)-O(1)#1	168.86(12)	O(1)-Co(1)-N(2)#1	92.29(11)
N(1)#1-Co(1)-O(1)#1	100.71(12)	N(1)-Co(1)-N(2)	88.22(12)
N(1)-Co(1)-O(1)	100.71(12)	N(1)#1-Co(1)-N(2)	85.28(12)
N(1)#1-Co(1)-O(1)	168.86(12)	O(1)#1-Co(1)-N(2)	92.29(11)
O(1)#1-Co(1)-O(1)	68.16(18)	O(1)-Co(1)-N(2)	95.36(12)
N(1)-Co(1)-N(2)#1	85.28(12)	N(2)#1-Co(1)-N(2)	170.77(16)
N(1)#1-Co(1)-N(2)#1	88.22(12)		

[Co(**6**)(OAc)]$(PF_6)_2$

Co(1)-N(1)	1.901(7)	Co(1)-O(1)	1.939(6)
Co(1)-N(3)	1.905(7)	Co(1)-N(2)	2.004(4)
Co(1)-O(2)	1.927(6)	Co(1)-N(4)	2.008(4)
N(1)-Co(1)-N(3)	90.85(19)	O(2)-Co(1)-N(2)	92.5(3)
N(1)-Co(1)-O(2)	168.5(3)	O(1)-Co(1)-N(2)	94.3(3)
N(3)-Co(1)-O(2)	100.6(3)	N(1)-Co(1)-N(4)	84.6(3)
N(1)-Co(1)-O(1)	101.0(3)	N(3)-Co(1)-N(4)	89.0(3)
N(3)-Co(1)-O(1)	168.2(3)	O(2)-Co(1)-N(4)	95.4(3)
O(2)-Co(1)-O(1)	67.57(19)	O(1)-Co(1)-N(4)	92.7(3)
N(1)-Co(1)-N(2)	88.6(3)	N(2)-Co(1)-N(4)	171.06(19)
N(3)-Co(1)-N(2)	85.3(3)		

[Co(**5**)(OAc)(H_2O)](PF_6)

O(1)-Co(1)	2.042(4)	N(2)-Co(1)	2.167(6)
N(1)-Co(1)	2.128(5)	N(4)-Co(1)	2.190(6)
N(3)-Co(1)	2.124(5)	Co(1)-O(1W)	2.111(5)
O(1)-Co(1)-O(1W)	88.18(18)	N(3)-Co(1)-N(2)	84.5(2)
O(1)-Co(1)-N(3)	172.38(19)	N(1)-Co(1)-N(2)	90.9(2)
O(1W)-Co(1)-N(3)	97.61(18)	O(1)-Co(1)-N(4)	95.27(18)
O(1)-Co(1)-N(1)	91.71(18)	O(1W)-Co(1)-N(4)	86.60(19)
O(1W)-Co(1)-N(1)	170.6(2)	N(3)-Co(1)-N(4)	90.0(2)
N(3)-Co(1)-N(1)	83.39(19)	N(1)-Co(1)-N(4)	84.1(2)
O(1)-Co(1)-N(2)	89.77(19)	N(2)-Co(1)-N(4)	173.0(2)
O(1W)-Co(1)-N(2)	98.4(2)		

[Ni(**1**)Cl_2]

Ni(1)-N(1)	2.122(3)	Ni(1)-N(2)#1	2.227(3)
Ni(1)-N(1)#1	2.122(3)	Ni(1)-Cl(1)	2.4338(9)
Ni(1)-N(2)	2.227(3)	Ni(1)-Cl(1)#1	2.4338(9)
N(1)-Ni(1)-N(1)#1	84.56(16)	N(2)-Ni(1)-Cl(1)	98.40(7)
N(1)-Ni(1)-N(2)	83.70(11)	N(2)#1-Ni(1)-Cl(1)	88.05(8)
N(1)#1-Ni(1)-N(2)	89.45(11)	N(1)-Ni(1)-Cl(1)#1	171.18(8)
N(1)-Ni(1)-N(2)#1	89.45(11)	N(1)#1-Ni(1)-Cl(1)#1	92.28(8)
N(1)#1-Ni(1)-N(2)#1	83.70(11)	N(2)-Ni(1)-Cl(1)#1	88.05(8)
N(2)-Ni(1)-N(2)#1	170.75(15)	N(2)#1-Ni(1)-Cl(1)#1	98.40(7)
N(1)-Ni(1)-Cl(1)	92.28(8)	Cl(1)-Ni(1)-Cl(1)#1	92.00(5)
N(1)#1-Ni(1)-Cl(1)	171.18(8)		

