Electronic Supplementary Material (ESI) for Dalton Transactions.

N,N´-substituted thioureas and their metal complexes: syntheses, structures and electronic properties

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Electronic Supplementary Information

Contents

Table S1. Data collection parameters for the X-ray crystallography.

Compound	**1**	**4**	**6**	**7**
Formula	$C_{30}H_{29}ClCuN_7O_6S_2$	$C_{14}H_{18}Cl_2N_6O_8S_2Zn$	$C_{26}H_{24}ClCuN_8O_6S_2$	$C_{14}H_{22}Cl_2N_8NiO_{10}S_2$
$D_{calc.}$/ g cm^{-3}	1.587	1.865	1.695	1.750
μ/mm^{-1}	0.975	1.656	1.094	1.228
Formula Weight	746.71	598.73	707.64	656.12
Colour	Red	Colourless	Dark Orange	Red
Shape	needle	prism	blade	blade
Size/mm^3	0.27×0.03×0.02	0.11×0.06×0.05	0.13×0.07×0.01	0.17×0.06×0.03
T/K	100(2)	100(2)	100(2)	100(2)
Crystal System	monoclinic	monoclinic	monoclinic	monoclinic
Space Group	$P2_1/n$	$P2_1$	$P2_1/c$	$C2/c$
a/Å	15.4602(11)	5.1243(2)	10.4870(7)	14.5374(10)
b/Å	9.7669(7)	11.4452(3)	17.9141(13)	17.6166(11)
c/Å	21.9107(15)	18.1830(5)	15.3930(11)	10.1978(7)
α/°	90	90	90	90
β/°	109.196(2)	91.109(3)	106.4260(10)	107.5720(10)
γ/°	90	90	90	90
V/Å^3	3124.5(4)	1066.21(6)	2773.8(3)	2489.8(3)
Z	4	2	4	4
Z'	1	1	1	0.5
Θ_{min}/°	2.509	2.103	2.925	3.121
Θ_{max}/°	27.485	27.548	27.484	27.479
Measured Refl's.	20514	7361	36950	17829
Indep't Refl's	7140	7361	6352	2849
Refl's I≥2 σ(I)	5054	7240	5291	2416
R_{int}	0.0528	.	0.0449	0.0439
Parameters	443	325	460	224
Restraints	0	7	3	371
Largest Peak	0.396	0.533	0.654	0.860
Deepest Hole	-0.574	-0.417	-0.334	-0.628
GooF	1.025	1.130	0.999	1.144
wR_2 (all data)	0.1133	0.1100	0.0963	0.1352
wR_2	0.1027	0.1058	0.0905	0.1295
R_1 (all data)	0.0699	0.0329	0.0460	0.0527
R_1	0.0439	0.0322	0.0355	0.0450
Flack Parameter		0.021(9)		
Hooft Parameter		0.0421(10)		

