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Pentanuclear M^{II}–Mn^{II} (M = Ni and Cu) complexes of N_2O_2 donor ligands with the variation of carboxylate anions: syntheses, structures, magnetic properties and catecholase-like activities

Sayantan Ganguly,[a,b] Pradip Bhunia,[a] Júlia Mayans,[c] Ashutosh Ghosh[a,d]*

[a]*Department of Chemistry, University College of Science, University of Calcutta, 92, A. P. C. Road, Kolkata-700 009, India; e-mail: ghosh_59@yahoo.com*

[b]*Department of Chemistry, Taki Government College, Taki, Hasnabad, West Bengal 743429, India*

[c]*Departament de Química Inorgànica i Orgànica and Institut de Nanociència i Nanotecnologia (IN²UB).Universitat de Barcelona (UB), Martí iFranqués 1-11, Barcelona-08028, Spain.*

[d]*Rani Rashmoni Green University, Tarakeswar, Hooghly 712410, West Bengal, India*

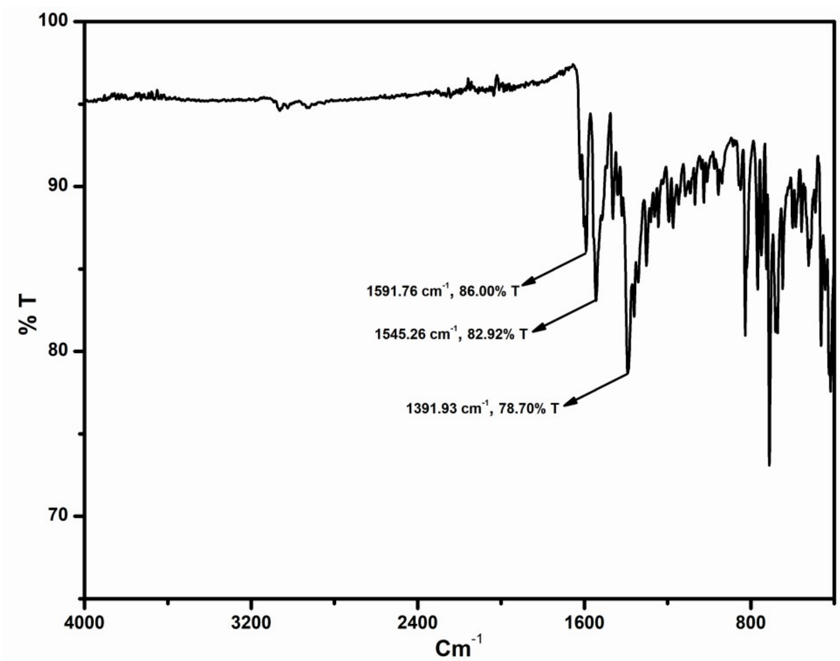

Figure S1. Representative IR spectrum of complex **1**.

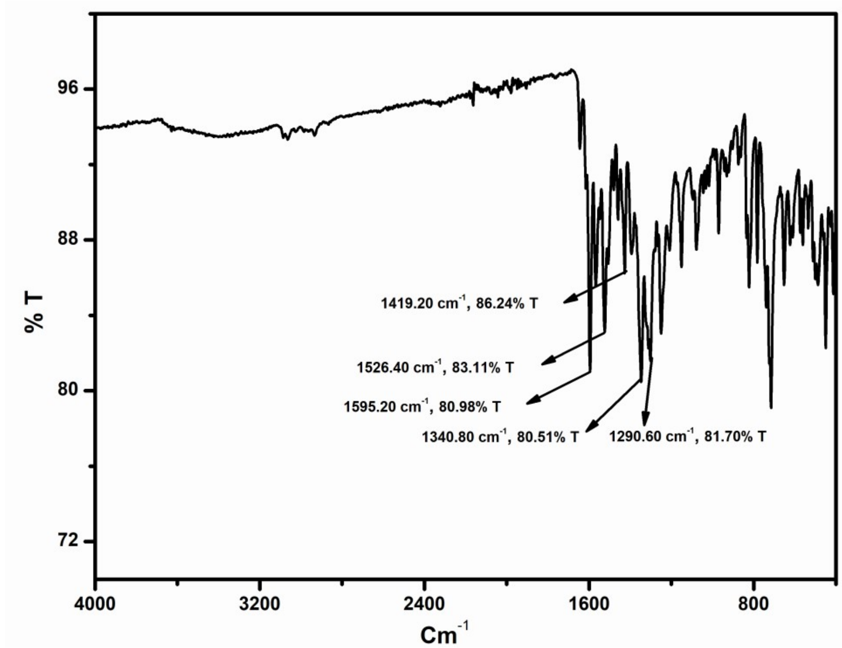

Figure S2. Representative IR spectrum of complex **2**.

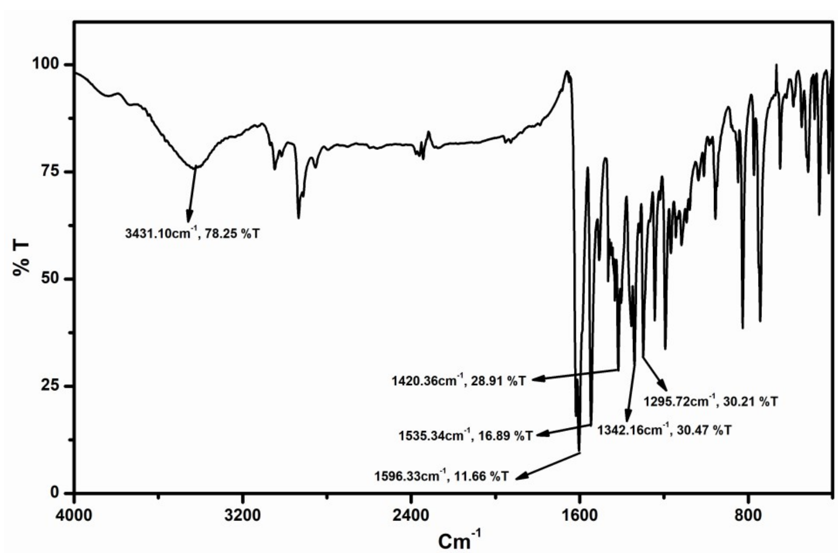

Figure S3. Representative IR spectrum of complex **3**.

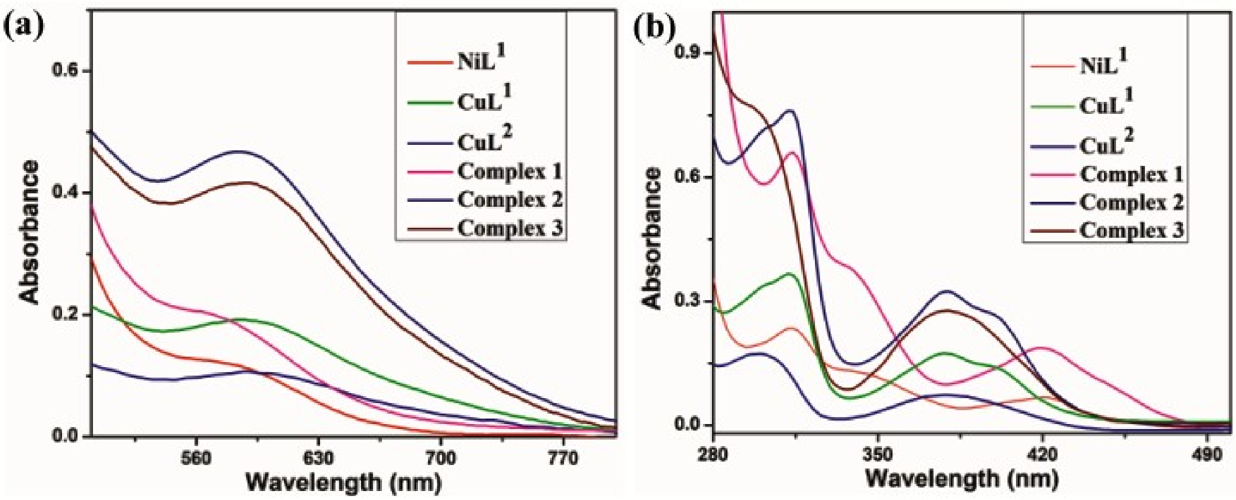

Figure S4. Representative UV-Vis spectra of NiL^1, CuL^1, CuL^2 and complexes (**1**–**3**) in DMF-acetonitrile solution (left) d-d transition and (right) charge transfer band.

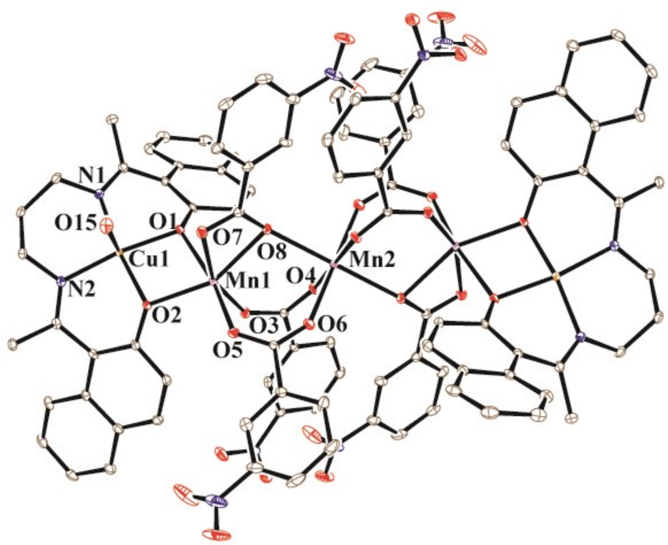

Figure S5. The structure of complex **3** with ellipsoid at 30% probability. Hydrogen atoms omitted for clarity.