[Ni(**2**)Cl_2]

Ni(1)-N(1)#1	2.0845(13)	Ni(1)-N(2)#1	2.1779(12)
Ni(1)-N(1)	2.0845(13)	Ni(1)-Cl(1)#1	2.4059(5)
Ni(1)-N(2)	2.1779(12)	Ni(1)-Cl(1)	2.4059(5)
N(1)#1-Ni(1)-N(1)	83.37(9)	N(2)-Ni(1)-Cl(1)#1	99.43(3)
N(1)#1-Ni(1)-N(2)	83.74(5)	N(2)#1-Ni(1)-Cl(1)#1	95.78(4)
N(1)-Ni(1)-N(2)	80.16(5)	N(1)#1-Ni(1)-Cl(1)	176.59(5)
N(1)#1-Ni(1)-N(2)#1	80.16(5)	N(1)-Ni(1)-Cl(1)	93.23(5)
N(1)-Ni(1)-N(2)#1	83.74(5)	N(2)-Ni(1)-Cl(1)	95.78(4)
N(2)-Ni(1)-N(2)#1	158.40(7)	N(2)#1-Ni(1)-Cl(1)	99.43(4)
N(1)#1-Ni(1)-Cl(1)#1	93.23(5)	Cl(1)#1-Ni(1)-Cl(1)	90.18(3)
N(1)-Ni(1)-Cl(1)#1	176.59(5)		

[Ni(**2**)(OAc)(H_2O)](PF_6)

Ni(1)-N(1)	2.0368(18)	Ni(1)-O(3)	2.0770(15)
Ni(1)-N(3)	2.0521(17)	Ni(1)-N(2)	2.1392(17)
Ni(1)-O(1)	2.0639(14)	Ni(1)-N(4)	2.1672(17)
N(1)-Ni(1)-N(3)	85.59(7)	O(1)-Ni(1)-N(2)	94.46(6)
N(1)-Ni(1)-O(1)	90.70(7)	O(3)-Ni(1)-N(2)	91.90(6)
N(3)-Ni(1)-O(1)	175.36(6)	N(1)-Ni(1)-N(4)	82.41(7)
N(1)-Ni(1)-O(3)	176.88(7)	N(3)-Ni(1)-N(4)	85.32(7)
N(3)-Ni(1)-O(3)	95.97(6)	O(1)-Ni(1)-N(4)	96.97(6)
O(1)-Ni(1)-O(3)	87.61(6)	O(3)-Ni(1)-N(4)	100.38(6)
N(1)-Ni(1)-N(2)	85.62(7)	N(2)-Ni(1)-N(4)	163.52(6)
N(3)-Ni(1)-N(2)	82.49(7)		

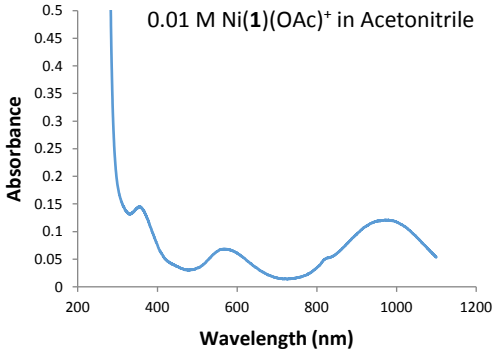
[Ni(**4**)(OAc)](PF_6)