Compound	**15**	**16**	**19**	**21**
Formula	$C_{24}H_{36}ClCuN_6O_7S_2$	$C_{12}H_{17}ClCuN_3OS$	$C_{22}H_{28}Cl_2CuN_8O_2S_2$	$C_{17}H_{26}ClCuN_5O_{6.5}S_2$
$D_{calc.}$/ g cm^{-3}	1.488	1.606	1.531	1.597
μ/mm^{-1}	0.992	1.830	1.175	1.261
Formula Weight	683.70	350.33	635.08	567.54
Colour	Orange	Red	Dark Orange	Yellow
Shape	plate	needle	plate	rod
Size/mm^3	0.11×0.09×0.01	0.29×0.01×0.01	0.08×0.06×0.01	0.13×0.04×0.01
T/K	100(2)	100(2)	100(2)	100(2)
Crystal System	orthorhombic	monoclinic	monoclinic	monoclinic
Space Group	$P2_12_12_1$	$P2_1/c$	$P2_1/c$	$P2_1$
a/Å	9.0770(3)	12.5881(9)	10.7026(8)	12.3999(3)
b/Å	17.2213(8)	6.0555(4)	16.3850(11)	14.2258(4)
c/Å	19.5201(6)	19.3671(14)	7.9196(5)	13.3826(3)
α/°	90	90	90	90
β/°	90	101.012(2)	97.287(2)	90.462(2)
γ/°	90	90	90	90
V/Å^3	3051.3(2)	1449.12(18)	1377.58(16)	2360.59(11)
Z	4	4	2	4
Z'	1	1	0.5	2
Θ_{min}/°	1.577	2.143	2.286	2.230
Θ_{max}/°	27.480	27.554	27.537	27.483
Measured Refl's.	35113	14550	20899	30299
Indep't Refl's	6990	3348	3166	10291
Refl's I≥2 σ(I)	4976	2880	2867	8684
R_{int}	0.1008	0.0518	0.0958	0.0477
Parameters	381	184	180	681
Restraints	33	0	0	157
Largest Peak	1.130	0.603	1.519	1.249
Deepest Hole	-0.700	-0.354	-0.671	-0.796
GooF	1.035	1.030	1.025	1.050
wR_2 (all data)	0.1439	0.0826	0.1671	0.1579
wR_2	0.1278	0.0786	0.1616	0.1509
R_1 (all data)	0.1073	0.0386	0.0651	0.0687
R_1	0.0662	0.0308	0.0619	0.0572
Flack Parameter	-0.019(12)			-0.003(8)
Hooft Parameter	0.005(9)			0.020(4)

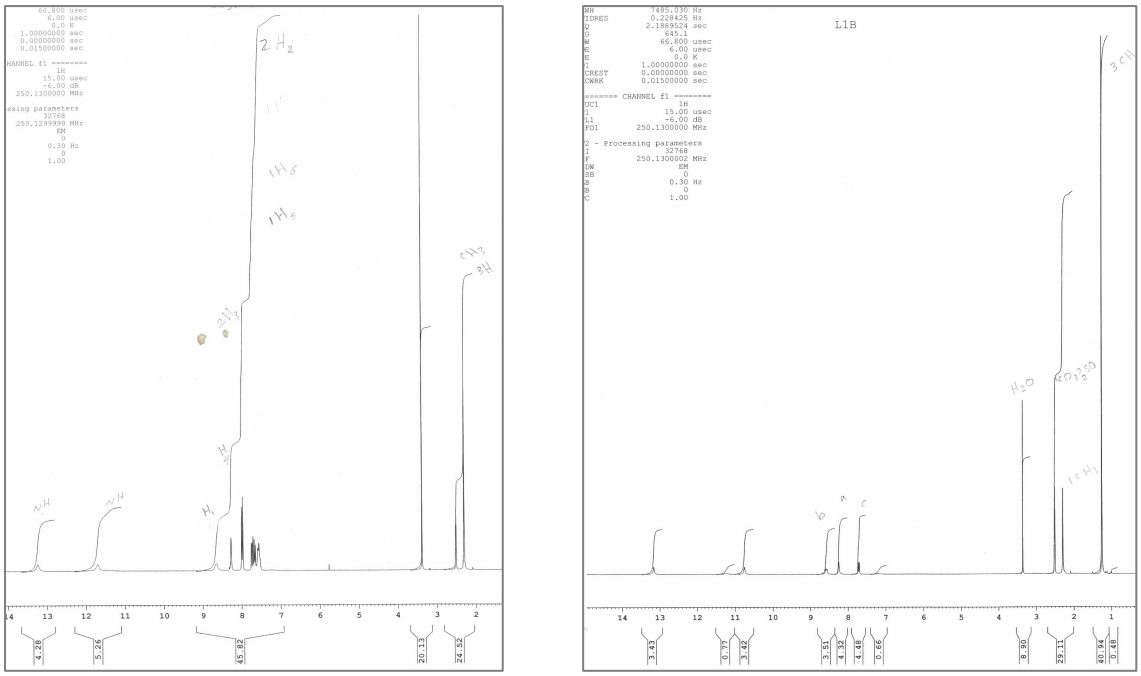

Figure S1. ^{1}H NMR spectra of ligands **L^{1a}** and **L^{1b}**.