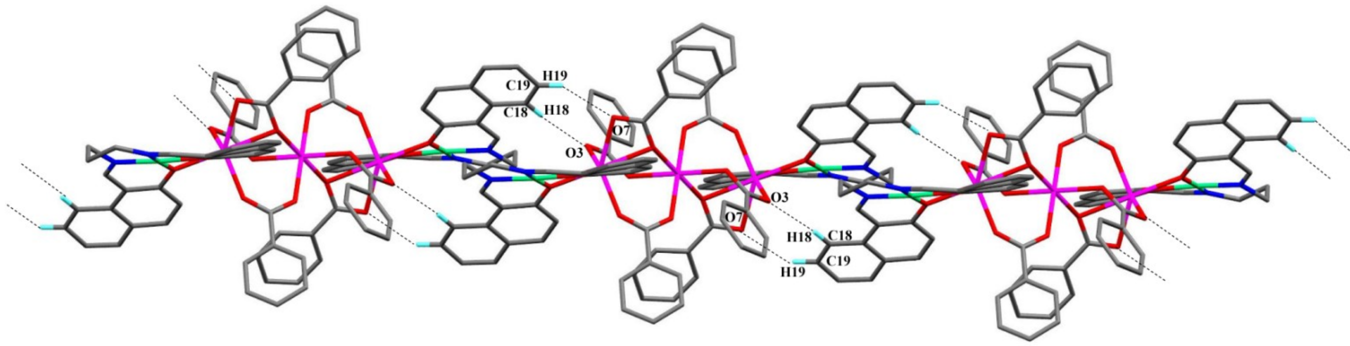

Figure S6. The 1D chain of complex **1** formed by intermolecular hydrogen bonding interactions. The other H-atoms are removed for picture clarity.

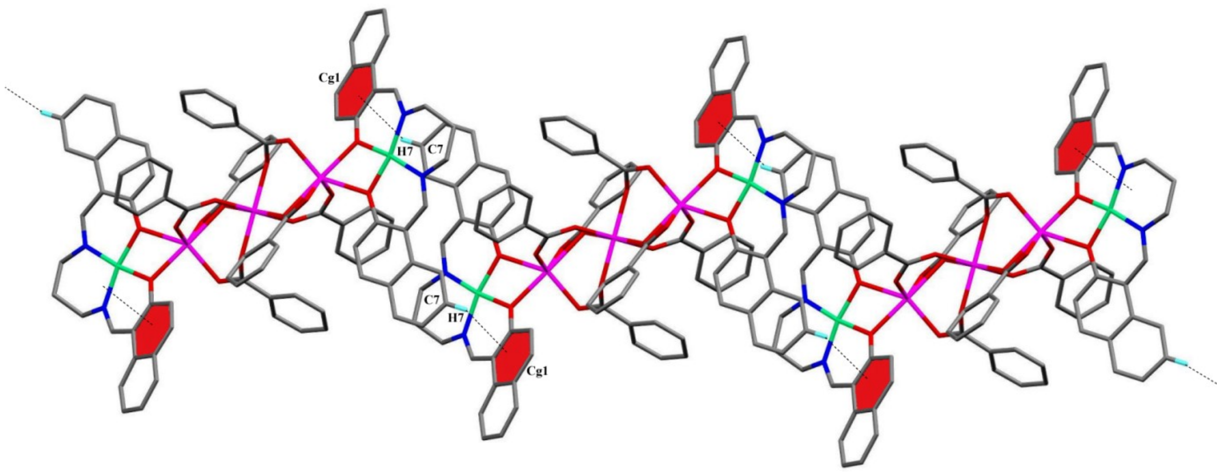

Figure S7. Formation of intermolecular C–H·····π in complex **1**. Other H-atoms are removed for picture clarity.

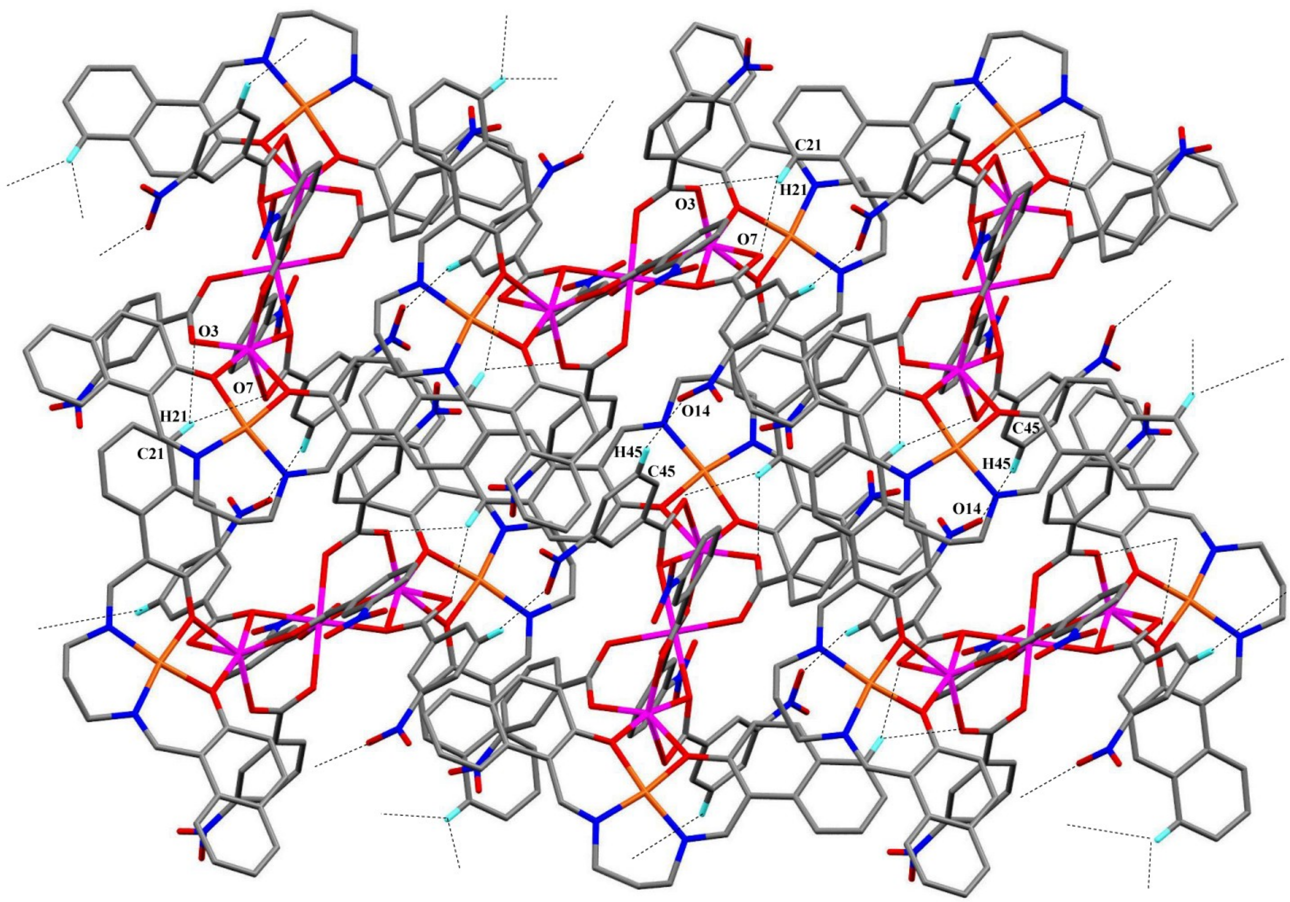

Figure S8. The 1D chain of complex **2** formed by intermolecular hydrogen bonding interactions. The other H-atoms are removed for picture clarity.

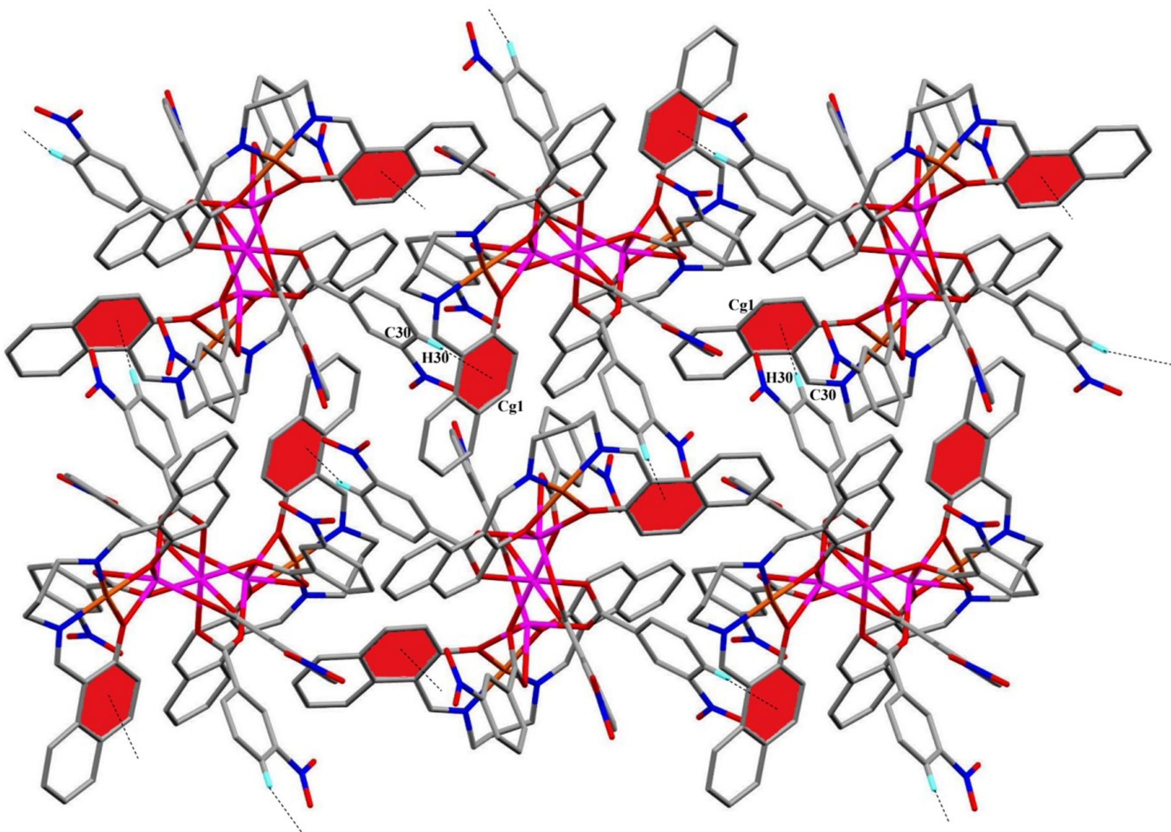

Figure S9. Formation of intermolecular C–H·····π in complex **2**. Other H-atoms are removed for picture clarity.

