Electronic Supplementary Information

Isonicotinate-Zn(II)/Cd(II) bridged Dicobaloximes: Synthesis, Characterization and Electrocatalytic Proton Reduction Studies

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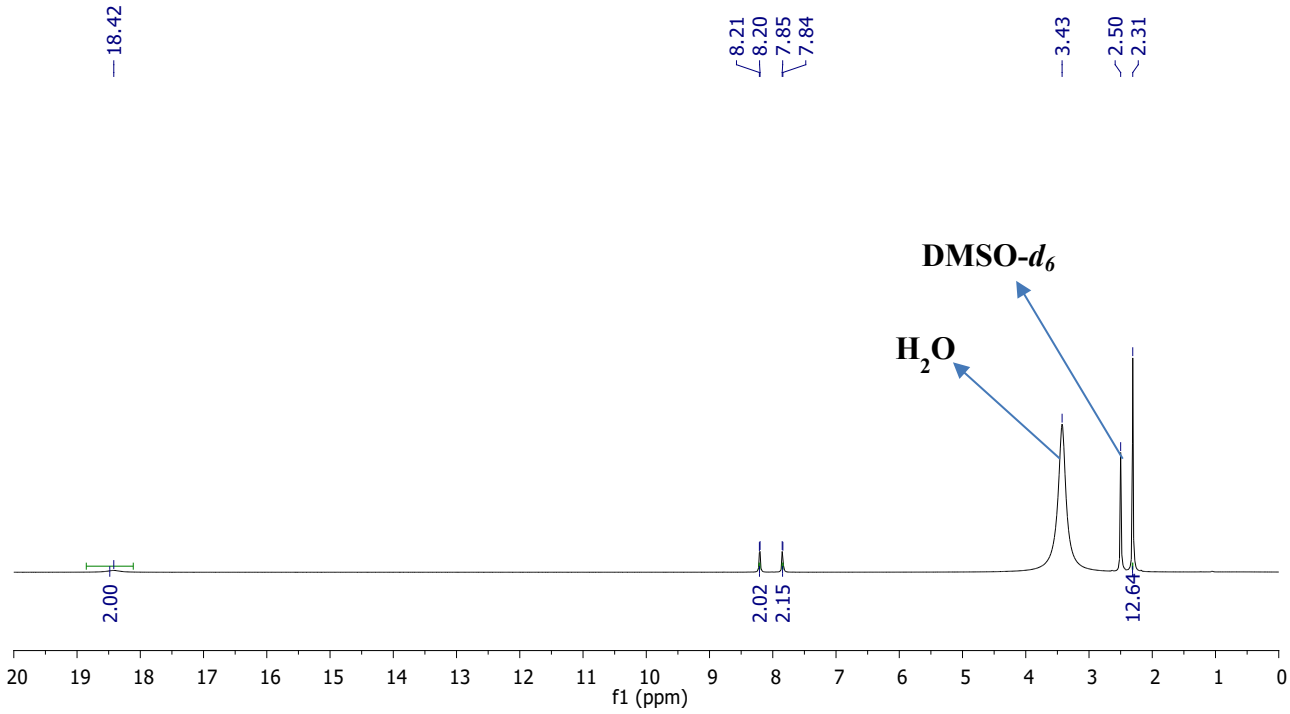

Figure S1: ^{1}H NMR spectrum (500 MHz, DMSO-*d6*) of [ClCo(dmgH)$_2$(4-PyCOOH)].

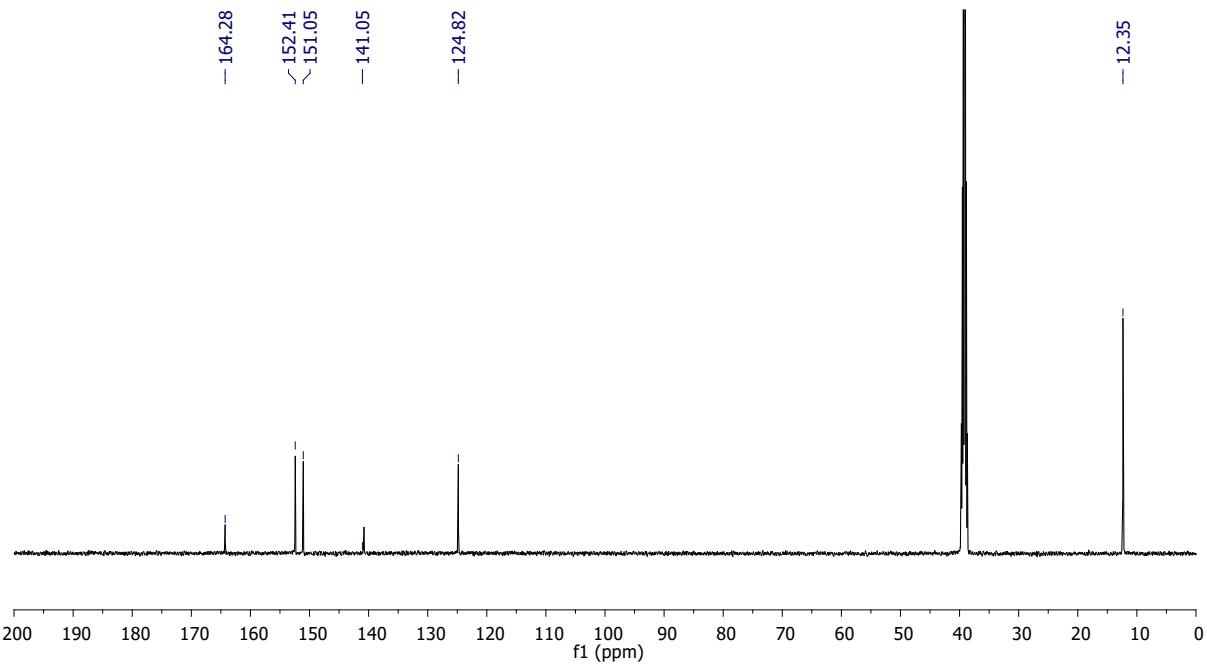

Figure S2: ^{13}C{^{1}H} NMR spectrum (125 MHz, DMSO-*d6*) of [ClCo(dmgH)$_2$(4-PyCOOH)].

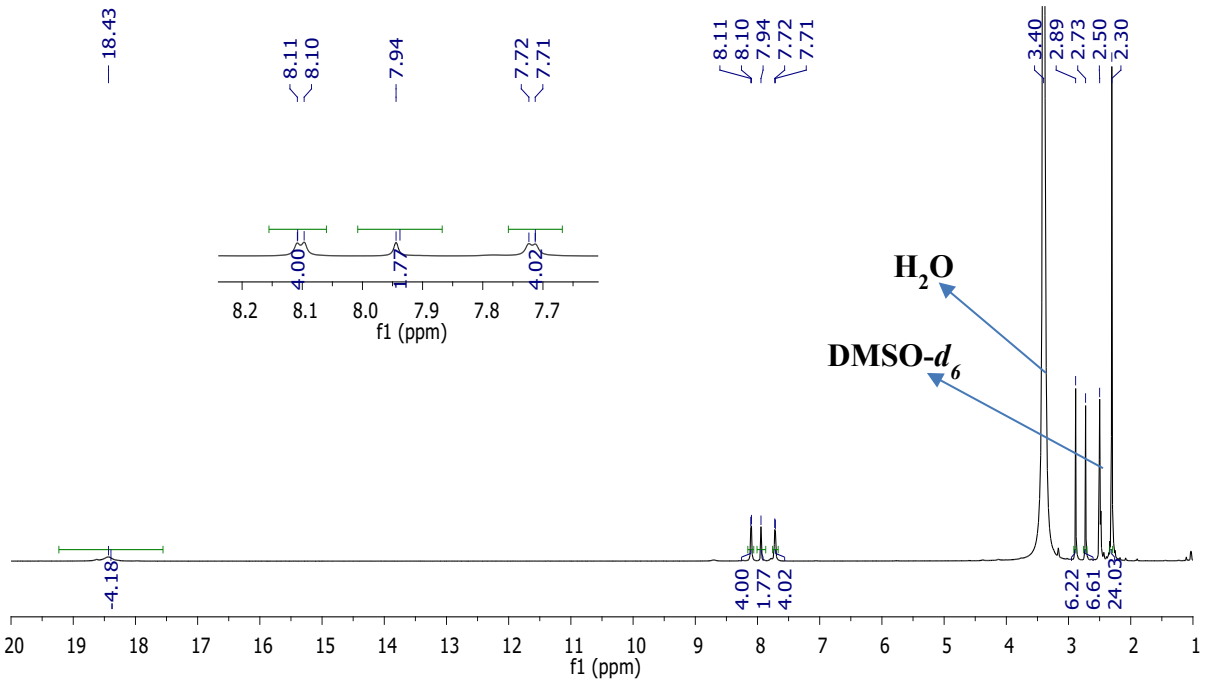

Figure S3: ^{1}H NMR spectrum (500 MHz, DMSO-*d6*) of [{ClCo(dmgH)$_2$(4-PyCOO)}$_2$Zn(DMF)$_2$] Complex **1**.

