Electronic Supplementary Information

Supramolecular and theoretical perspective of 2,2′:6′,2″-terpyridine based Ni(II) and Cu(II) complexes: On the importance of C–H···Cl and π···π interaction

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Contents of the Supporting Information

Table S1. Selected crystallographic features of structures **1** and **2**

Compound	**1**	**2**
Empirical formula	$C_{15}H_{15}Cl_2N_3NiO_2$	$C_{15}H_{11}Cl_2CuN_3$
Formula weight	398.89	367.72
Temperature (K)	293 K	273 K
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	P 2_1/n	P 2_1/c
Unit cell dimensions		
a (Å)	12.485(6)	10.671(10)
b (Å)	9.687(4)	8.258(7)
c (Å)	14.318(6)	16.090(16)
α (˚)	90	90
β (˚)	105.290(15)	94.686(3)
γ (˚)	90	90
Volume ($Å^3$)	1670.4(13)	1413.2(2)
Crystal size (mm^3)	0.07x0.13x0.21	0.08x0.12x0.17
z	4	4
Densitycal (Mg m^{-3})	1.586	1.728
Absorption coefficient (mm^{-1})	1.492	1.917
F(000)	816.0	740.0
θ Range (˚) for data collection	2.87 – 25.88	1.915 – 27.218
Index ranges	$-16 \le h \le 16$ $-12 \le k \le 12$ $-18 \le l \le 18$	$-13 \le h \le 13$ $-10 \le k \le 10$ $-20 \le l \le 20$
Goodness-of-fit on F^2	0.893	0.938
Independent reflections [Rint]	3686 (0.035)	3130
Absorption correction	Multi-scan	Multi-scan
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F^2
Data/restraints/parameters	3686/ 0/ 224	3130/ 0/ 234
Reflections collected	24244	20311
Final R indices[I > 2σ (I)]	R=0.0273 wR_2=0.1204	R=0.0240 wR_2=0.1103
Largest difference peak & hole($eÅ^{-3}$)	-1.27, 0.83	-0.92, 0.83

Table S2. Selected bond distances (Å) and angles (°) in **1** and **2**

Selected Bonds	Value (Å)	Selected Angles	(°)
Complex 1			
Ni1 - N1	2.105(2)	N1 - Ni1 - N2	78.65(9)
Ni1 - N2	1.9854(19)	N2 - Ni1 - N3	78.69(9)
Ni1 - N3	2.087(2)	N2 - Ni1 - O2	174.33(8)
Ni1 - O1	2.097(2)	N2 - Ni1 - O1	91.07(8)
Ni1 - O2	2.0557(18)	N3 - Ni1 - O2	98.01(8)
Ni1 – Cl1	2.386(13)	N3 - Ni1 - N1	157.34(9)
		Cl1 - Ni1 - O1	174.75(6)
		Cl1 - Ni1 - O2	90.51(5)
		N1 - Ni1 - O2	104.59(8)
		N3 - Ni1 - O1	89.04(9)
		Cl1 - Ni1 - N1	89.67(6)
		Cl1 - Ni1 - N2	94.18(6)
		Cl1 - Ni1 - N3	91.90(6)
		O2 - Ni1 - O1	84.25(8)
Complex 2			
Cu1 - N1	2.0552(18)	N1 - Cu1 - N2	78.96(7)
Cu1 - N2	1.9614(16)	N2 - Cu1 - N3	78.82(7)
Cu1 - N3	2.0572(17)	Cl1 - Cu1 - N1	99.51(5)
Cu1 - Cl1	2.4699(6)	Cl1 - Cu1 - N2	98.36(5)
Cu1 - Cl2	2.2496(6)	Cl1 - Cu1 - N3	92.57(5)
		Cl1 - Cu1 - Cl2	104.39(2)
		Cl2 - Cu1 - N1	97.24(5)
		Cl2 - Cu1 - N2	157.25(5)
		Cl2 - Cu1 - N3	99.74(5)
		N1 - Cu1 - N3	156.00(7)

Table S3. Geometric features (distances in Å and angles in degrees) of π···π interactions obtained for **1** and **2**