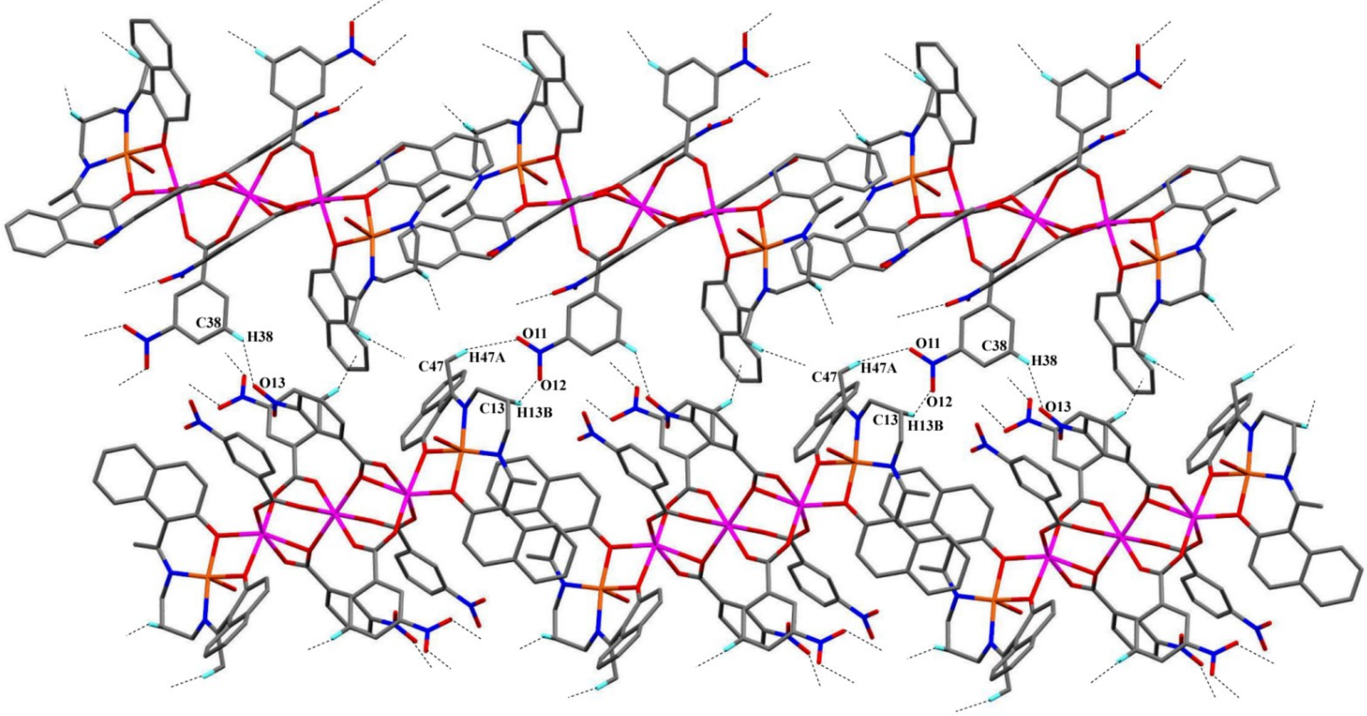

Figure S10. The 1D chain of complex **3** formed by intermolecular hydrogen bonding interactions. The other H-atoms are removed for picture clarity.

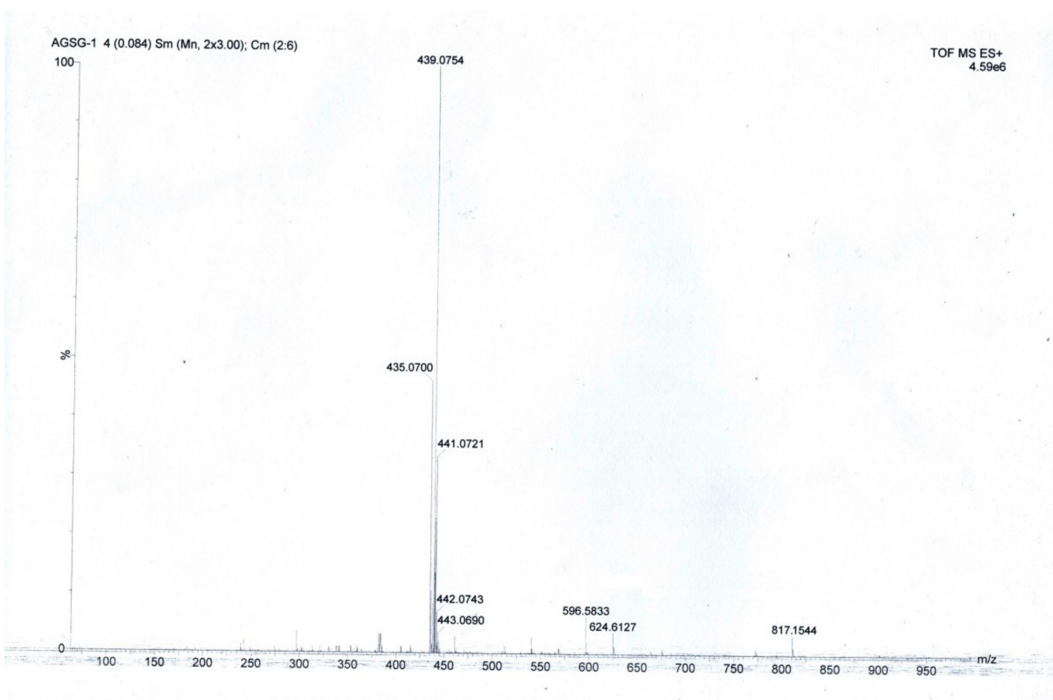

Figure S11. Representative ESI mass spectrum of complex **1**.

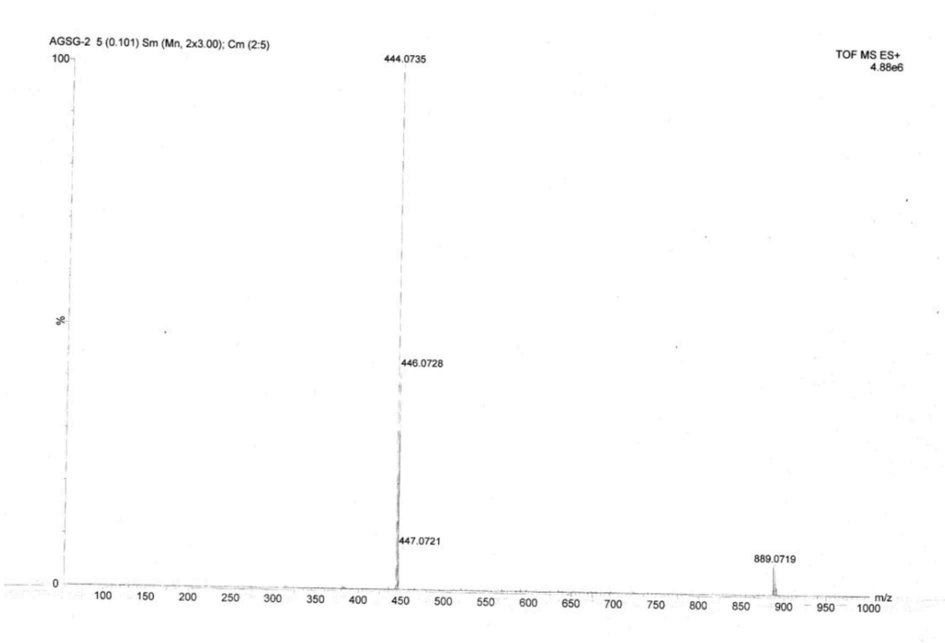

Figure S12. Representative ESI mass spectrum of complex **2**.

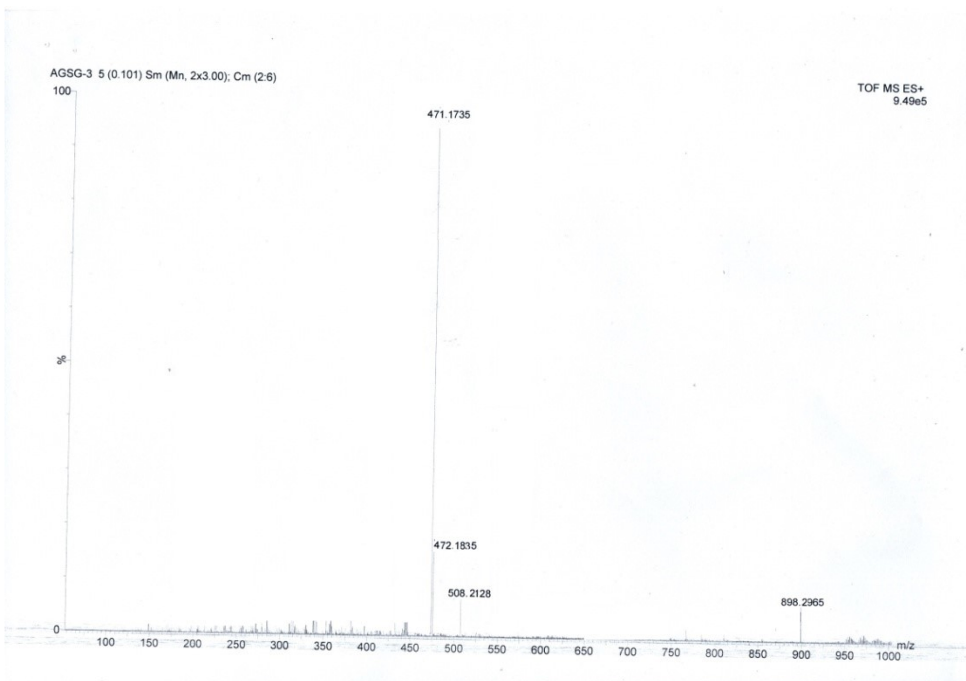

Figure S13. Representative ESI mass spectrum of complex **3**.