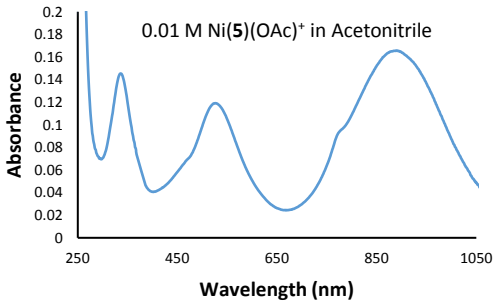
Ni(1)-N(1)	2.023(3)	Ni(1)-O(2)	2.109(3)
Ni(1)-N(3)	2.026(4)	Ni(1)-N(2)	2.139(3)
Ni(1)-O(1)	2.102(3)	Ni(1)-N(4)	2.160(3)
N(1)-Ni(1)-N(3)	87.69(14)	O(1)-Ni(1)-N(2)	94.76(12)
N(1)-Ni(1)-O(1)	166.80(13)	O(2)-Ni(1)-N(2)	98.66(13)
N(3)-Ni(1)-O(1)	105.49(13)	N(1)-Ni(1)-N(4)	82.67(13)
N(1)-Ni(1)-O(2)	103.84(13)	N(3)-Ni(1)-N(4)	85.12(14)
N(3)-Ni(1)-O(2)	168.45(13)	O(1)-Ni(1)-N(4)	98.98(12)
O(1)-Ni(1)-O(2)	63.01(12)	O(2)-Ni(1)-N(4)	95.37(12)
N(1)-Ni(1)-N(2)	85.95(13)	N(2)-Ni(1)-N(4)	163.71(13)
N(3)-Ni(1)-N(2)	82.79(14)		

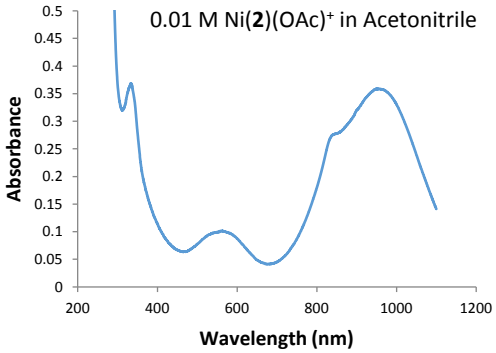
[Ni(**6**)(OAc)]PF_6

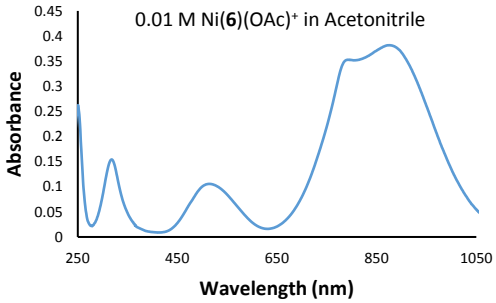
Ni(1)-N(3)	2.018(4)	Ni(1)-O(2)	2.102(3)
Ni(1)-N(1)	2.027(4)	Ni(1)-N(4)	2.142(4)
Ni(1)-O(1)	2.086(3)	Ni(1)-N(2)	2.147(4)
N(3)-Ni(1)-N(1)	87.08(14)	O(1)-Ni(1)-N(4)	96.30(14)
N(3)-Ni(1)-O(1)	105.08(13)	O(2)-Ni(1)-N(4)	98.84(14)
N(1)-Ni(1)-O(1)	167.82(13)	N(3)-Ni(1)-N(2)	85.46(15)
N(3)-Ni(1)-O(2)	167.82(14)	N(1)-Ni(1)-N(2)	82.62(15)
N(1)-Ni(1)-O(2)	105.04(14)	O(1)-Ni(1)-N(2)	97.57(14)
O(1)-Ni(1)-O(2)	62.78(13)	O(2)-Ni(1)-N(2)	94.89(14)
N(3)-Ni(1)-N(4)	82.92(15)	N(4)-Ni(1)-N(2)	163.82(14)
N(1)-Ni(1)-N(4)	85.58(15)		