Cg(ring I) - Cg(ring J)	Cg···Cg (Å)	Cg(I) ···perp (Å)	Cg(J) ···perp (Å)	α (°)	β (°)	γ (°)	Symmetry
Complex 1							
Cg(3)···Cg(5)	3.593(2)	3.453	3.493	2.84	13.53	16.04	-1/2+x, 1/2-y, -1/2+z
Cg(5)···Cg(3)	3.593(2)	3.493	3.453	2.84	16.04	13.53	1/2+x, 1/2-y,1/2+z
Complex 2							
Cg(1)···Cg(5)	3.4970(12)	3.277	3.342	5.59	17.11	20.43	1-x, 1-y, 1-z
Cg(5)···Cg(1)	3.4969(12)	3.342	3.277	5.59	20.43	17.11	1-x, 1-y, 1-z
Cg(2)···Cg(2)	3.5839(11)	3.348	3.348	0.02	20.90	20.90	1-x, 1-y, 1-z
Cg(2)···Cg(5)	3.5184(12)	3.346	3.354	2.51	17.56	18.02	1-x, 1-y, 1-z
Cg(5)···Cg(2)	3.5183(12)	3.354	3.346	2.51	18.02	17.56	1-x, 1-y, 1-z
Cg(3)···Cg(4)	3.7469(12)	3.341	3.473	4.93	22.05	26.9	-x, 1-y, 1-z
Cg(4)···Cg(3)	3.7468(12)	3.473	3.341	4.93	26.9	22.05	-x, 1-y, 1-z
Cg(4)···Cg(5)	3.6812(13)	3.299	3.281	2.31	26.95	26.34	1-x, 1-y, 1-z
Cg(5)···Cg(4)	3.6811(13)	3.281	3.299	2.31	26.34	26.95	1-x, 1-y, 1-z
Cg(5)···Cg(5)	3.6706(13)	3.288	3.288	0.02	26.40	26.40	1-x, -y, 1-z

α = Dihedral angle between ring I and ring J (°); β = Cg(I) →Cg(J) or Cg(I) → Me vector and normal to plane I (°); γ = Cg(I) → Cg(J) vector and normal to plane J (°); Cg–Cg = distance between ring centroids (Å); CgI···Perp = perpendicular distance of Cg(I) on ring J (Å); CgJ···Perp = perpendicular distance of Cg(J) on ring I (Å).

Cg(3) = Centre of gravity of ring [N1/C1/C2/C3/C4/C5] and Cg(5) = Centre of gravity of ring [N3/C11/C12/C13/C14/C15] for complex **1,** Cg(1) = Centre of gravity of ring [Cu1/N1/C5/C6/N2], Cg(2) = Centre of gravity of ring [Cu1/N2/C10/C11/N3], Cg(3) = Centre of gravity of ring [N1/C1/C2/C3/C4/C5], Cg(4) = Centre of gravity of ring [N2/C6/C7/C8/C9/C10] and Cg(5) = Centre of gravity of ring [N3/C11/C12/C13/C14/C15].

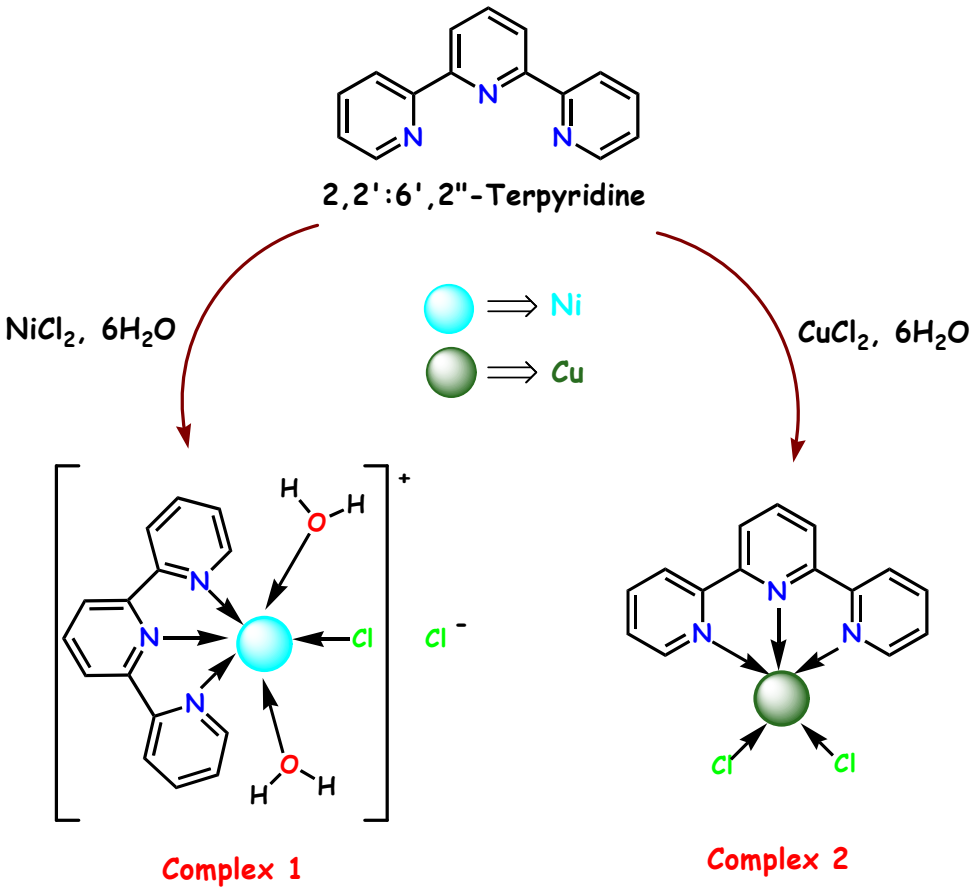
Table S4. Details of Hydrogen bond distances (Å) and angles (°) for **1** and **2**