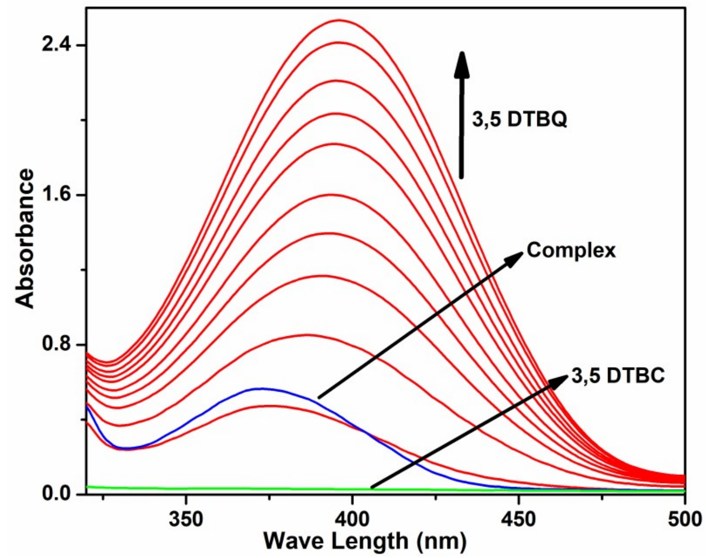

Figure S14. Increase in absorbance around 400 nm, after mixing equal volumes of DMF-acetonitrile solutions of 3,5-DTBC (1.0×10^{-2} M) and **3** (1.5×10^{-5} M). The spectra were recorded in every 5 min interval.

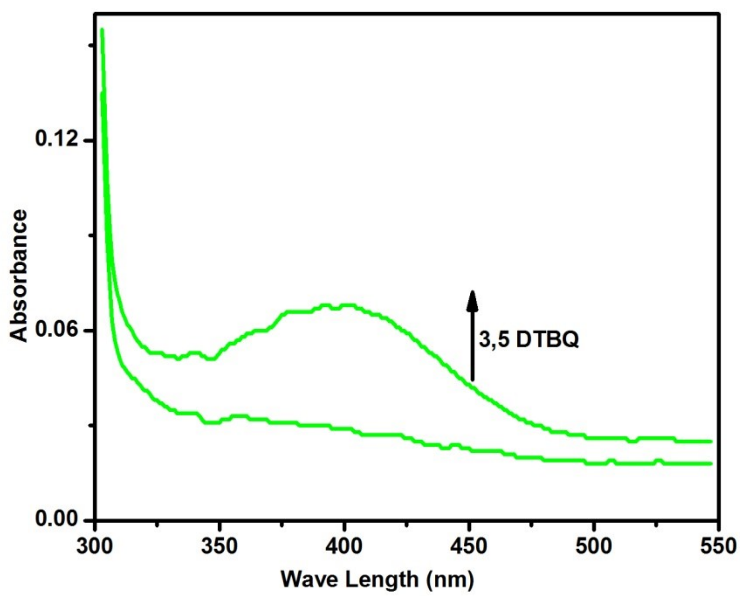

Figure S15. Representative UV-vis spectra of 3,5-DTBC (Blank) in DMF-acetonitrile solution.

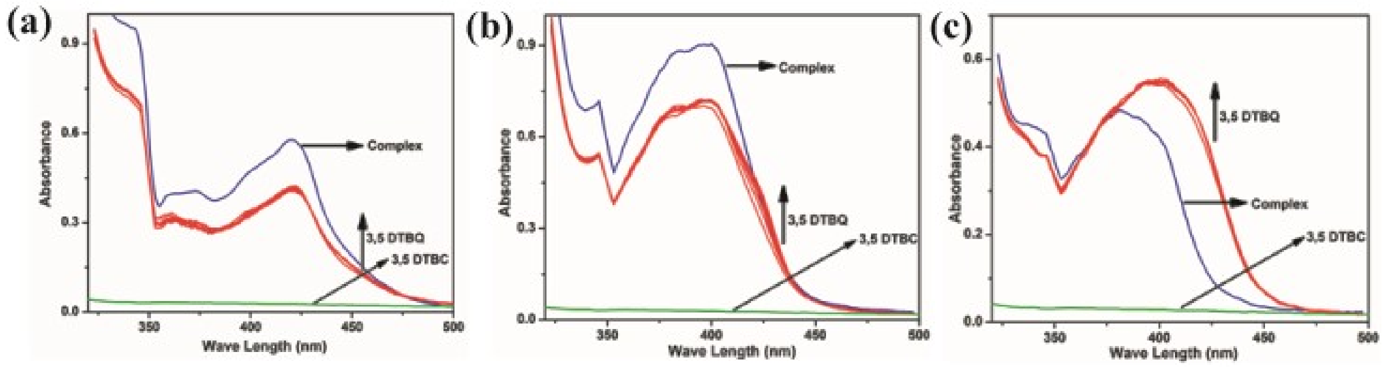

Figure S16. Representative UV-vis spectra of the "metalloligand" (a) [NiL^1], (b) [CuL^1] and (c) [CuL^2] with 3,5-DTBC in DMF-acetonitrile solution. The spectra were recorded in every 3 mininterval.

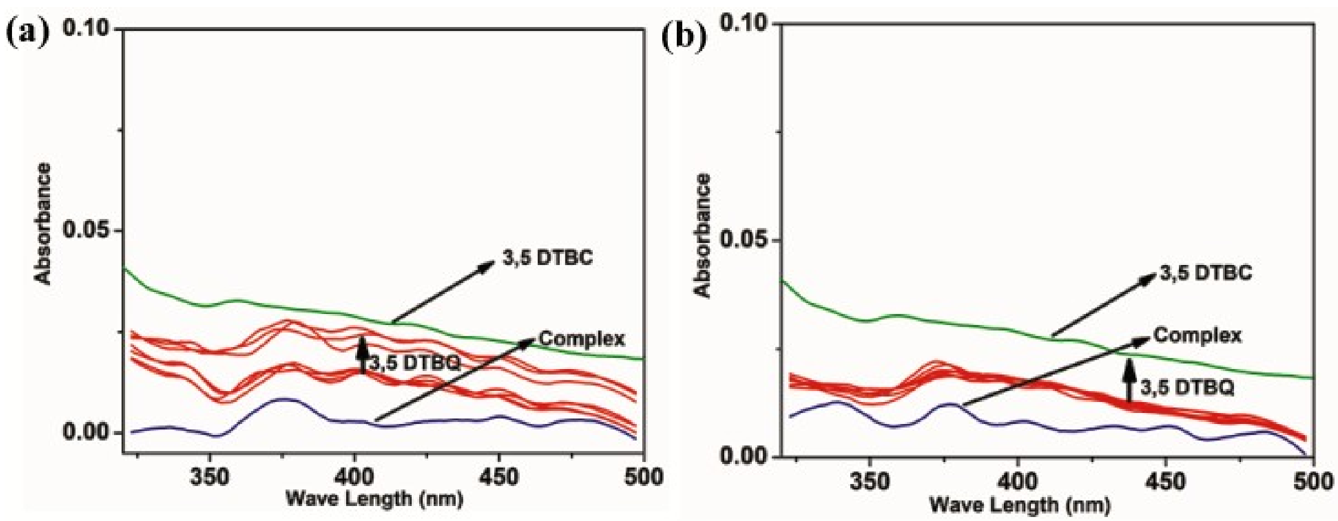

Figure S17. Representative UV-vis spectra of (a) $Mn(C_6H_5CO_2)_2 \cdot 4H_2O$ and (b)$Mn(m\text{-}(NO_2)C_6H_4CO_2)_2 \cdot 2H_2O$ with 3,5-DTBC in DMF-acetonitrile solution. The spectra were recorded in every 3 min interval.

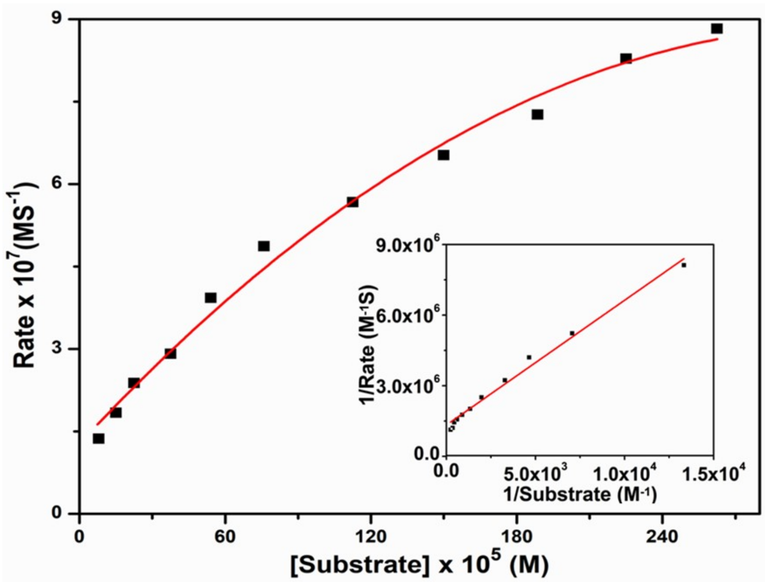

Figure S18. Plot of initial rates *vs.* substrate concentration for the oxidation reaction of 3,5-DTBC catalyzed by complex **3**. Inset shows the Lineweaver−Burk plot. Symbols and solid lines represent the experimental and simulated profiles, respectively.