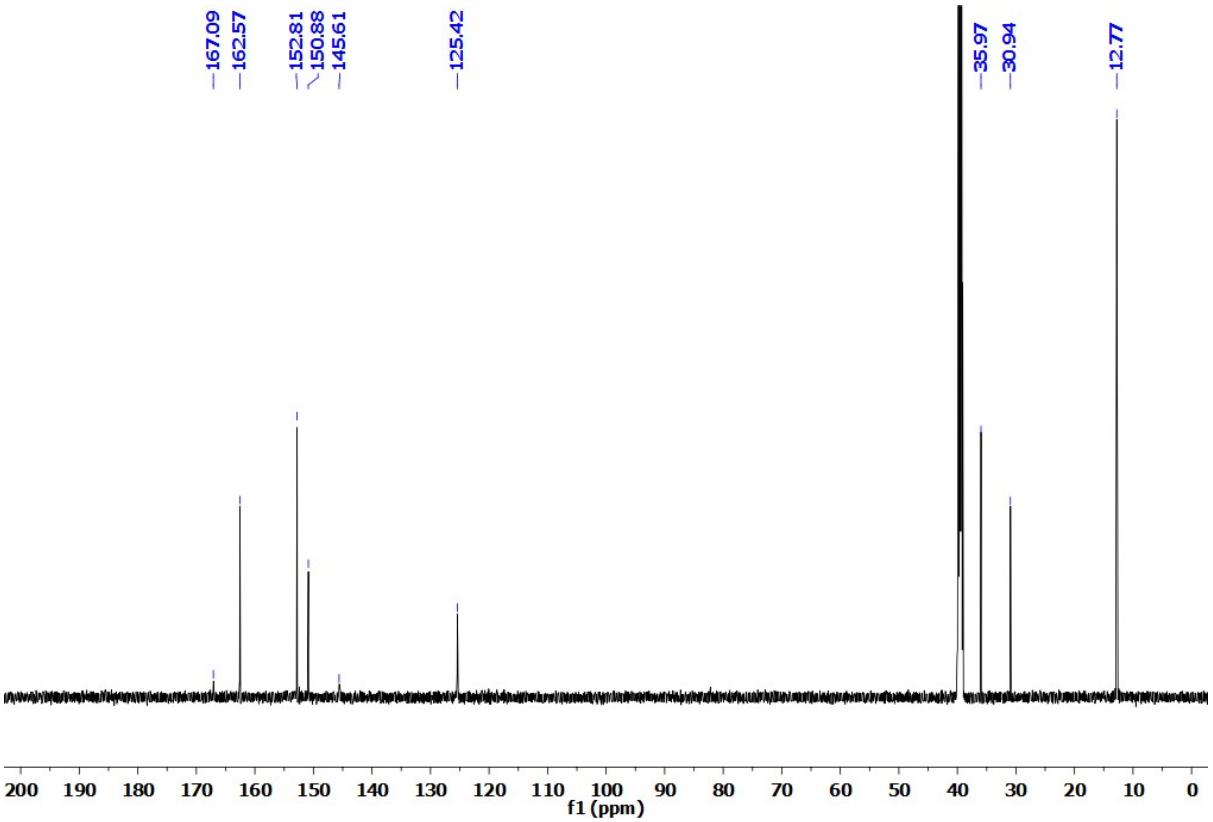

Figure S4: $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, DMSO-*d6*) of [{ClCo(dmgH)$_2$(4-PyCOO)}$_2$Zn(DMF)$_2$] Complex **1**.

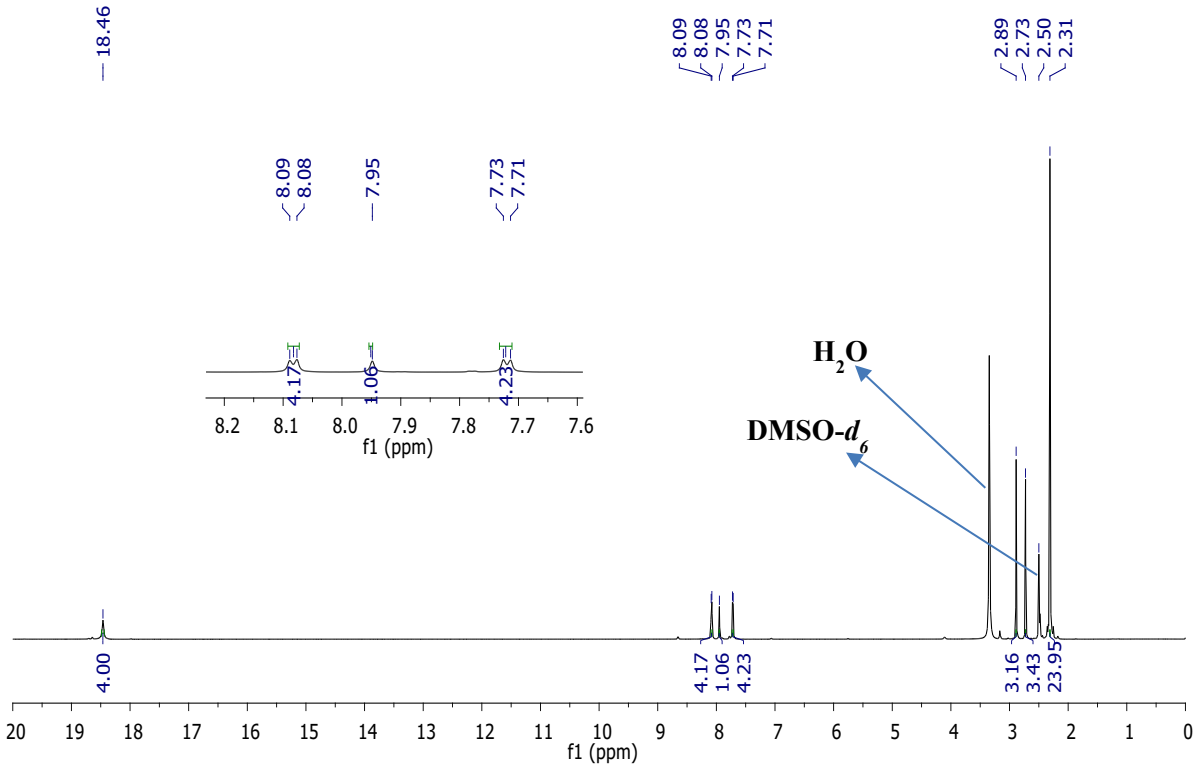

Figure S5: ^{1}H NMR spectrum (500 MHz, DMSO-*d6*) of [{ClCo(dmgH)$_2$(4-PyCOO)}$_2$Cd(H$_2$O)$_3$(DMF)].4H$_2$O (Complex **2**).