D – H ⋯A	D (D – H)	D (HA)	D(D⋯A)	<DHA
Complex 1				
O1–H12⋯Cl2	0.78(4)	2.28(4)	3.052(3)	173(3)
O1–H13⋯Cl2	0.72(3)	2.44(4)	3.115(3)	156(4)
O2–H15⋯Cl1	0.83(4)	2.26(4)	3.073(2)	167(3)
C4–H4⋯Cl1	0.93	2.82	3.693(3)	156
Complex 2				
C2–H2⋯Cl1	0.97(3)	2.76(3)	3.446(2)	128(2)
C4–H4⋯Cl1	0.88(3)	2.64(3)	3.479(2)	159(2)

Table S5. Geometric features (distances in Å and angles in degrees) of metal cation⋯π interaction obtained for complex **2**

Cation ⋯Cg	Cg(I) ⋯Cation (Å)	Cation(J) ⋯Perp (Å)	β (°)	Symmetry
Cu1⋯Cg (5)	3.848	3.465	25.8	1-x, 1-y, 1-z

Cg(5) = Centre of gravity of ring [N3/C11/C12/C13/C14/C15]



Scheme S1. Schematic representations of the synthesis of complex **1** and **2**

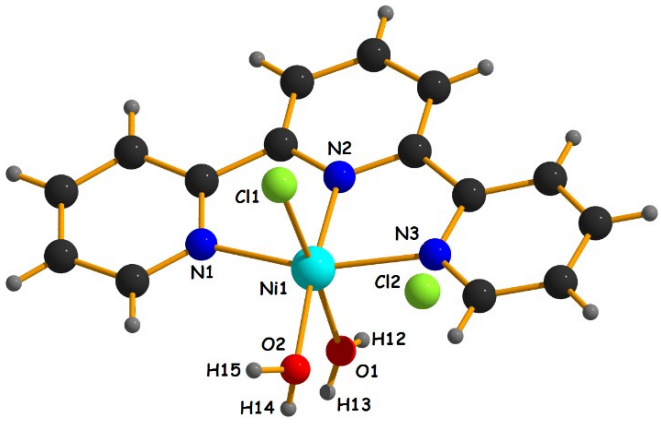


Figure S1. Asymmetric unit of Complex **1**

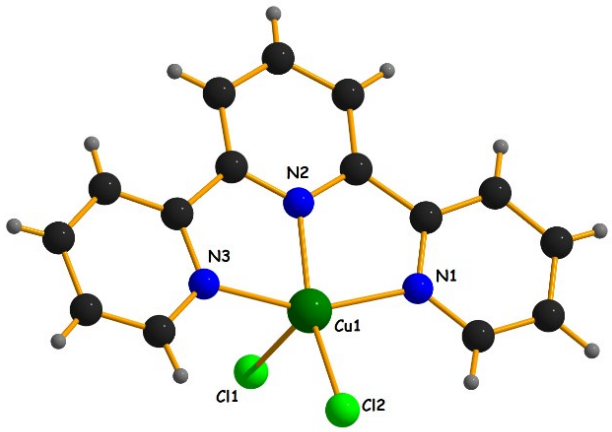
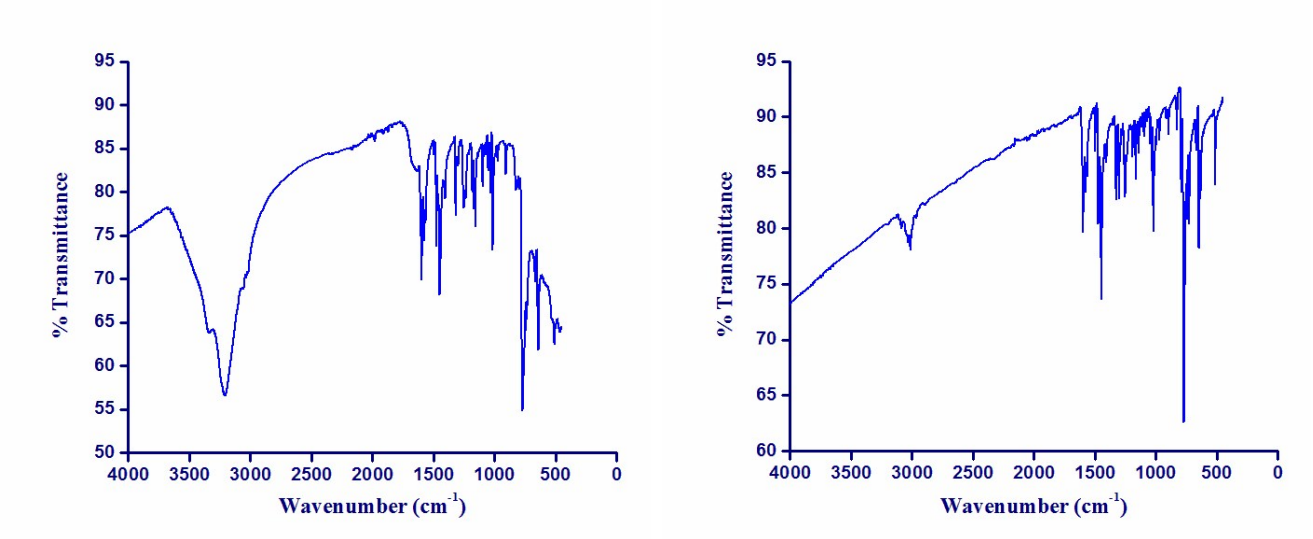
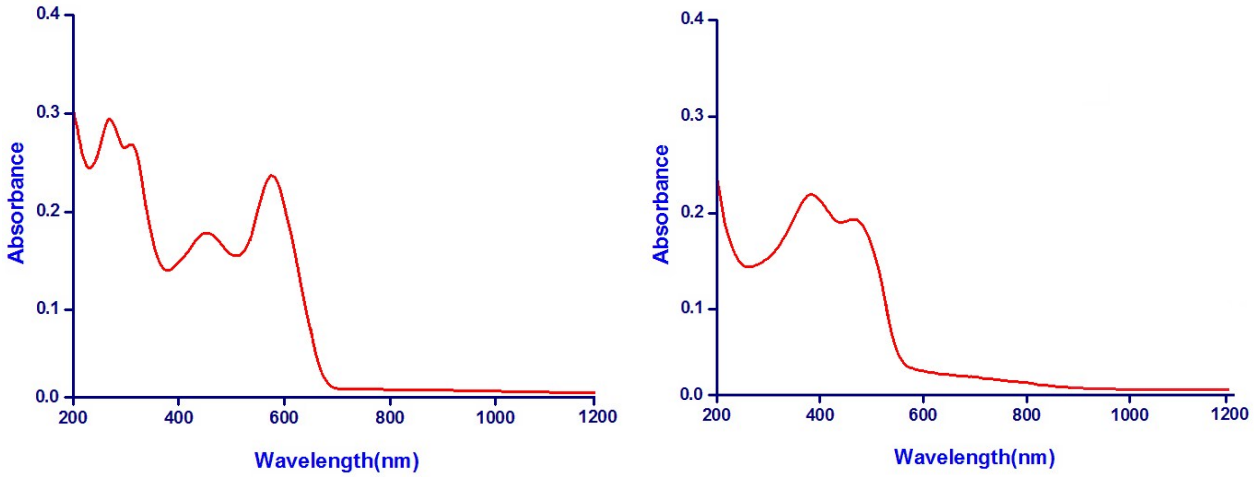