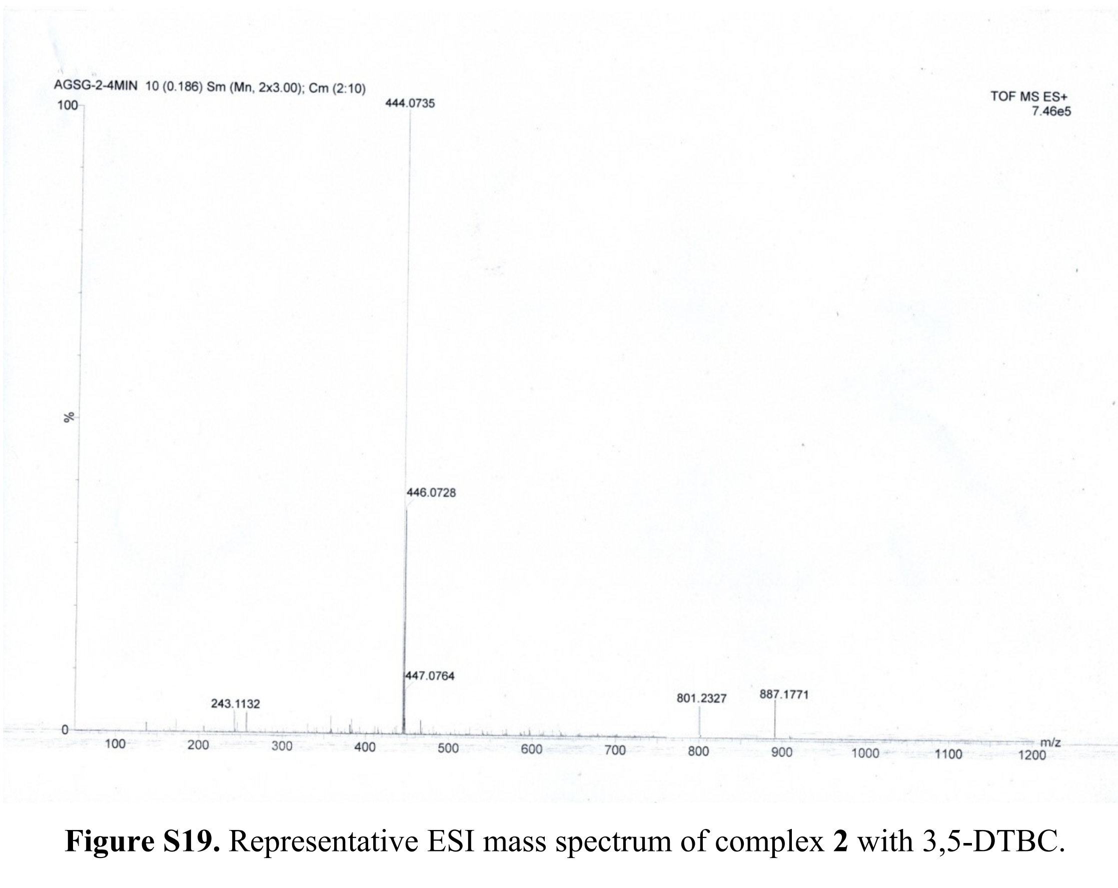

Figure S19. Representative ESI mass spectrum of complex **2** with 3,5-DTBC.

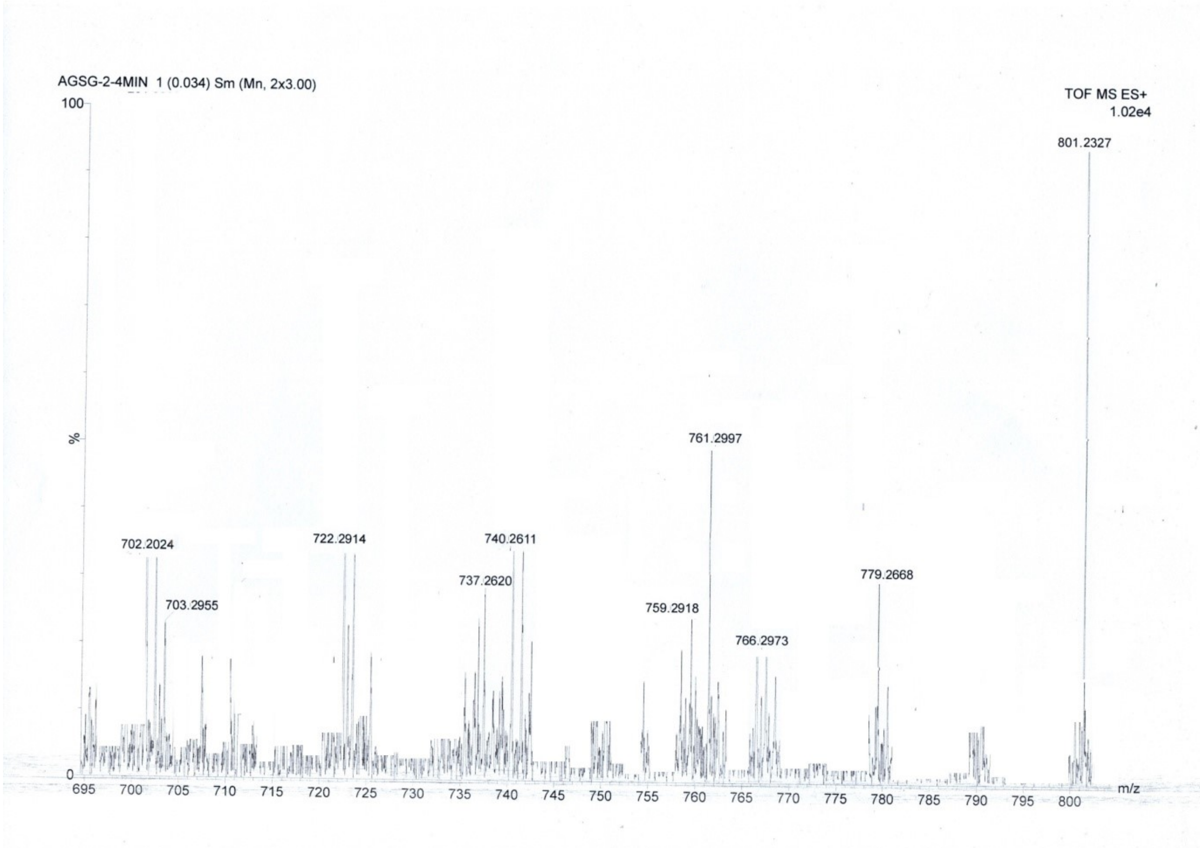

Figure S20. Representative ESI mass spectrum of complex **2** with 3,5-DTBC. (Expanded)

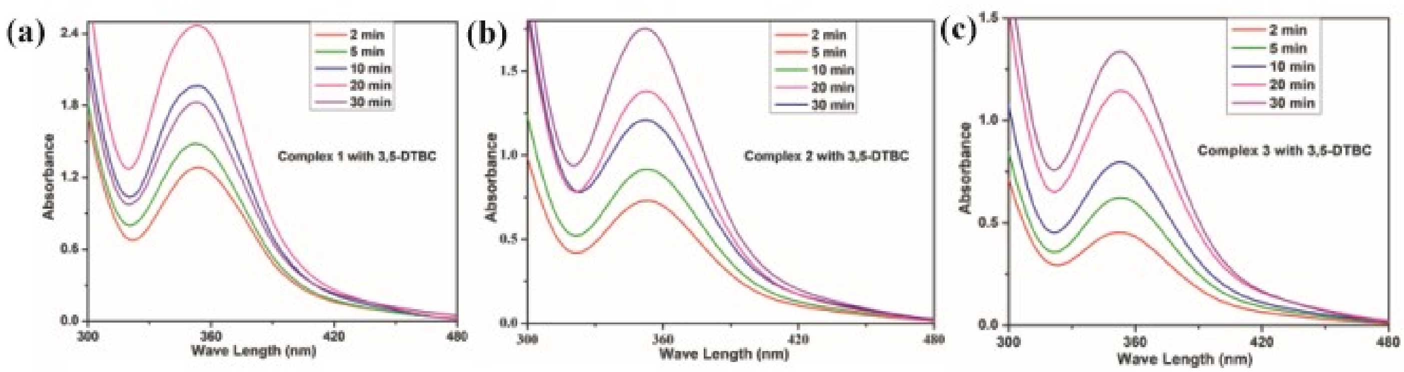

Figure S21. Increase of the absorption band at around 353 nm during the estimation of H_2O_2 iodometrically forcomplexes (**1–3**). The spectra were recorded at different time interval for complexes (**1–3**).

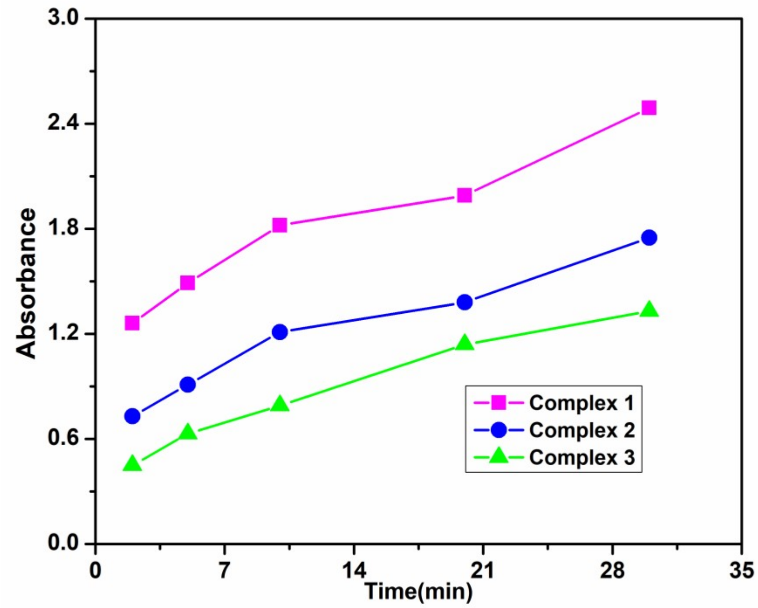

Figure S22. Plot of H_2O_2 estimation of complexes (**1–3**).