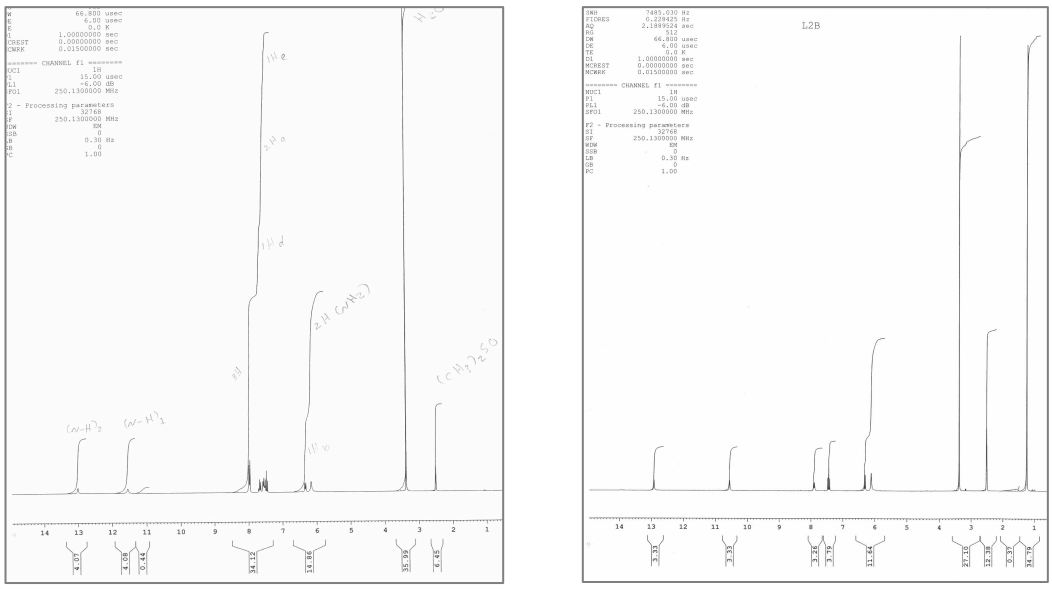

Figure S2. ^{1}H NMR spectra of ligands **L^{2a}** and **L^{2b}**.