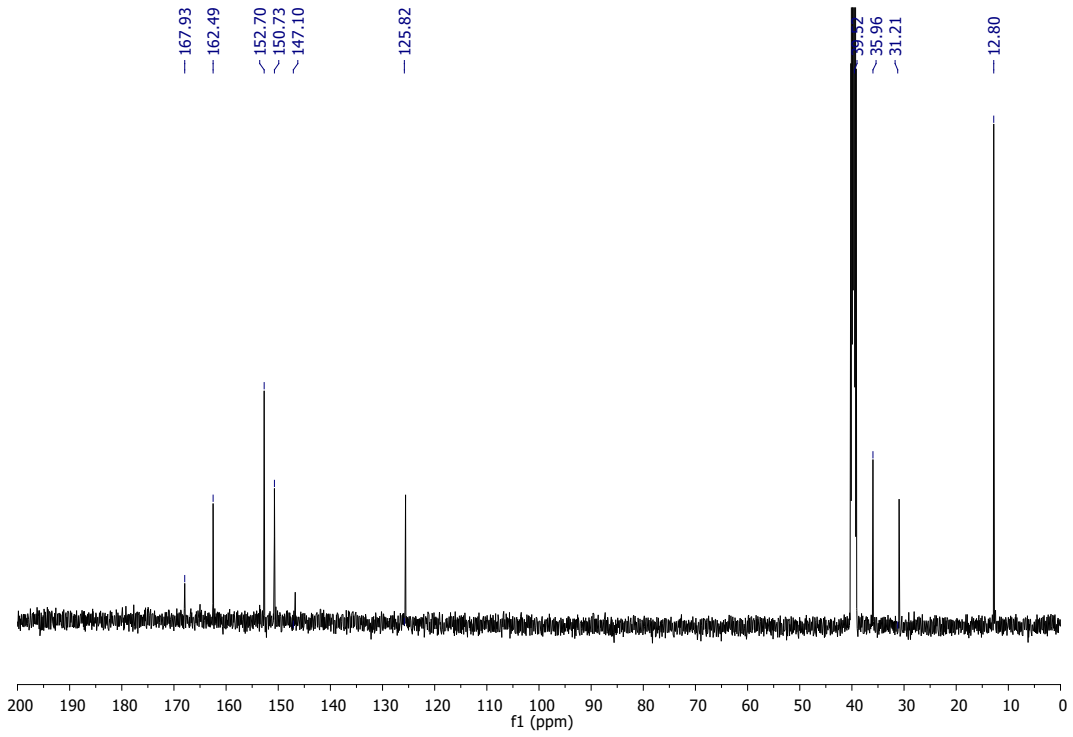

Figure S6: $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, DMSO-*d6*) of [{ClCo(dmgH)$_2$(4-PyCOO)}$_2$Cd(H$_2$O)$_3$(DMF)].4H$_2$O (Complex **2**).

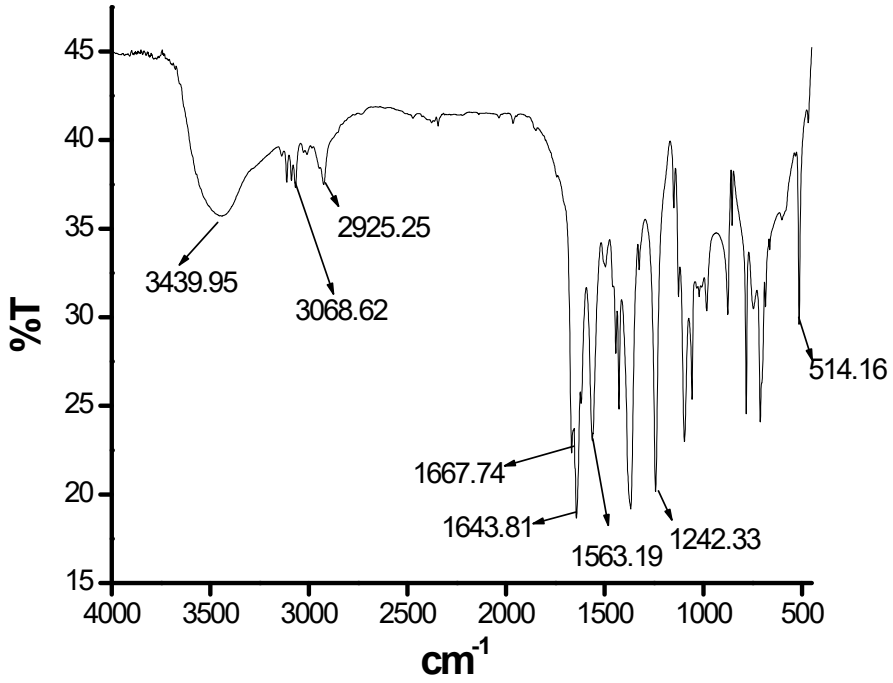

Figure S7: IR Spectrum of complex $[\{ClCo(dmgH)_2(4\text{-}PyCOO)\}_2Zn(DMF)_2]$ Complex **1**.

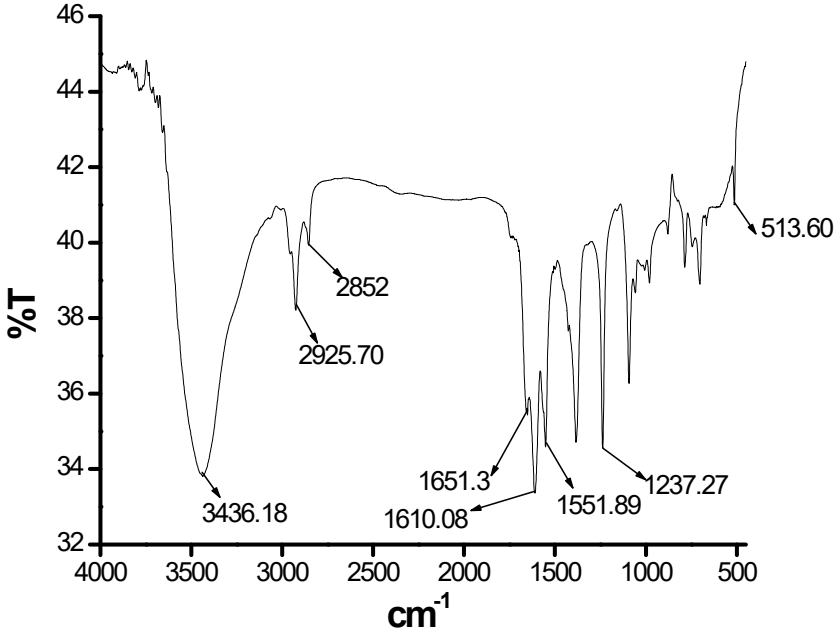

Figure S8: IR Spectrum of complex $[\{ClCo(dmgH)_2(4\text{-}PyCOO)\}_2Cd(H_2O)_3(DMF)].4H_2O$ (Complex **2**).

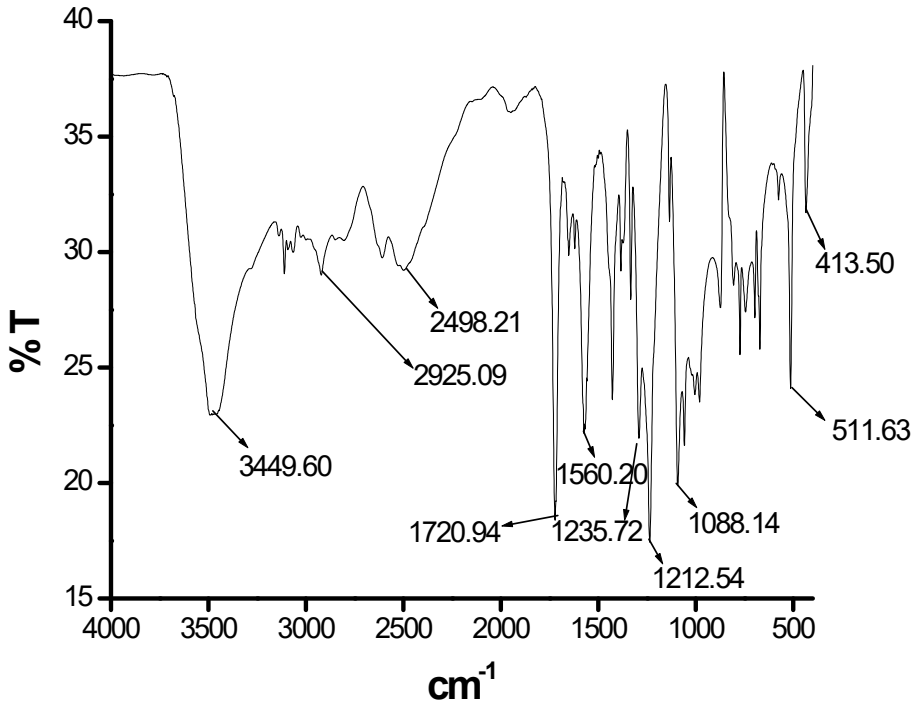

Figure S9: IR Spectrum of complex [ClCo(dmgH)$_2$(4-PyCOOH)].