Table ST1. Selected bond distances (Å) and angles (°) for complex **1**

1			
Bond distances (Å)			
Mn1–O1	2.254(5)	Mn1–O2	2.197(5)
Mn1–O3	2.146(5)	Mn1–O5	2.085(5)
Mn1–O7	2.287(5)	Mn1–O8	2.310(5)
Mn2–O4	2.188(4)	Mn2–O6	2.127(4)
Mn2–O8	2.181(5)	Ni1–O1	1.876(5)
Ni1–O2	1.854(5)	Ni1–N1	1.897(5)
Ni1–N2	1.891(5)		
Bond angles(°)			
O1–Mn1–O2	65.13(18)	O1–Mn1–O3	139.02(17)
O1–Mn1–O4	165.93(15)	O1–Mn1–O5	87.28(18)
O1–Mn1–O7	82.59(17)	O1–Mn1–O8	113.16(18)
O2–Mn1–O3	86.21(18)	O2–Mn1–O4	112.18(16)
O2–Mn1–O5	91.53(19)	O2–Mn1–O7	121.66(17)

O2–Mn1–O8	178.10(18)	O3–Mn1–O4	51.26(15)
O3–Mn1–O5	123.90(19)	O3–Mn1–O7	89.24(18)
O3–Mn1–O8	94.85(17)	O4–Mn1–O5	78.91(17)
O4–Mn1–O7	109.22(15)	O4–Mn1–O8	69.69(15)
O5–Mn1–O7	135.89(19)	O5–Mn1–O8	89.19(18)
O7–Mn1–O8	56.83(16)	O4–Mn2–O6	92.33(18)
O4–Mn2–O8	84.76(17)	O4–Mn2–O6^a	87.67(18)
O4–Mn2–O8^a	95.24(17)	O6–Mn2–O8	89.67(18)
O6–Mn2–O8^a	90.33(18)	O1–Ni1–O2	80.00(2)
O1–Ni1–N1	92.10(2)	O1–Ni1–N2	169.00(2)
O2–Ni1–N1	171.40(2)	O2–Ni1–N2	90.40(2)
N1–Ni1–N2	97.90(2)	Ni1–O1–Mn1	103.50(2)
Ni1–O2–Mn1	106.40(2)	Mn1–O4–Mn2	90.33(17)
Mn1–O8–Mn2	104.8(2)		
Symmetry Element^a = 1-x,1-y,1-z			

Table ST2. Selected bond distances (Å) and angles (°) for complexes **2** & **3**

	2	**3**
Bond distances (Å)		
Mn1–O1	2.188(3)	2.201(2)
Mn1–O2	2.197(3)	2.151(2)
Mn1–O3	2.110(3)	2.086(2)
Mn1–O5	2.097(3)	2.127(3)
Mn1–O7	2.351(3)	2.237(2)
Mn1–O8	2.251(3)	2.311(2)
Mn2–O4	2.134(3)	2.167(2)
Mn2–O6	2.151(3)	2.136(3)
Mn2–O8	2.206(3)	2.278(2)

Cu1–O1	1.918(3)	1.959(2)
Cu1–O2	1.936(4)	1.953(2)
Cu1–N1	1.955(5)	1.978(3)
Cu1–N2	1.952(3)	1.974(3)
Cu1–O15		2.569(3)
Bond angles(°)		
O1–Mn1–O2	68.09(13)	73.24(8)
O1–Mn1–O3	90.42(13)	97.59(9)
O1–Mn1–O5	93.65(13)	167.79(10)
O1–Mn1–O7	111.61(13)	82.89(9)
O1–Mn1–O8	167.57(13)	89.01(8)
O2–Mn1–O3	146.43(14)	98.79(9)
O2–Mn1–O5	95.86(12)	97.86(9)
O2–Mn1–O7	81.53(11)	101.77(9)
O2–Mn1–O8	103.33(13)	155.29(9)
O3–Mn1–O5	111.56(14)	91.95(10)
O3–Mn1–O7	83.16(14)	158.62(10)
O3–Mn1–O8	92.90(13)	100.54(9)
O5–Mn1–O7	151.05(14)	91.00(9)
O5–Mn1–O8	96.25(13)	96.73(9)
O7–Mn1–O8	57.03(12)	58.08(9)
O4–Mn2–O6	94.94(12)	88.79(9)
O4–Mn2–O8	89.90(12)	91.31(8)
O4–Mn2–O6[a]	85.06(12)	91.21(9)
O4–Mn2–O8[a]	90.10(12)	88.69(8)
O6–Mn2–O8	89.48(11)	90.60(9)
O6–Mn2–O8[a]	90.53(12)	89.40(9)
O1–Cu1–O2	79.12(14)	83.16(10)
O1–Cu1–N1	92.19(18)	89.05(10)
O1–Cu1–N2	167.90(2)	172.36(11)

O2–Cu1–N1	171.30(18)	171.31(10)
O2–Cu1–N2	90.56(18)	89.78(11)
N1–Cu1–N2	98.10(2)	98.18(12)
O1–Cu1–O15		93.75(9)
O2–Cu1–O15		86.92(10)
O15–Cu1–N1		89.77(10)
O15–Cu1–N2		88.79(10)
Cu1–O1–Mn1	102.41(15)	99.62(10)
Cu1–O2–Mn1	101.46(14)	101.50(10)
Mn1–O8–Mn2	107.35(14)	106.62(9)
Symmetry elements: [a] = 1-x,1-y,1-z for complex **2**; [a] = -x,1-y,1-z for complex **3**		

Table ST3. Representation of the d-d band and CT band in the complexes (**1**–**3**)

Complex	**d-d band** (λ_{max}(nm) (ε,$M^{-1}cm^{-1}$) in DMF)	**CT band** (λ_{max}(nm) (ε,$M^{-1}cm^{-1}$) in DMF
[NiL^1]	581(114)	422 (6806), 314(23249)
[CuL^1]	593(193)	378 (17285), 312(36459)
[CuL^2]	595(106)	381 (7252), 300 (17118)
1	572(200)	419(18901), 315(65832)
2	588(468)	379(32445), 312(75865)
3	591(416)	378(30104), 298(76980)

Table ST4. Bond valence sum (BVS)[a] calculations for complex **1**.

Atom	**Mn^{II}**	**Mn^{III}**
Mn1	1.81	1.67
Mn2	2.04	1.86

Table ST5. Bond valence sum (BVS)[a] calculations for complex **2**.

Atom	**Mn^{II}**	**Mn^{III}**
Mn1	1.91	1.75
Mn2	2.04	1.88

Table ST6. Bond valence sum (BVS)[a] calculations for complex **3**.

Atom	**Mn^{II}**	**Mn^{III}**
Mn1	<u>1.97</u>	1.79
Mn2	<u>1.92</u>	1.74

[a]The underlined value is the one closest to the charge for which it was calculated. The oxidation state is the nearest whole number to the underlined value.

Table ST7. Geometric features (Distances in (Å) and Angles in (^{0})) of the H-bond interactions obtained for complex 1

Donor–H·····Acceptor	**D–H (Å)**	**H·····A (Å)**	**D·····A (Å)**	**∠D–H·····A (^{0})**	**Symmetry Element**
C18–H18 ···O3	0.95	2.51	3.439(7)	168	1-x, 1-y, 2-z
C19–H19 ···O7	0.95	2.52	3.355(7)	146	1-x, 1-y, 2-z

Table ST8. Geometric features (Distances in (A^0) and Angles in (^{0})) of the C-H /π interactions obtained for complex **1**

C–H·····Cg(Ring)	**H·····Cg (Å)**	**∠C–H·····Cg (^{0})**	**C·····Cg (Å)**	**Symmetry Element**
C7–H7···Cg1	2.97	133	3.691(8)	2-x,2-y,2-z

Table ST9 Geometric features (Distances in (Å) and Angles in (^{0})) of the H-bond interactions obtained for complex **2**

Donor–H·····Acceptor	**D–H (Å)**	**H·····A (Å)**	**D·····A (Å)**	**∠D–H·····A (^{0})**	**Symmetry Element**
C21–H21 ···O3	0.95	2.58	3.262(7)	129	x, 1/2-y, -1/2+z

C21–H21 ···O7	0.95	2.56	3.470(7)	160	x, 1/2-y, -1/2+z
C45–H45 ···O14	0.95	2.38	3.310(7)	168	x, 1/2-y, 1/2+z

Table ST10. Geometric features (Distances in (A^0) and Angles in (^{0})) of the C-H /π interactions obtained for complex **2**

C–H·····Cg(Ring)	**H·····Cg (Å)**	**∠C–H·····Cg (^{0})**	**C·····Cg (Å)**	**Symmetry Element**
C30–H30···Cg1	2.50	156	3.397(7)	1-x,1/2+y,3/2-z

Cg1 = C16─C17─C22─C23─C24─C25─

Table ST11. Geometric features (Distances in (Å) and Angles in (^{0})) of the H-bond interactions obtained for complex **3**

Donor–H·····Acceptor	**D–H (Å)**	**H·····A (Å)**	**D·····A (Å)**	**∠D–H·····A (^{0})**	**Symmetry Element**
C13–H13B ···O12	0.99	2.57	3.438(8)	147	1-x, 1/2+y, 3/2-z
C38–H38 ···O13	0.95	2.26	3.050(6)	140	-x, -1/2+y, 1/2-z
C47–H47A ···O11	0.98	2.45	3.405(7)	165	1-x, 1/2+y, 3/2-z

Table ST12. Different concentrations of substrate (3,5-DTBC) in DMF/Acetonitrile for kinetic measurement