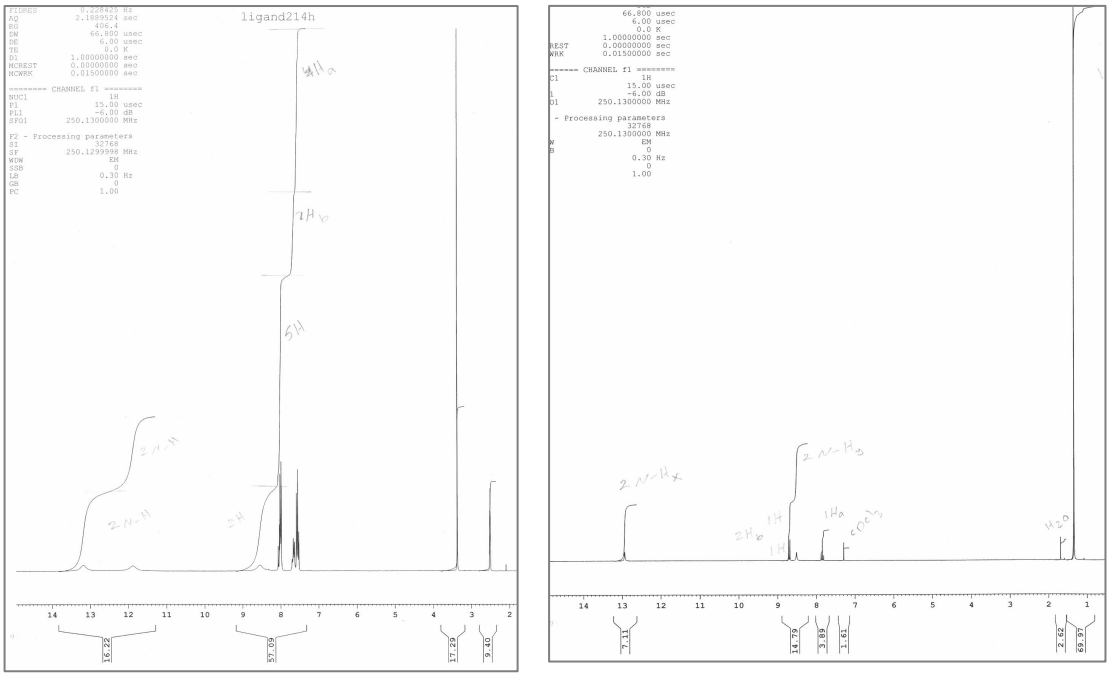

Figure S3. ^{1}H NMR spectra of ligands **L^{3a}** and **L^{3b}**.

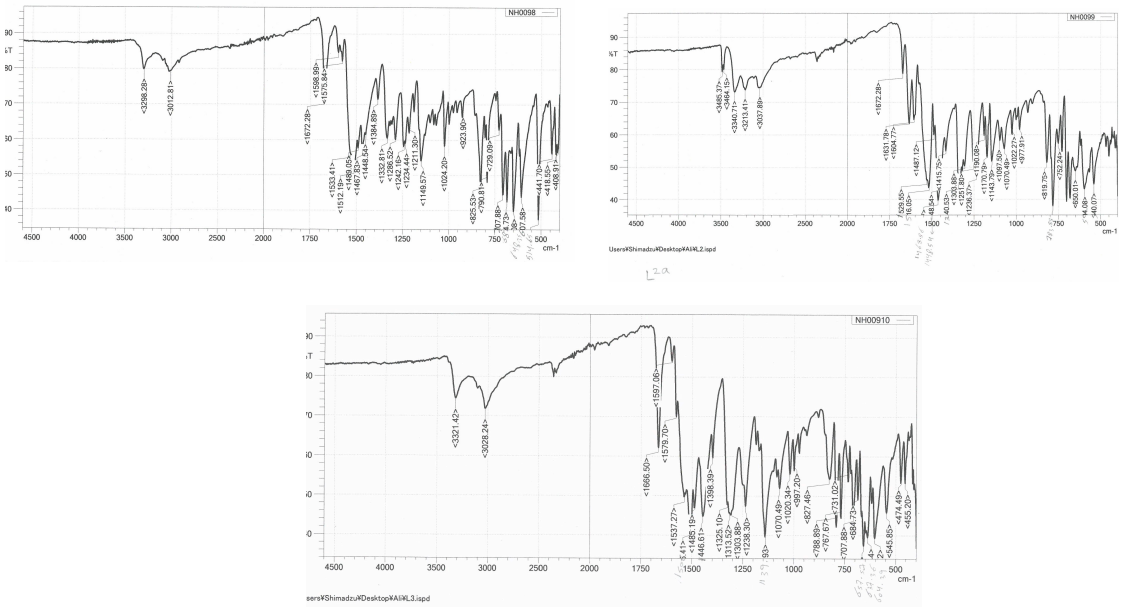

Figure S4. Examples of IR spectra of ligands **L^{1a}** (top left), **L^{2a}** (top right) and **L^{3a}** (bottom).