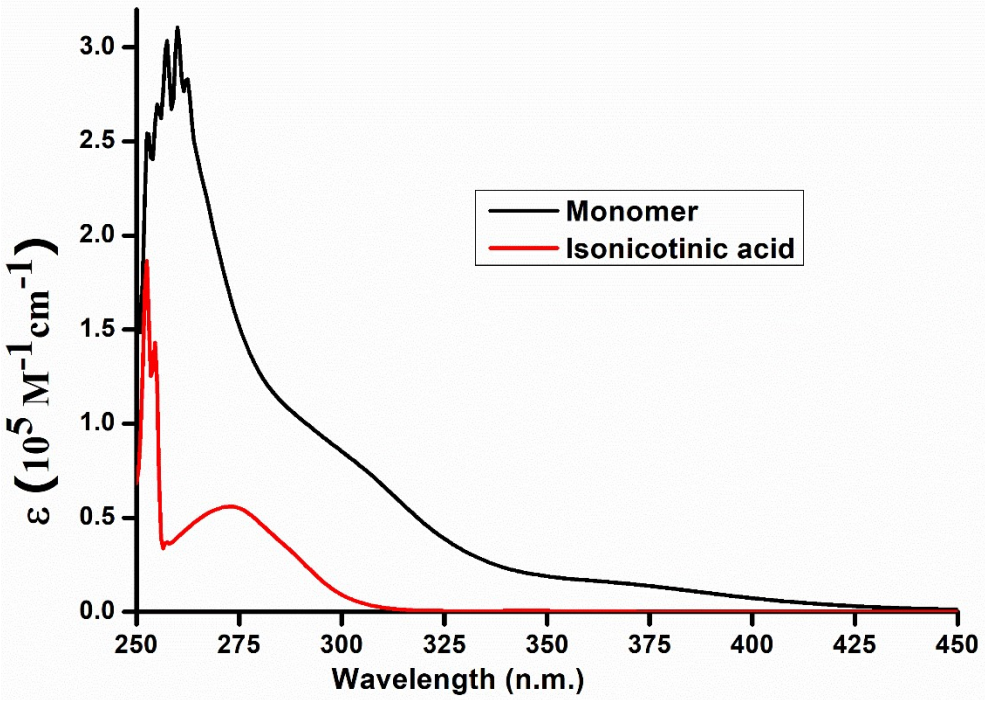

Figure S10: UV-Vis spectra of monomer *[ClCo(dmgH)$_2$(4-PyCOOH)]* and isonicotinic acid in DMSO solution at 10^{-5} molar concentration.

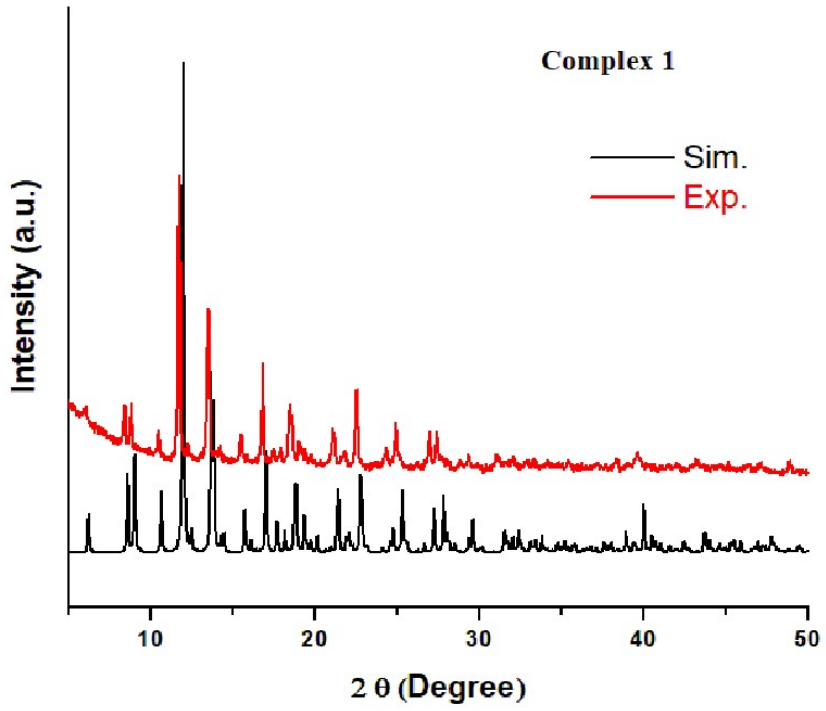

Figure S11: Simulated and experimental PXRD patterns of complex **1**.

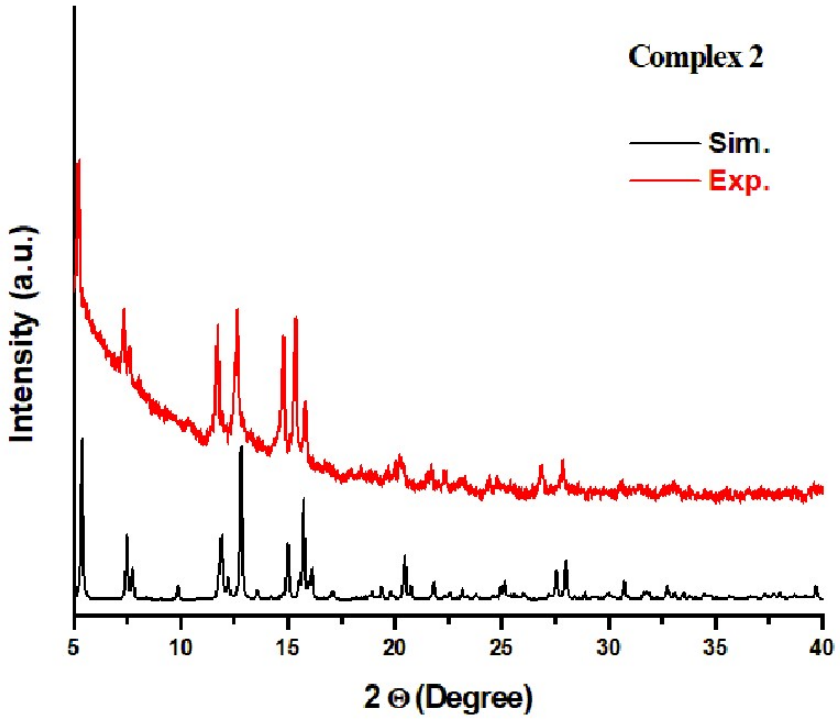

Figure S12: Simulated and experimental PXRD patterns of complex **2**.

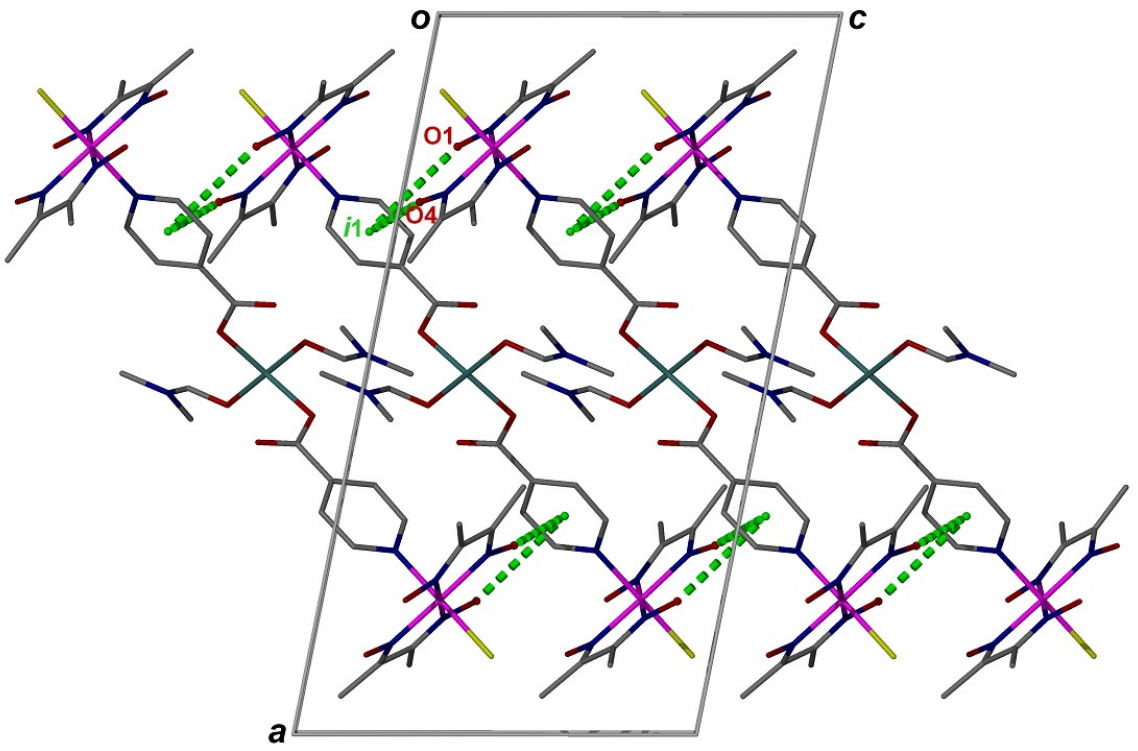

Figure S13: View showing intermolecular *p*···π interaction between the oxygen atoms (O4 and O1) of the cobaloxime unit and centroid (i1) of the pyridine ring along *ac* plane in complex **1** (hydrogen atoms are omitted for clarity).