Metal complex and its concentration (M)	**Concentration of 3,5-DTBC (M)**
1(5.0×10^{-6})	5.0×10^{-5}, 1.0×10^{-4}, 1.5×10^{-4}, 2.5×10^{-4}, 3.5×10^{-4}, 5.0×10^{-4}, 7.5×10^{-4}, 1.0×10^{-3}, 1.5×10^{-3}, 1.75×10^{-3}
2(7.5×10^{-6})	7.5×10^{-5}, 1.5×10^{-4}, 2.25×10^{-4}, 3.75×10^{-4}, 5.25×10^{-4}, 7.5×10^{-4}, 1.125×10^{-3}, 1.5×10^{-3}, 1.875×10^{-3}, 2.25×10^{-3}, 2.625×10^{-3}
3(7.5×10^{-6})	7.5×10^{-5}, 1.5×10^{-4}, 2.25×10^{-4}, 3.75×10^{-4}, 5.25×10^{-4}, 7.5×10^{-4}, 1.125×10^{-3}, 1.5×10^{-3}, 1.875×10^{-3}, 2.25×10^{-3}, 2.625×10^{-3}

Table ST13. Kinetic parameters for catalytic activities of complexes (**1–3**) on 3,5-DTBC

Complex	V_{max} (M S^{-1})	Std. Error	K_M (M)	Std. Error	k_{cat} (h^{-1})
1	1.02×10^{-6}	2.22×10^{-7}	4.01×10^{-4}	3.00×10^{-5}	734.0
2	9.43×10^{-7}	4.25×10^{-8}	4.14×10^{-4}	1.52×10^{-5}	450.0
3	7.46×10^{-7}	9.23×10^{-8}	3.98×10^{-4}	2.56×10^{-5}	358.0

Table ST14. Kinetic parameters for the oxidation of 3,5-DTBC to 3,5-DTBQ catalyzed by different Cu^{II}, Ni^{II}, Mn^{II}, Ni^{II}–Mn^{II} and Cu^{II}–Mn^{II} complexes.[a]

	Complexes	k_{cat} (h^{-1}) in CH_3OH	k_{cat} (h^{-1}) in CH_3CN	k_{cat} (h^{-1}) in DMF	References
Cu^{II} complexes	$[Cu^{II}_2(L^1)_2(NCO)_2]$	64.2	Not performed	Not performed	26a
	$[Cu^{II}_2(L^2)_2(NCO)_2]\cdot 2CH_3OH$	98.4	Not performed	Not performed	26a
	$[Cu^{II}L^3(NCO)]$	23.6	Not performed	Not performed	26b
	$[Cu^{II}(L^4)bpy]ClO_4$	83.5	Not performed	Not performed	26c
	$[Cu^{II}(L^4)phen]ClO_4$	73.5	Not performed	Not performed	26c
	$[Cu^{II}_2L^5_4(\mu\text{-cl})](ClO_4)_2$	183.6	Not performed	Not performed	26d
	$[Cu^{II}_4(\mu_3\text{-OH})_2(\mu_2\text{-OH})_2 L^5_4(\mu\text{-}ClO_4)](ClO_4)_2$	172.8	Not performed	Not performed	26d
	$[Cu^{II}_2(L^6H)_2(H_2O)_2(NO_3)_2] (NO_3)_2$	29600.0	Not performed	Not performed	26e
	$[Cu^{II}_2L^7(OH)(H_2O)(NO_3)] (NO_3)$	3310.0	Not performed	Not performed	26e

	$[Cu^{II}_2L^8(H_2O)(NO_3)]\ (NO_3)$	7200.0	Not performed	Not performed	26e
	$[Cu^{II}_2L^9(H_2O)_2(NO_3)]\ (NO_3)_2$	2350.0	Not performed	Not performed	26e
	$[Cu^{II}_2L^{10}(N_3)_2(H_2O)_2$	18000.0	21600.0	Not performed	26f
	$[Cu^{II}_2L^{11}(N_3)_2(H_2O)_2]$	Not performed	10800.0	Not performed	26f
	$[Cu^{II}_2L^{12}(N_3)_2(H_2O)_2]$	Not performed	18000.0	Not performed	26f
	$[Cu^{II}_2L^{13}(N_3)_2(H_2O)_2]$	21600.0	72000.0	Not performed	26f
	$[Cu^{II}_2(HL^{14})(O_2CPh)(H_2O)]$- $PhCO_2\cdot H_2O$	25.8	Not performed	Not performed	26g
	$[Cu^{II}_2L^{15}{}_2]$	720.0	Not performed	Not performed	26h
	$[Cu^{II}_2L^{16}(H_2O)_4](ClO_4)_4\cdot 2H_2O$	63.0	Not performed	Not performed	30a
	$[Cu^{II}_2(H_2L^{17})(ClO_4)](ClO_4)$	58.6	Not performed	Not performed	30a
	$[Cu^{II}L^{18}{}_2]\ \cdot 4H_2O$	2796.0	Not performed	Not performed	26i
	$[Cu^{II}L^{19}]$	722.0	Not performed	Not performed	26j
	$[Cu^{II}_4(L^{20}H)_2\ L^{20}{}_2(H_2O)_2]\ (ClO_4)_2\cdot 3H_2O$	113.0	Not performed	Not performed	26k
	$[Cu^{II}_4(L^{20}H)_2\ L^{20}{}_2(H_2O)_2]$ $(ClO_4)\cdot(tp)_{0.5}\cdot 3H_2O$	97.0	Not performed	Not performed	26k
	$[(Cu^{II}L^{21})_2(\mu_{1,1}\text{-}N_3)_2Cu(H_2O)]\cdot CH_3OH$	125.8	Not performed	Not performed	26l

	$[(Cu^{II}L^{22})_2(\mu_{1,1}\text{-}N_3)_2Cu(H_2O)]\cdot CH_3OH$	118.9	Not performed	Not performed	26l
	$[(Cu^{II}L^{23})_2(\mu_{1,1}\text{-}N_3)_2Cu(H_2O)]\cdot CH_3OH$	114.7	Not performed	Not performed	26l
Ni^{II} complexes	$[Ni^{II}_2(L^{24})(SCN)_2(CH_3COO)\text{-}(H_2O)]$	863.9	Not performed	Not performed	27a
	$[Ni^{II}_2(L^{25})(SCN)_3(CH_3OH)_2]$	161.1	Not performed	Not performed	27a
	$[Ni^{II}_2(L^{24})(SCN)_3(H_2O)(CH_3OH)]$	154.0	Not performed	Not performed	27a
	$[Ni^{II}_2(L^{25})(SCN)\ CH_3COO)_2]$	303.7	Not performed	Not performed	27a
	$[Ni^{II}_2(L^{24})(N_3)3(H_2O)_2]$	172.8	Not performed	Not performed	27a
	$[Ni^{II}_2(L^{25})(N_3)3(H_2O)_2]$	264.1	Not performed	Not performed	27a
	$[Ni^{II}_2L^{24}_2(CH_3CN)_4](ClO_4)_2\cdot 2CH_3CN$	7.9	Not performed	Not performed	27a
	$[Ni^{II}_3(L^{25})_2(NCS)_2(H_2O)_4]\cdot H_2O$	14.5	Not performed	Not performed	27a
	$[Ni^{II}_2(L^{26})(CH_3COO)_2(N(CN)_2)]_n$	128.6	Not performed	Not performed	27a
	$[Ni^{II}_2(L^{27})(CH_3COO)_2(N(CN)_2)]$	275.0	Not performed	Not performed	27a
	$[Ni^{II}_2L^{28}_2(CH_3CN)_4](ClO_4)_2\cdot 2CH_3CN$	7.9	Not performed	Not performed	6e
	$[Ni_3(L^{29})_2(NCS)_2(H_2O)_4]\cdot H_2O$	14.5	Not performed	Not performed	6e
	$[Ni^{II}_2(L^{30})_2(NCS)_2]$	Not performed	64.1	Not performed	27b

	$[Ni^{II}_2(L^{31})_2(NCS)_2]$	Not performed	51.1	Not performed	27b
	$[Ni^{II}_2(L^{32})_2(NCS)_2]$	Not performed	81.7	Not performed	27b
	$[Ni^{II}L^{33}(H_2O)_3]I_2 \cdot H_2O$	92.6	Not performed	Not performed	3d
	$[Ni^{II}L^{33}(H_2O)_3]Br_2 \cdot H_2O$	84.8	Not performed	Not performed	3d
	$[Ni^{II}_2(L^{34})_2(H_2O)_4](NO_3)_2$	474	Not performed	Not performed	3d
	$[Ni^{II}_5(L^{35})_2(CH_3COO)_6(OH)_2] \cdot 5.5\ H_2O$	477	Not performed	Not performed	3d
	$[Ni^{II}L^{33}(H_2O)_3](NO_3)_2$	52.6	Not performed	Not performed	3d
	$[Ni^{II}L^{36}(H_2O)_3](NO_3)_2$	129	Not performed	Not performed	3d
	$[Ni^{II}_4(L^{37})_2(H_2O)_8(\mu_2H_2O)_2](NO_3)6(H_2O)_6$	Not performed	Not performed	12	27c
	$[Ni^{II}_2L^{38}(PhCOO)(H_2O)_2]ClO_4$	167.4	Not performed	Not performed	27d
Mn^{II} complexes	$[Mn^{II}(HL^{39})(H_2O)_2(CH_3CN)](ClO_4)_2$	Not performed	Not performed	48.8	28a
	$[Mn^{II}(L^{40})_2(OH_2)_2]$	598.0	Not performed	Not performed	28b
	$[Mn^{II}(HL^{41})_2] \cdot 2ClO_4$	1038.0	Not performed	Not performed	28c
	$[Mn^{II}(HL^{41})(N(CN)_2)$	871.2	Not performed	Not performed	28c
	$[Mn^{II}(o\text{-}(NO_2)\ C_6H_4COO)_2(L^{42})(H_2O)]_n$	Not performed	177.0	Not performed	28d