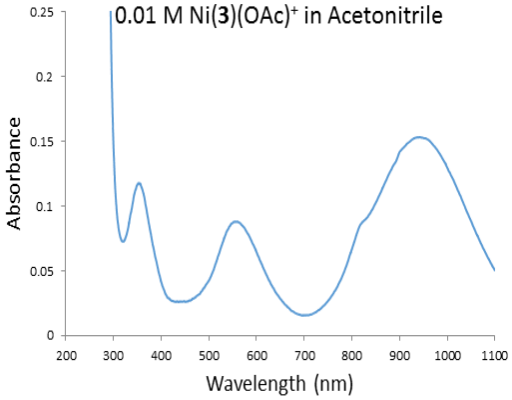
UV-Vis Spectra of Complexes

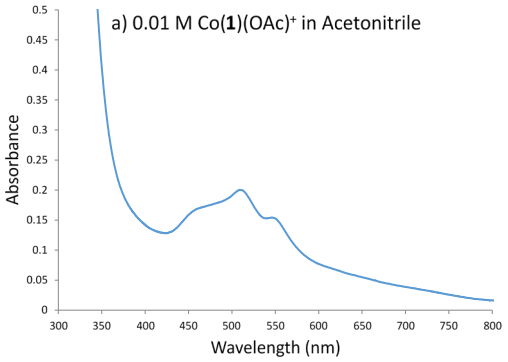


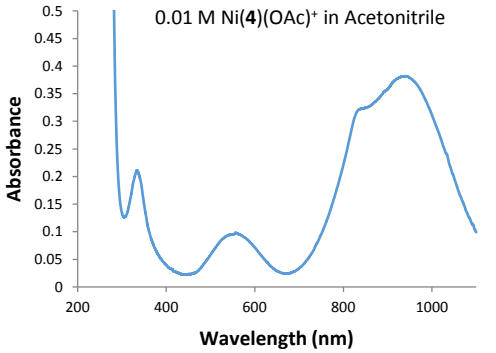


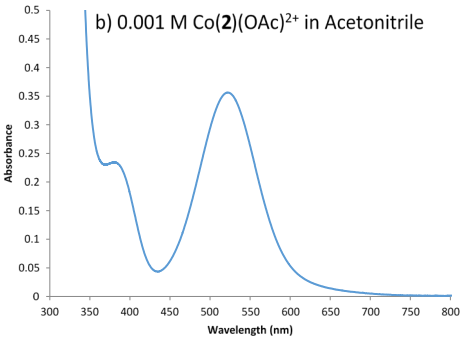


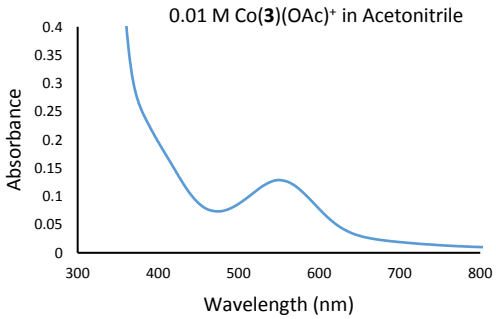


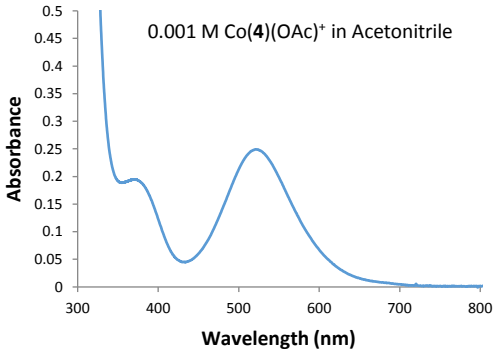


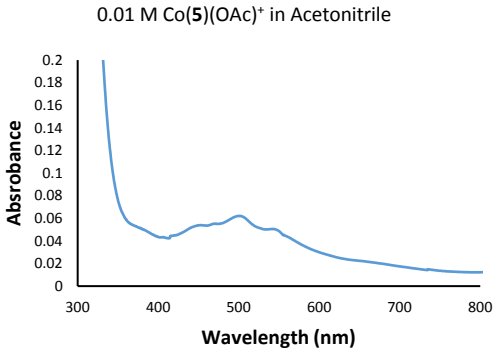


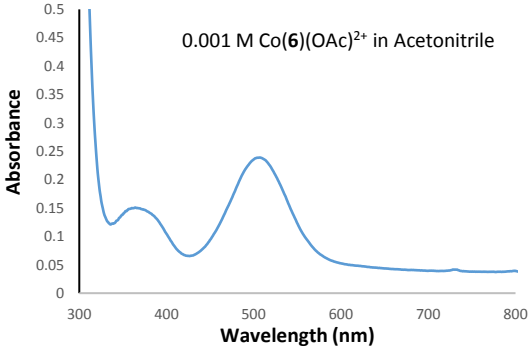




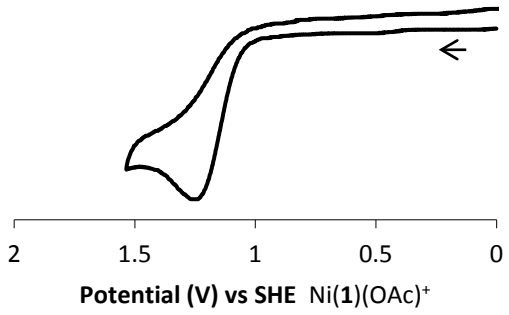

0.01 M Co(3)(OAc)+ in Acetonitrile
Absorbance
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
300
400
500
600
700
800
Wavelength (nm)