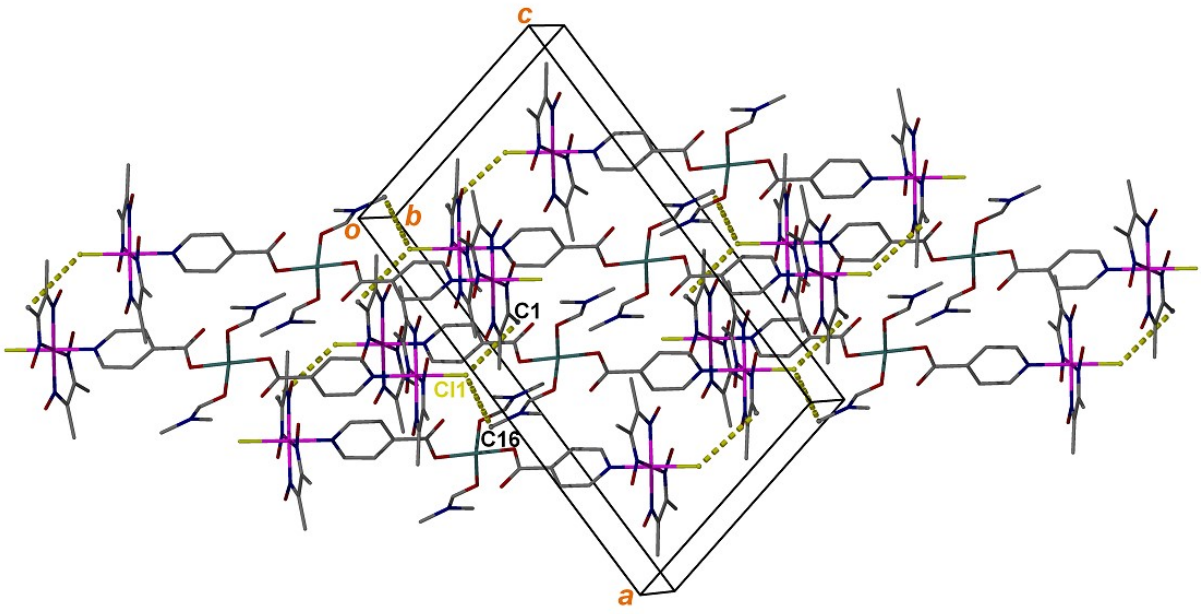

Figure S14: Diagram showing weak intermolecular interaction between the terminal chloride (Cl1) and the methyl group of dimethylglyoxime and DMF molecule in complex **1** (hydrogen atoms are omitted for clarity).

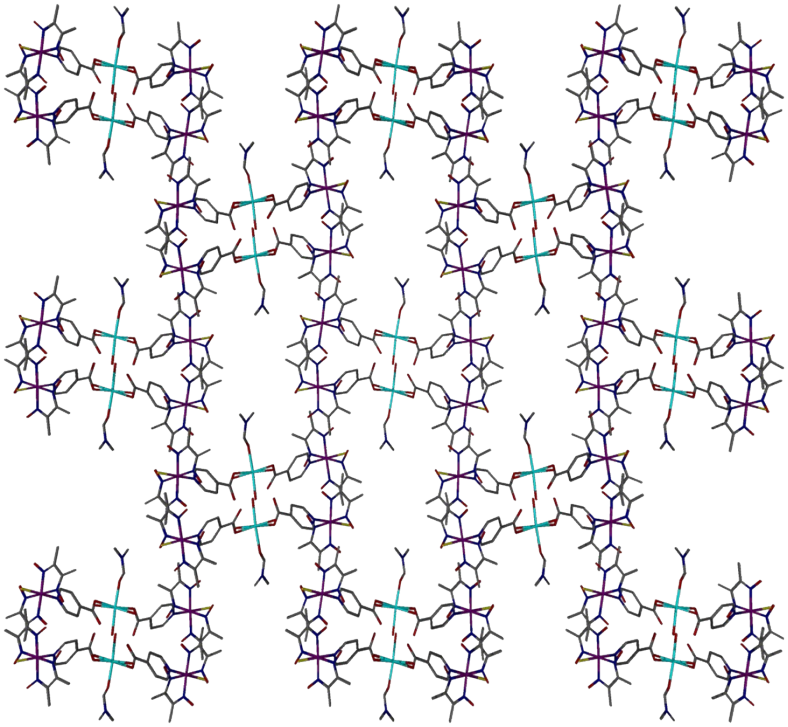

Figure S15: View showing 3D architecture of complex **2** along *a* axis (lattice solvent molecules, minor disorder fractions and hydrogen atoms are omitted for clarity).

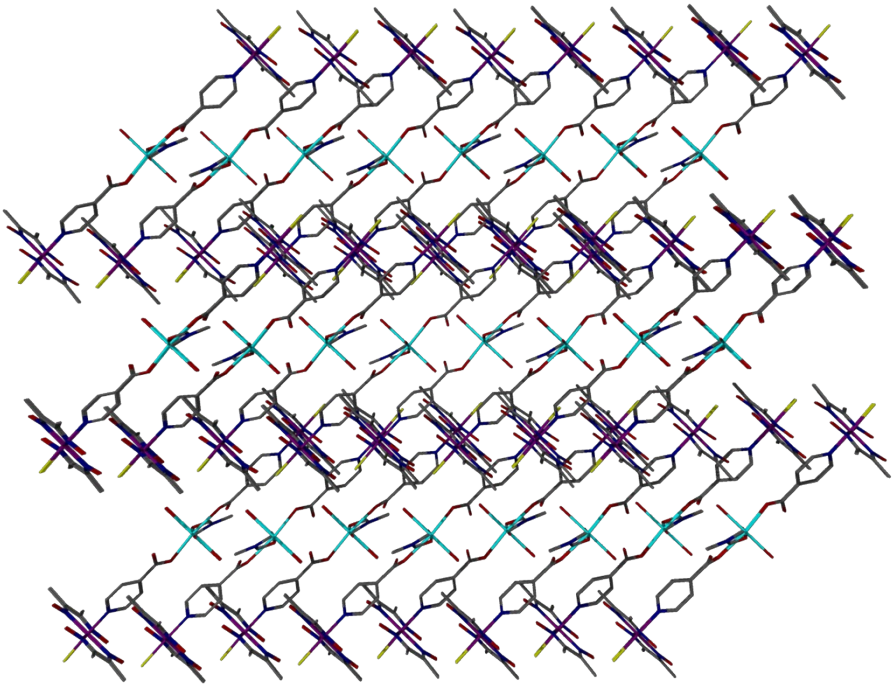

Figure S16: View showing 3D architecture of complex **2** along *b* axis (lattice solvent molecules, minor disorder fractions and hydrogen atoms are omitted for clarity).