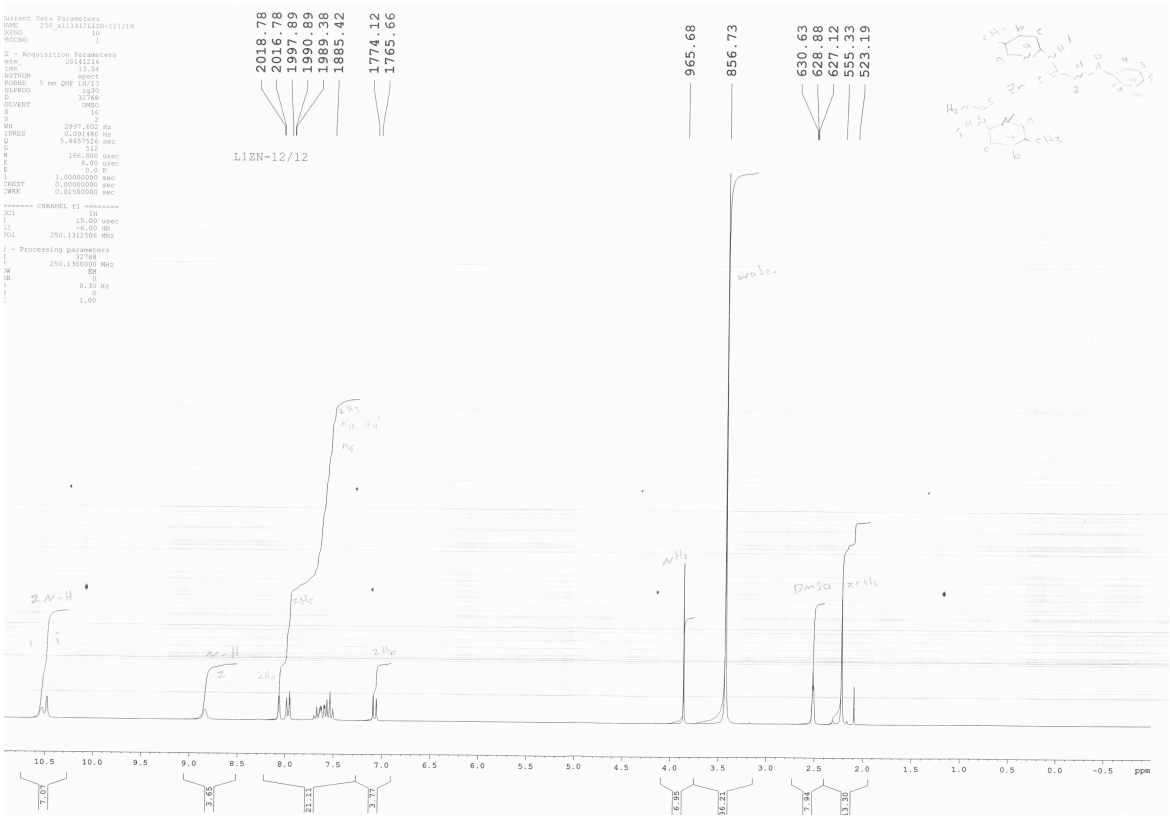

Figure S5. ^{1}H NMR spectrum of complex **5**.