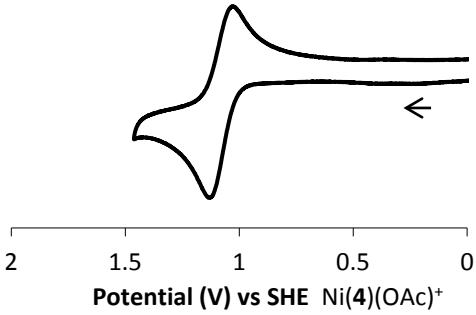

0.001 M Co(4)(OAc)+ in Acetonitrile
Absorbance
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
300
400
500
600
700
800
Wavelength (nm)

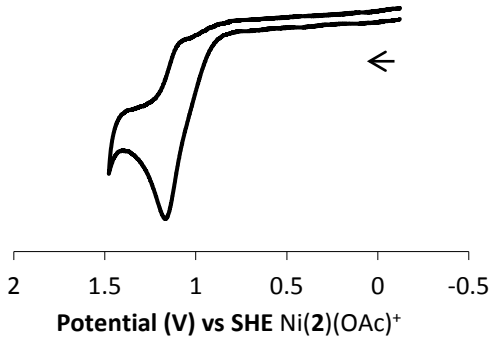

0.01 M Co(5)(OAc)+ in Acetonitrile
Absrobance
0.2
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
300
400
500
600
700
800
Wavelength (nm)

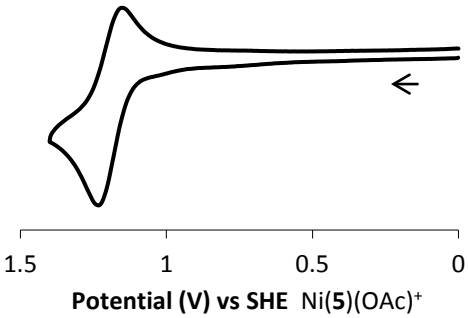

0.001 M Co(6)(OAc)2+ in Acetonitrile
Absorbance
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
300
400
500
600
700
800
Wavelength (nm)