Table S1: List of hydrogen bonding interactions in dicobaloximes 1 and 2

For complex 1

No.	Donor(D)-H···Acceptor(A)	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)
1	C16-H16C···O2	0.979(3)	2.661(1)	3.376(3)	130.0(1)
2	C17-H17A···O2	0.980(4)	2.701(1)	3.317(4)	121.2(2)
3	C16-H16A···O6	0.980(3)	2.626(1)	3.599(3)	171.9(1)
4	C1-H1C···Cl1	0.980(2)	2.786(1)	3.758(2)	171.5(1)
5	C16-H16B···Cl1	0.980(2)	2.920(1)	3.861(3)	161.1(1)

For complex 2

No.	Donor(D)-H···Acceptor(A)	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)
1	C12-H12···O2W[1]	0.95	2.44	3.084(4)	125.3
2	C29B-H29B···O11	0.95	1.91	2.665(19)	134.8
3	O5W-H5WA···O4W[2]	0.87	2.00	2.845(5)	164.3
4	O4W-H4WA···O5W	0.87	1.98	2.771	150.4
5	O4W-H4WB···O7WA[3]	0.87	2.13	2.943(6)	155.0
6	O6W-H6WA···O5W	0.87	2.10	2.933	159.1
7	O6W-H6WB···O7WA	0.87	2.21	2.978	146.4
8	O7WA-H7WA···O14A	0.87	2.06	2.807(6)	143.2
9	O7WA-H7WB···O3[4]	0.87	1.96	2.784(4)	156.6
10	O9-H9···O8	0.973(2)	1.524(2)	2.491(3)	171.62(17)
11	O9-H9···N7	0.973(2)	2.203(3)	3.019(4)	140.52(15)
12	O4-H4···O1	0.960(2)	1.552(2)	2.495(3)	166.34(17)
13	O4-H4···N1	0.960(2)	2.234(3)	3.011(4)	137.42(15)
14	O2-H2···O3	0.960(2)	1.559(2)	2.513(3)	172.29(17)
15	O2-H2···N3	0.960(2)	2.196(3)	3.035(4)	145.33(15)
16	O10-H10···O7	0.978(2)	1.505(2)	2.477(3)	172.52(16)
17	O10-H10···N6	0.978(2)	2.201(3)	2.989(4)	136.82(15)
18	O1W-H1WA···O12[5]	0.858(19)	1.95(2)	2.804(4)	171(5)
19	O2W-H2WA···O12[5]	0.851(19)	2.05(2)	2.893(4)	172(6)
20	O2W-H2WB···O6	0.876(19)	1.80(2)	2.646(3)	163(4)
21	O3W-H3WA···O6[1]	0.871(19)	1.84(2)	2.712(3)	175(5)
22	O3W-H3WB···O8[6]	0.862(19)	2.02(2)	2.833(3)	157(4)
23	C5-H5C···O6W	0.980(4)	3.796(2)	4.649(5)	147.1(2)
24	C22-H22C···O4W	0.980(4)	2.794(3)	3.337(5)	118.7(2)
25	O5W-H5WB···Cl1	0.869(3)	2.326(1)	3.191(3)	173.2(2)

[1]1-X,1-Y,1-Z; [2]2-X,2-Y,1-Z; [3]1-X,2-Y,1-Z; [4]+X,3/2-Y,1/2+Z; [5]2-X,1-Y,1-Z; [6] -1+X,+Y,+Z

Table S2: Bond lengths for complex 1

Bond Lengths for complex 1					
Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Zn1	O5	1.9108(14)	N3	C6	1.297(3)
Zn1	O5[1]	1.9108(14)	N4	C7	1.298(3)
Zn1	O7	2.0077(15)	N5	C13	1.346(3)
Zn1	O7[1]	2.0078(15)	N5	C9	1.350(3)
Co1	N3	1.8862(17)	N6	C15	1.300(3)
Co1	N2	1.8891(17)	N6	C17	1.453(3)
Co1	N4	1.8903(17)	N6	C16	1.460(3)
Co1	N1	1.8923(17)	C1	C2	1.491(3)
Co1	N5	1.9563(17)	C2	C3	1.470(3)
Co1	Cl1	2.2411(6)	C3	C4	1.491(3)
O1	N1	1.344(2)	C5	C6	1.494(3)
O2	N2	1.346(2)	C6	C7	1.466(3)
O3	N3	1.341(2)	C7	C8	1.497(3)
O4	N4	1.337(2)	C9	C10	1.377(3)
O5	C14	1.285(3)	C10	C11	1.386(3)
O6	C14	1.225(3)	C11	C12	1.387(3)
O7	C15	1.253(3)	C11	C14	1.506(3)
N1	C2	1.295(3)	C12	C13	1.376(3)
N2	C3	1.293(3)			
[1]1-X,+Y,1/2-Z					

Table S3: Bond angles for complex 1

Bond Angles for complex 1							
Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
O5	Zn1	O5[1]	138.99(10)	C7	N4	O4	121.14(17)
O5	Zn1	O7	110.33(6)	C7	N4	Co1	116.38(14)
O5[1]	Zn1	O7	98.23(6)	O4	N4	Co1	122.22(13)
O5	Zn1	O7[1]	98.23(6)	C13	N5	C9	118.14(18)
O5[1]	Zn1	O7[1]	110.33(6)	C13	N5	Co1	120.48(14)
O7	Zn1	O7[1]	91.12(9)	C9	N5	Co1	121.38(14)
N3	Co1	N2	98.49(8)	C15	N6	C17	121.2(2)
N3	Co1	N4	81.39(7)	C15	N6	C16	121.60(19)
N2	Co1	N4	178.87(7)	C17	N6	C16	117.2(2)
N3	Co1	N1	178.89(7)	N1	C2	C3	112.83(18)
N2	Co1	N1	81.52(7)	N1	C2	C1	123.37(19)
N4	Co1	N1	98.58(7)	C3	C2	C1	123.80(18)

Bond Angles for complex 1							
Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
N3	Co1	N5	89.10(7)	N2	C3	C2	112.56(18)
N2	Co1	N5	89.60(7)	N2	C3	C4	123.08(19)
N4	Co1	N5	89.28(7)	C2	C3	C4	124.35(19)
N1	Co1	N5	89.79(7)	N3	C6	C7	112.72(18)
N3	Co1	Cl1	91.53(5)	N3	C6	C5	122.5(2)
N2	Co1	Cl1	90.05(5)	C7	C6	C5	124.8(2)
N4	Co1	Cl1	91.07(5)	N4	C7	C6	112.40(18)
N1	Co1	Cl1	89.58(5)	N4	C7	C8	123.1(2)
N5	Co1	Cl1	179.32(5)	C6	C7	C8	124.46(19)
C14	O5	Zn1	113.70(13)	N5	C9	C10	122.31(19)
C15	O7	Zn1	118.67(14)	C9	C10	C11	119.39(19)
C2	N1	O1	121.43(17)	C10	C11	C12	118.33(19)
C2	N1	Co1	116.26(14)	C10	C11	C14	120.90(18)
O1	N1	Co1	122.31(13)	C12	C11	C14	120.74(19)
C3	N2	O2	120.90(17)	C13	C12	C11	119.41(19)
C3	N2	Co1	116.60(14)	N5	C13	C12	122.41(19)
O2	N2	Co1	122.44(13)	O6	C14	O5	125.21(19)
C6	N3	O3	121.04(18)	O6	C14	C11	120.90(19)
C6	N3	Co1	116.50(14)	O5	C14	C11	113.90(18)
O3	N3	Co1	122.38(14)	O7	C15	N6	124.1(2)
[1]1-X,+Y,1/2-Z							

Table S4: Bond lengths for complex 2

Bond lengths for complex 2					
Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Cd1	O5	2.323(2)	N10	C23	1.348(4)
Cd1	O11	2.252(3)	N10	C27	1.348(4)
Cd1	O13	2.265(3)	C1	C2	1.485(5)
Cd1	O1W	2.339(3)	C2	C3	1.460(5)
Cd1	O2W	2.302(3)	C3	C4	1.495(5)
Cd1	O3W	2.338(2)	C5	C6	1.487(5)
Co1	Cl1	2.2371(9)	C6	C7	1.471(5)
Co1	N1	1.899(3)	C7	C8	1.486(5)
Co1	N2	1.895(3)	C9	C10	1.384(5)
Co1	N3	1.900(3)	C10	C11	1.376(5)
Co1	N4	1.894(3)	C11	C12	1.389(5)
Co1	N5	1.956(3)	C11	C14	1.523(5)
Co2	Cl2	2.2291(9)	C12	C13	1.387(5)
Co2	N6	1.883(3)	C16	C17	1.467(5)