	$[Mn^{II}_4L^{43}_2(\mu_3\text{-}Cl)_2Cl_2]$	2265.5	Not performed	Not performed	28e
	$[Mn^{II}_4L^{43}(\mu_{1,1,1}\text{-}N_3)_2(N_3)_2]$	2132.2	Not performed	Not performed	28e
Ni^{II}-Mn^{II} complexes	$[(Ni^{II}L^{44})_2Mn^{II}(NCS)_2]$	104.5	Not performed	Not performed	7e
	$[(Ni^{II}L^{44})_2Mn^{II}(NCO)_2]$	77.0	Not performed	Not performed	7e
	$[\{Ni^{II}L^{44}(EtOH)\}_2Mn^{II}(NO_2)_2]\cdot 2EtOH$	25.8	Not performed	Not performed	7e
	$[(Ni^{II}L^{45})_2\,Mn^{II}N_3](ClO_4)$	768.0	Not performed	Not performed	7c
	$[(Ni^{II}L^{45})_2\,Mn^{II}_2(N_3)_2(\mu_{1,1}\text{-}N_3)_2(CH_3OH)_2]$	1985.0	Not performed	Not performed	7c
	$[\{(Ni^{II}L^{45})_2Mn^{II}\}_2(\mu_{1,3}\text{-}N_3)(H_2O)]\cdot(CH_3OH),(ClO_4)_3$	2309.0	Not performed	Not performed	7c
	$[(Ni^{II}L^{45})_2\,Mn^{II}_2(N_3)_2(\mu_{1,1}\text{-}N_3)_2(CH_3OH)_2]$	935.0	Not performed	Not performed	7d
	$[(Ni^{II}L^{46})_2\,Mn^{II}_2(N_3)_2(\mu_{1,1}\text{-}N_3)_2(CH_3OH)_2]$	984.0	Not performed	Not performed	7g
	$[(Ni^{II}L^{46})_2\,Mn^{II}_2(N_3)_2(\mu_{1,1}\text{-}N_3)_2(CH_3OH)_2]$	2081.0	Not performed	Not performed	7g
	Complex **1**	Not performed	734.0	Not performed	Present Study
Cu^{II}-Mn^{II} complexes	$[(Cu^{II}L^{47})\,Mn^{II}(PhCOO)(H_2O)]_2\cdot(Cu\,L^{42})_2(ClO_4)_2$	Not performed	399.0	Not performed	10g
	$[(Cu^{II}L^{48})_2Mn^{II}(N_3)(H_2O)](ClO_4)\cdot H_2O$	1118.0	Not performed	Not performed	7b
	$[(Cu^{II}L^{49})_2\,Mn^{II}(CH_3COO)_2]$	Not performed	139.0	Not performed	7f

	$[(Cu^{II}L^{49})_2Mn^{II}(PhCOO)(H_2O)]Cl$	Not performed	439.0	Not performed	7f
	$[(Cu^{II}L^{49})_2Mn^{II}((p\text{-}OH)PhCOO)(H_2O)]ClO_4$	Not performed	348.0	Not performed	7f
	$[(Cu^{II}L^{49})_2Mn^{II}(HCOO)(H_2O)]ClO_4$	Not performed	730.0	Not performed	7f
	$\{[(Cu^{II}L^{49})_2Mn^{II}(nic)(H_2O)_2](ClO_4)(0.5H_2O)\}_n$	Not performed	1075.0	Not performed	3e
	$[(Cu^{II}L^{49})_2Mn^{II}(nic)_2]\cdot 2CH_3OH$	Not performed	683.0	Not performed	3e
	$[(Cu^{II}L^{50})_2Mn^{II}_3(PhCOO)_6]$	Not performed	595.0	Not performed	12c
	$[(Cu^{II}L^{50})_2Mn^{II}(CH_3COO)_2]$	Not performed	39.9	Not performed	12c
	$\{[(Cu^{II}L^{50})_2Mn^{II}(PhCH_2CO_2)_2]\cdot 2CH_3CN\}$	Not performed	204.5	Not performed	12c
	Complex **2**	Not performed	450.0	Not performed	Present Study
	Complex **3**	Not performed	358.0	Not performed	Present Study

[a]Where HL^1 = 2-dimethylamino-ethylamino)-methyl]-phenol, HL^2 = 2-[(2-diethylamino-ethylamino)-methyl]-phenol, HL^3 = 2-methoxy-6-(8-iminoquinolinylmethyl)phenol, HL^4 = 2-[(3-methylamino-propylimino)-methyl]phenol, L^5 = 2-aminoethylpyridine, HL^6 = 2-formyl-4-methyl-6-(4-(aminomethyl)-piperidine)-iminomethyl-phenol, HL^7 = 2,6-bis(2-amino-2-methyl-1-propanol)-iminomethyl-4-methyl-phenol, HL^9 = 2,6-bis(2-aminoethylpyridine)-iminomethyl-4-methyl-phenol, HL^8= 2-formyl-4-methyl-6-(aminobenzyl)-iminomethyl-phenol, H_2L^9 = condensation product of 4-methyl-2,6-diformylphenol with 1,3-diaminopropane, H_2L^{10} = condensation product of 4-methyl-2,6-diformylphenol with 1,2-diaminoethane, H_2L^{11} = condensation product of 4-methyl-2,6-diformylphenol with 1,2-diaminopropane, H_2L^{12} = condensation product of 4-methyl-2,6-diformylphenol with 1,2-diamino-2-methylpropane, H_2L^{13} = condensation product of 4-methyl-2,6-diformylphenol with 1,2- diaminocyclohexane, H_3L^{14} =2,6-bis[{(2-hydroxybenzyl)(N-(2-pyridylmethyl)amino}methyl]-4-methylphenol, L^{15} = N,N′-

(ethane-1,2-diyldi-o-phenylene)-bis(pyridine-2-carboxamidide), L^{16} = 2,8-dimethyl-5,11-bis(pyridin-2-ethyl)-1,4,5,6,7,10,11,12-octahydroimidazo [4,5-h]imidazo[4,5c][1,6]-diazecine, H_2L^{17} = N,N´-bis{(2-hydroxy-3-formyl-5-methylbenzyl)(dimethyl)}-ethylenediamine, L^{18} = 3-methoxy-2-oxo-benzaldehyde, H_2L^{19} =N,N´-bis(2-hydroxy-3,5-di tertiarybutylbenzyl)homopiperazine,H_2L^{20} = 2-[(2-hydroxy ethylimino)-propylimino)-methyl]-6-methoxy-phenol, H_2L^{21} = N,N-bis(3,5-dimethyl-2-hydroxybenzyl)-N′,N′-dimethyl-1,3-diaminopropane ,H_2L^{22} = N,N-bis(3,5-dimethyl-2-hydroxybenzyl)-N′,N′-dimethyl-1,2-diaminoethane, H_2L^{23} = N,N-bis(3,5-dimethyl-2-hydroxybenzyl)-N′,N′-diethyl-1,2-diaminoethane, HL^{24}=2,6-bis(R_2-iminomethyl)-4-R_1-phenol; R_1 = tert-butyl, R_2 = N,N-dimethylethylene, HL^{25}=2,6-bis(R_2-iminomethyl)-4-R_1-phenol; R_1 = tert-butyl, R_2 = 2-(N-ethyl) pyridine, HL^{26}=2,6-bis(R_2-iminomethyl)-4-R_1-phenol ; R_1 = methyl, R_2 = N,N-dimethylethylene, HL^{27}=2,6-bis(R_2-iminomethyl)-4-R_1-phenol ; R_1 = methyl, R_2 = 2-(N-ethyl) pyridine, deen = 2-(diethylamino) ethylamine, dmpn = 3-(dimethylamino)-1-propylamine, and modaH= diacetyl monoxime, HL^{28}=2-[1-(3-methylamino-propylamino)-ethyl]-phenol, HL^{29}=2-[1-(2-dimethylamino-ethylamino)-ethyl]-phenol, HL^{30}=2-[1-(3-dimethylamino-propylamino)-ethyl]-phenol, HL^{31} = 2-[(2-piperazin-1-ylethylimino)methyl]phenol, HL^{32}= 2-formyl-4-methyl-6-(1-(2-aminomethyl)piperidine)-iminomethylphenol, HL^{33}= 4-methyl-2,6-bis(1-(2-aminomethyl)piperidine)-iminomethylphenol, HL^{34}=2-[(2-piperazin-1-ylethylimino)methyl]-4-chlorophenol, HL^{35}= 2,6 diformyl-4-isopropyl phenol, HL^{36}= 2-[(3-methylamino-propylamino)-methyl]-4-nitrophenol,HL^{37}=2-[(3-methylamino-propylamino)-methyl]-4-phenol, L^{39} = 1,3-Bis(6′-methyl-2-pyridylimino)isoindoline, L^{40}= 3-methoxy-4-hydroxy-benzaldehyde, HL^{41}= 4-tert-butyl-2,6-bis-[(2-pyridin-2-yl-ethylimino)-methyl]-phenol, L^{42}= Pyrazine, H_2L^{43}=N,N´-dimethyl-N,N'-bis(2-hydroxy-3-methoxy-5-methylbenzyl)ethylenediamine, H_2L^{44} = N,N´_-bis(salicylidene)-1,3-propanediamine, H_2L^{45} = N-α-methylsalicylidene-N´-3-methoxysalicylidene-1,3-propanediamine,H_2L^{46} = N-α-methylsalicylidene-N′-salicylidene-1,3-propanediamineH_2L^{47} = N-salicylidene-N′-3-methoxysalicylidene-1,2-ethylenediamine, H_2L^{48} = N-(2-Hydroxyacetophenylidene)-N′-salicylidene-1,3-propanediamine, H_2L^{49} =N,N´-bis(α-methylsalicylidene)-1,3-propanediamine, H_2L^{50} = N,N′-bis(2-hydroxynaphthyl-methylidene)-1,3-propanediamine.