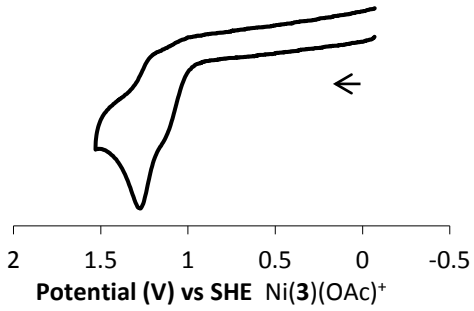
Cyclic Voltammograms of Complexes 0.001 M in Acetonitrile with 0.1 M $TBAPF_6$ supporting electrolyte

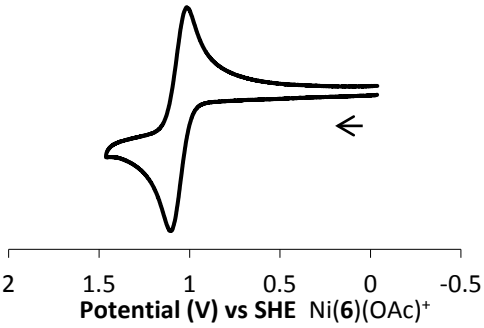


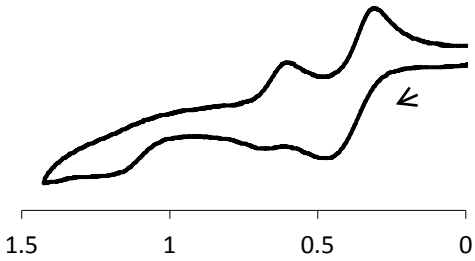




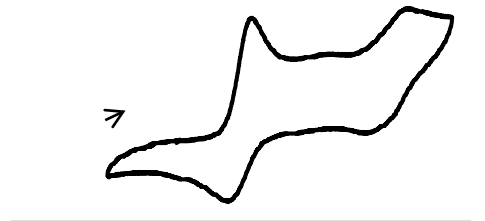




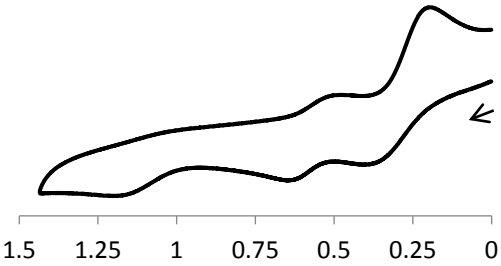




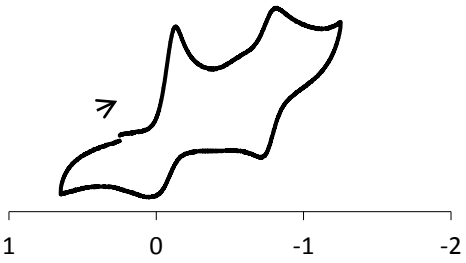
Potential (V) vs SHE Co(**1**)$(OAc)^{+}$



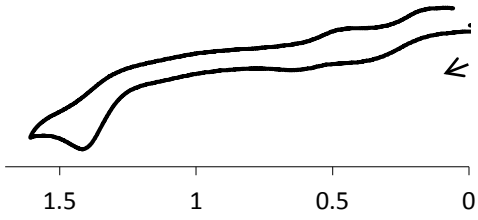
Potential (V) vs SHE Co(**2**)$(OAc)^{2+}$



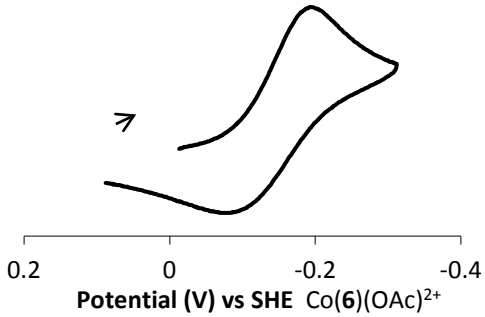
Potential (V) vs SHE Co(**3**)$(OAc)^{+}$



Potential (V) vs SHE Co(**4**)$(OAc)^{2+}$



Potential (V) vs SHE Co(**5**)$(OAc)^{+}$



Potential (V) vs SHE Co(**6**)$(OAc)^{2+}$