Bond lengths for complex 2					
Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Co2	N7	1.899(3)	C16	C32	1.491(5)
Co2	N8	1.900(3)	C17	C18	1.495(5)
Co2	N9	1.898(3)	C19	C20	1.489(5)
Co2	N10	1.957(3)	C20	C21	1.479(5)
O1	N1	1.349(4)	C21	C22	1.491(5)
O2	N2	1.350(3)	C23	C24	1.384(5)
O3	N3	1.341(3)	C24	C25	1.382(5)
O4	N4	1.363(3)	C25	C26	1.382(5)
O5	C14	1.254(4)	C25	C28	1.513(5)
O6	C14	1.255(4)	C26	C27	1.374(5)
O7	N6	1.345(3)	O14A	C32A	1.202(7)
O8	N7	1.347(4)	N11A	C29A	1.298(6)
O9	N8	1.358(3)	N11A	C30A	1.415(10)
O10	N9	1.350(4)	N11A	C31A	1.465(7)
O11	C28	1.260(4)	N12A	C32A	1.303(8)
O12	C28	1.252(5)	N12A	C33A	1.425(10)
O13	C29A	1.275(5)	N12A	C34A	1.470(8)
O13	C29B	1.254(18)	O14B	C32B	1.07(4)
N1	C2	1.303(4)	N11B	C29B	1.34(2)
N2	C3	1.294(4)	N11B	C30B	1.39(4)
N3	C6	1.297(4)	N11B	C31B	1.46(3)
N4	C7	1.293(4)	N12B	C32B	1.34(4)
N5	C9	1.348(4)	N12B	C33B	1.48(2)
N5	C13	1.342(4)	N12B	C34B	1.47(3)
N6	C16	1.302(4)	O14C	C32C	1.23451(5)
N7	C17	1.293(4)	N12C	C32C	1.31196(5)
N8	C20	1.283(4)	N12C	C33C	1.47155(5)
N9	C21	1.290(4)	N12C	C34C	1.47740(8)

Table S5: Bond angles for complex 2

Bond Angles for complex 2							
Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
O5	Cd1	O1W	91.44(9)	C20	N8	O9	119.9(3)
O5	Cd1	O3W	87.16(9)	O10	N9	Co2	121.9(2)
O11	Cd1	O5	166.31(9)	C21	N9	Co2	116.8(2)
O11	Cd1	O13	83.20(10)	C21	N9	O10	121.2(3)
O11	Cd1	O1W	98.31(10)	C23	N10	Co2	121.4(2)

Bond Angles for complex 2							
Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
O11	Cd1	O2W	102.79(10)	C27	N10	Co2	120.6(2)
O11	Cd1	O3W	84.55(9)	C27	N10	C23	117.9(3)
O13	Cd1	O5	86.31(9)	N1	C2	C1	123.3(3)
O13	Cd1	O1W	95.62(10)	N1	C2	C3	112.2(3)
O13	Cd1	O2W	173.82(9)	C3	C2	C1	124.5(3)
O13	Cd1	O3W	92.60(9)	N2	C3	C2	113.7(3)
O2W	Cd1	O5	87.54(9)	N2	C3	C4	122.6(3)
O2W	Cd1	O1W	85.10(10)	C2	C3	C4	123.7(3)
O2W	Cd1	O3W	86.52(9)	N3	C6	C5	125.7(3)
O3W	Cd1	O1W	171.56(10)	N3	C6	C7	112.6(3)
N1	Co1	Cl1	90.99(9)	C7	C6	C5	121.7(3)
N1	Co1	N3	179.49(13)	N4	C7	C6	112.6(3)
N1	Co1	N5	90.09(12)	N4	C7	C8	123.6(3)
N2	Co1	Cl1	87.68(9)	C6	C7	C8	123.8(3)
N2	Co1	N1	81.33(12)	N5	C9	C10	122.4(3)
N2	Co1	N3	99.13(12)	C11	C10	C9	119.7(3)
N2	Co1	N5	91.11(12)	C10	C11	C12	118.2(3)
N3	Co1	Cl1	89.26(9)	C10	C11	C14	121.0(3)
N3	Co1	N5	89.68(12)	C12	C11	C14	120.7(3)
N4	Co1	Cl1	89.58(9)	C13	C12	C11	119.3(3)
N4	Co1	N1	98.43(12)	N5	C13	C12	122.4(3)
N4	Co1	N2	177.25(12)	O5	C14	O6	126.5(3)
N4	Co1	N3	81.12(12)	O5	C14	C11	116.5(3)
N4	Co1	N5	91.63(12)	O6	C14	C11	117.0(3)
N5	Co1	Cl1	178.24(9)	N6	C16	C17	112.5(3)
N6	Co2	Cl2	88.95(9)	N6	C16	C32	123.0(3)
N6	Co2	N7	81.47(12)	C17	C16	C32	124.5(3)
N6	Co2	N8	177.05(13)	N7	C17	C16	112.8(3)
N6	Co2	N9	98.90(12)	N7	C17	C18	124.1(3)
N6	Co2	N10	91.40(12)	C16	C17	C18	123.0(3)
N7	Co2	Cl2	92.12(9)	N8	C20	C19	124.1(3)
N7	Co2	N8	98.62(12)	N8	C20	C21	112.6(3)
N7	Co2	N10	90.45(12)	C21	C20	C19	123.2(3)
N8	Co2	Cl2	88.11(9)	N9	C21	C20	112.5(3)
N8	Co2	N10	91.55(12)	N9	C21	C22	125.2(3)
N9	Co2	Cl2	88.44(9)	C20	C21	C22	122.1(3)
N9	Co2	N7	179.34(13)	N10	C23	C24	122.0(3)
N9	Co2	N8	81.05(12)	C25	C24	C23	119.9(3)
N9	Co2	N10	88.99(12)	C24	C25	C26	117.8(3)
N10	Co2	Cl2	177.43(9)	C24	C25	C28	122.2(3)
C14	O5	Cd1	127.5(2)	C26	C25	C28	120.0(3)
C28	O11	Cd1	113.7(2)	C27	C26	C25	119.9(3)

Bond Angles for complex 2							
Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
C29A	O13	Cd1	123.5(3)	N10	C27	C26	122.4(3)
C29B	O13	Cd1	110.2(9)	O11	C28	C25	116.3(3)
O1	N1	Co1	122.2(2)	O12	C28	O11	125.7(3)
C2	N1	Co1	116.5(2)	O12	C28	C25	118.0(3)
C2	N1	O1	121.2(3)	C29A	N11A	C30A	121.7(5)
O2	N2	Co1	123.4(2)	C29A	N11A	C31A	121.3(5)
C3	N2	Co1	116.2(2)	C30A	N11A	C31A	117.0(6)
C3	N2	O2	120.4(3)	C32A	N12A	C33A	124.1(6)
O3	N3	Co1	121.3(2)	C32A	N12A	C34A	117.5(6)
C6	N3	Co1	116.6(2)	C33A	N12A	C34A	118.2(7)
C6	N3	O3	122.1(3)	O13	C29A	N11A	124.5(5)
O4	N4	Co1	123.2(2)	O14A	C32A	N12A	128.3(7)
C7	N4	Co1	117.0(2)	C29B	N11B	C30B	124(2)
C7	N4	O4	119.8(3)	C29B	N11B	C31B	122.2(18)
C9	N5	Co1	120.9(2)	C30B	N11B	C31B	114(2)
C13	N5	Co1	121.2(2)	C32B	N12B	C33B	123.7(18)
C13	N5	C9	117.9(3)	C32B	N12B	C34B	121.4(19)
O7	N6	Co2	122.2(2)	C34B	N12B	C33B	114.7(17)
C16	N6	Co2	116.7(2)	O13	C29B	N11B	120.6(16)
C16	N6	O7	121.1(3)	O14B	C32B	N12B	124(3)
O8	N7	Co2	121.6(2)	C32C	N12C	C33C	119.340(4)
C17	N7	Co2	116.4(2)	C32C	N12C	C34C	121.212(2)
C17	N7	O8	122.0(3)	C33C	N12C	C34C	118.855(2)
O9	N8	Co2	123.1(2)	O14C	C32C	N12C	132.210(1)
C20	N8	Co2	117.0(2)				