Figure S2. Asymmetric unit of Complex **2**



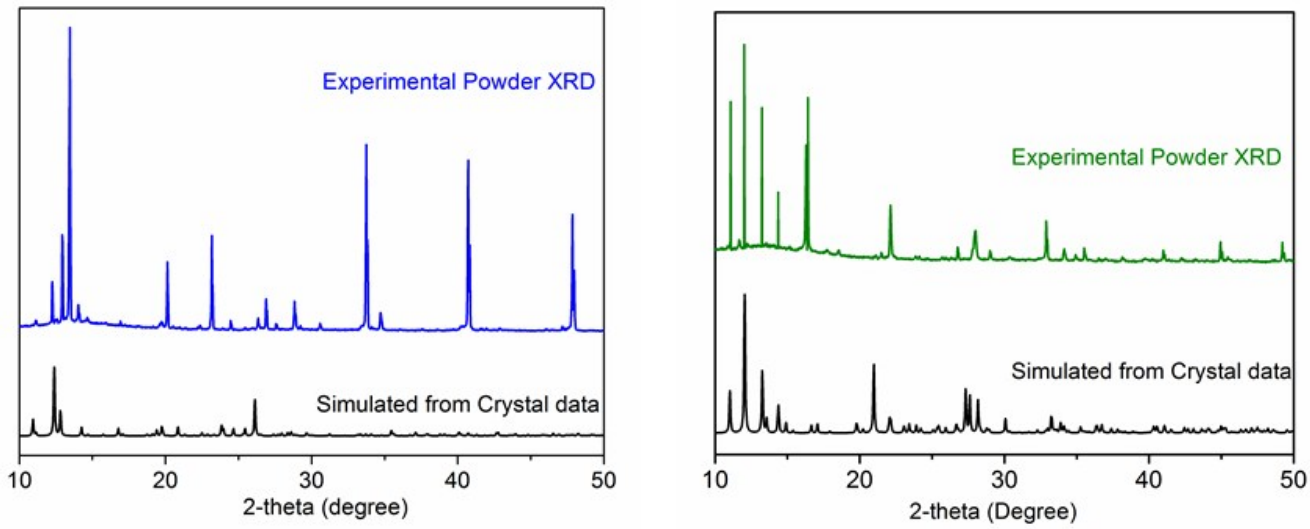
Complex **1** Complex **2**

Figure S3. IR spectra for Complex **1** and **2**



Complex **1** Complex **2**

Figure S4. UV – Vis -NIR spectra for Complex **1** and **2**



Complex 1 **Complex 2**

Figure S5. PXRD patterns of experimental powder XRD (blue) for complex **1** and green for complex **2** and simulated pattern from single crystal data (black)

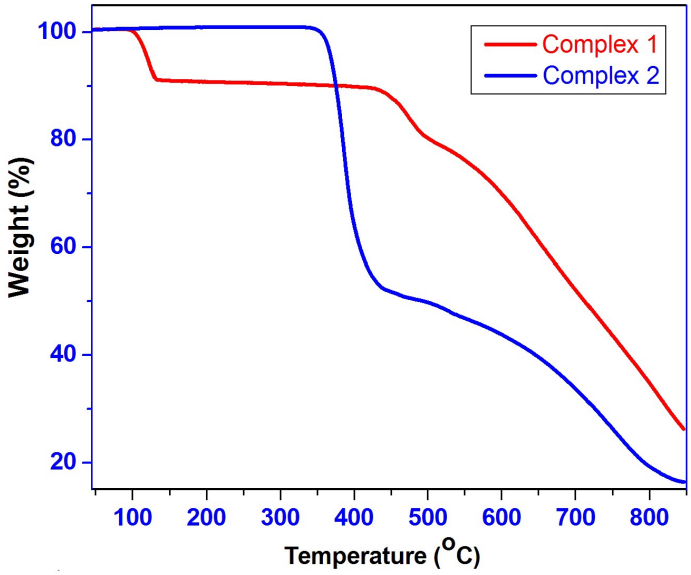


Figure S6. TGA of Complex **1** and **2** measured under N_2 atmosphere