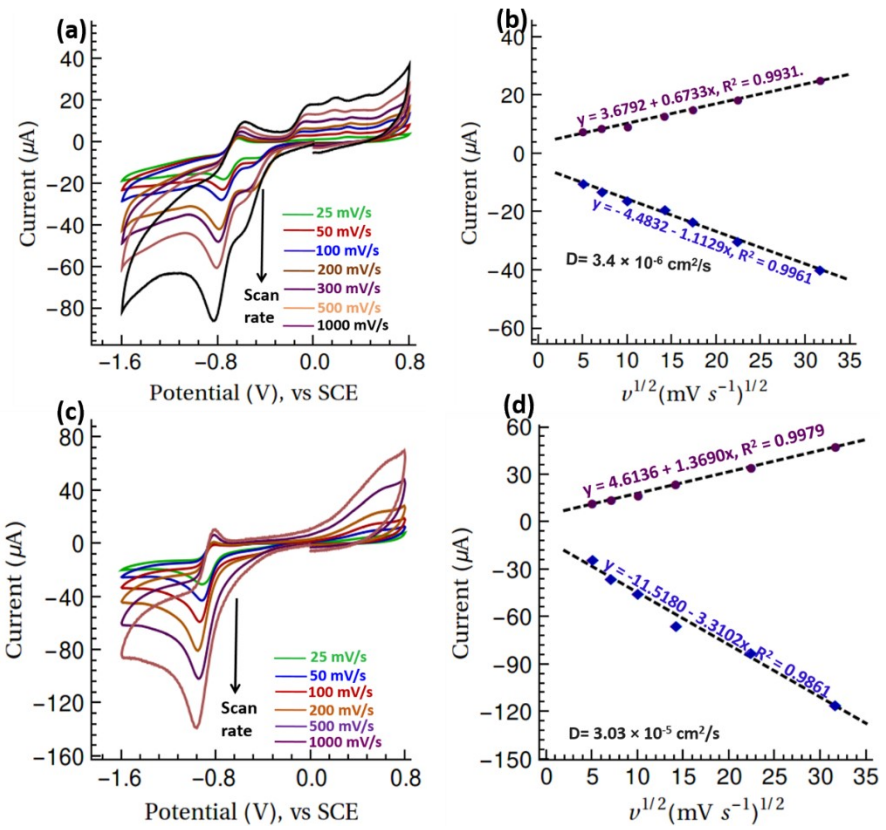

Figure S17: (a) Effect of variation of scan rate from 25 mV/s to 1000 mV/s on cyclic voltammogram of 1 mM complex **1** (a) and **2** (c) in DMF/water (95/5, v/v) containing 0.1 M $[NBu_4][PF_6]$. Fig. (b) and (d) show the variation of peak current with the square root of scan rate for complexes **1** and **2,** respectively.

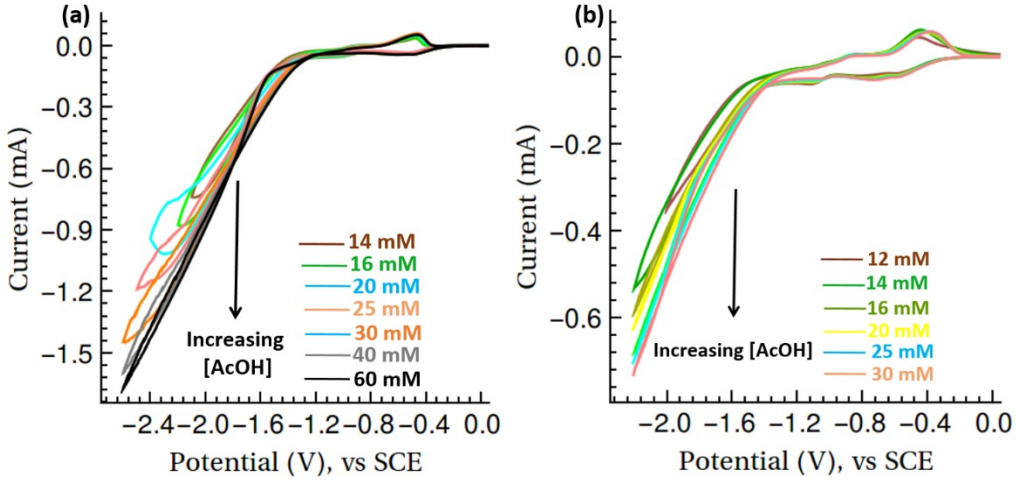

Figure S18: Variation of high acid concentration for complex **1** and **2** in DMF/water (95/5, v/v) containing 0.1 M $[NBu_4][PF_6]$.

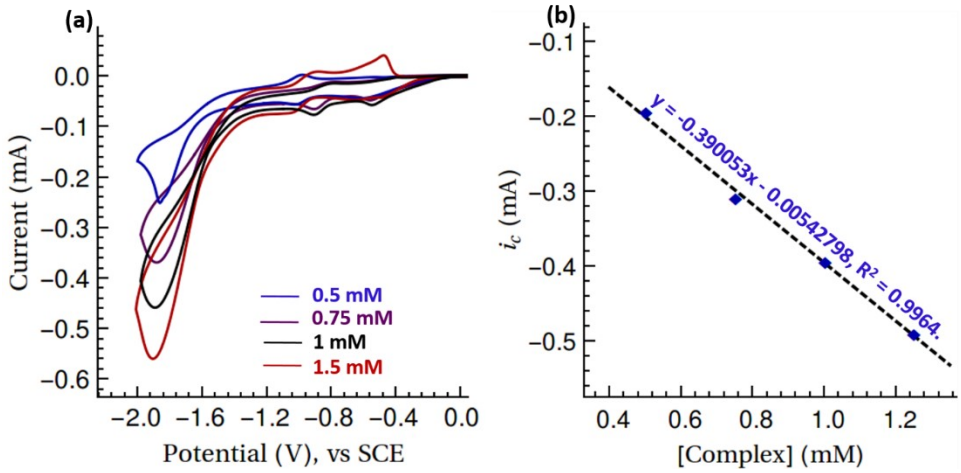

Figure S19: (a) CV of complex **1** on varying complex concentration in DMF/water (95/5, v/v) containing 0.1 M $[NBu_4][PF_6]$.

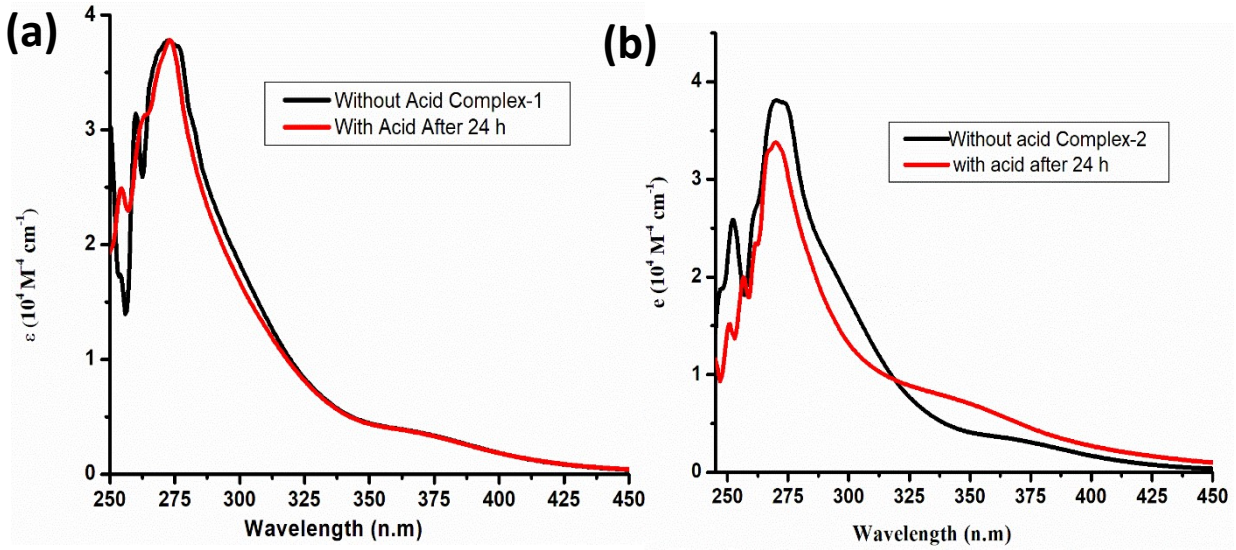

Figure S20: Time dependent U.V –Vis spectra of Complex **1** and **2** in DMF solution at 10^{-4} molar concentration (Stability measurement)