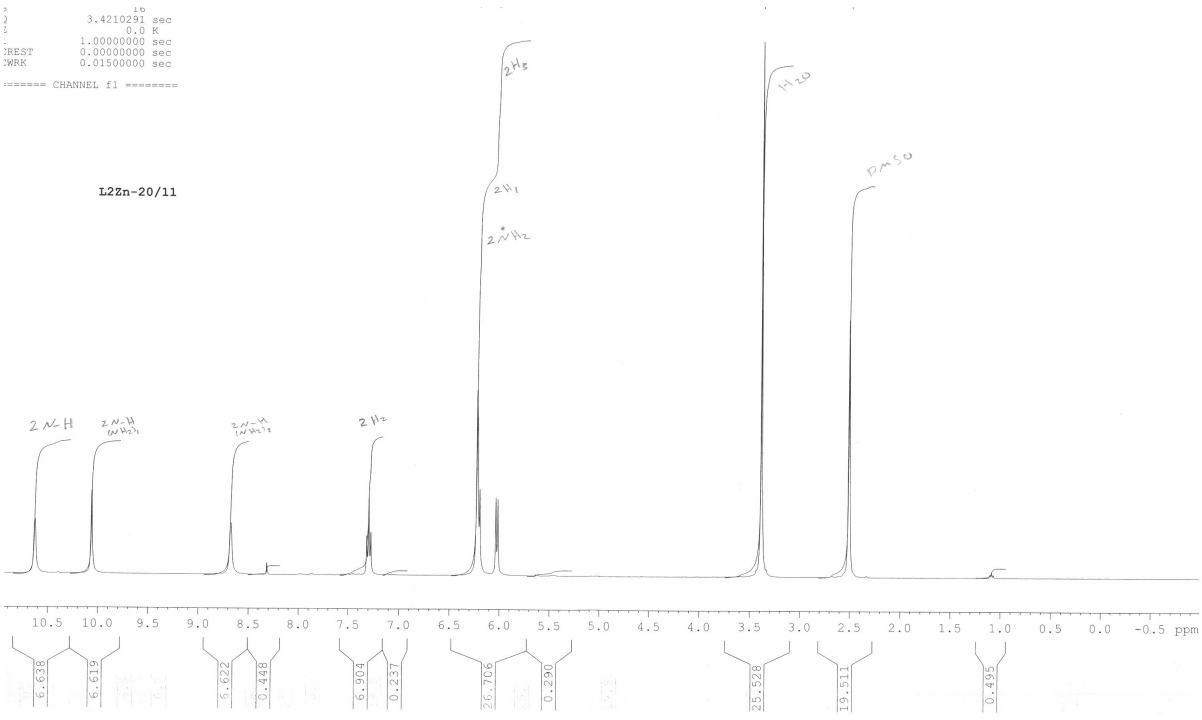

Figure S6. ^{1}H NMR spectrum of complex **9**.

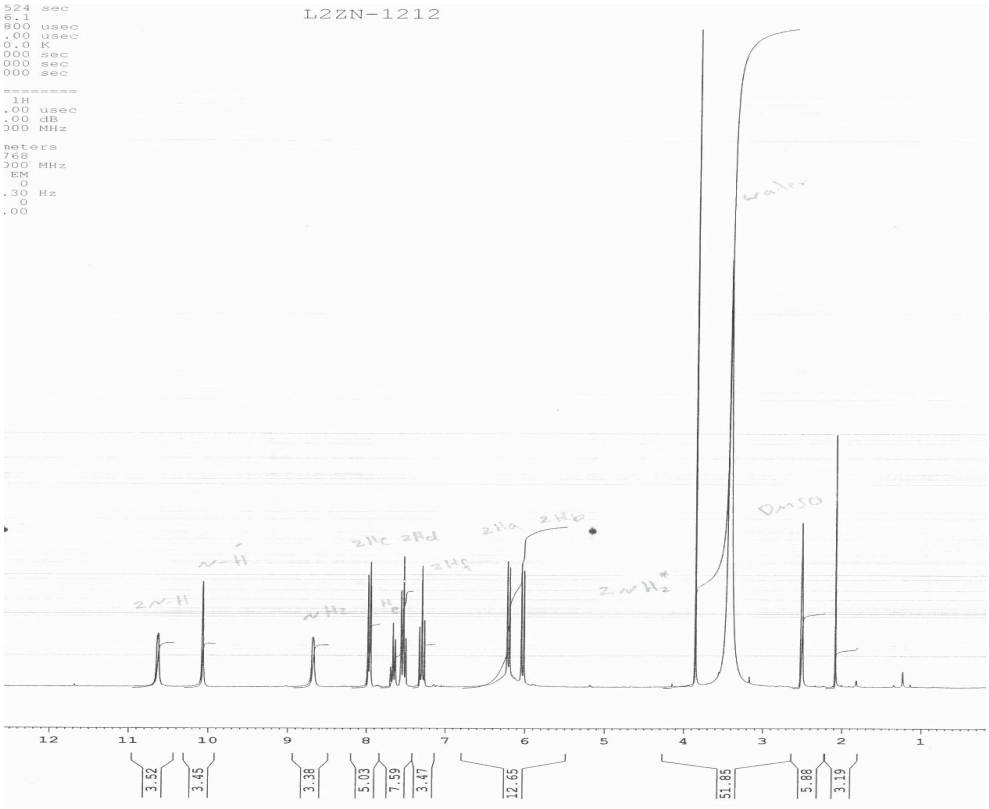

Figure S7. ^{1}H NMR spectrum of complex **10**.

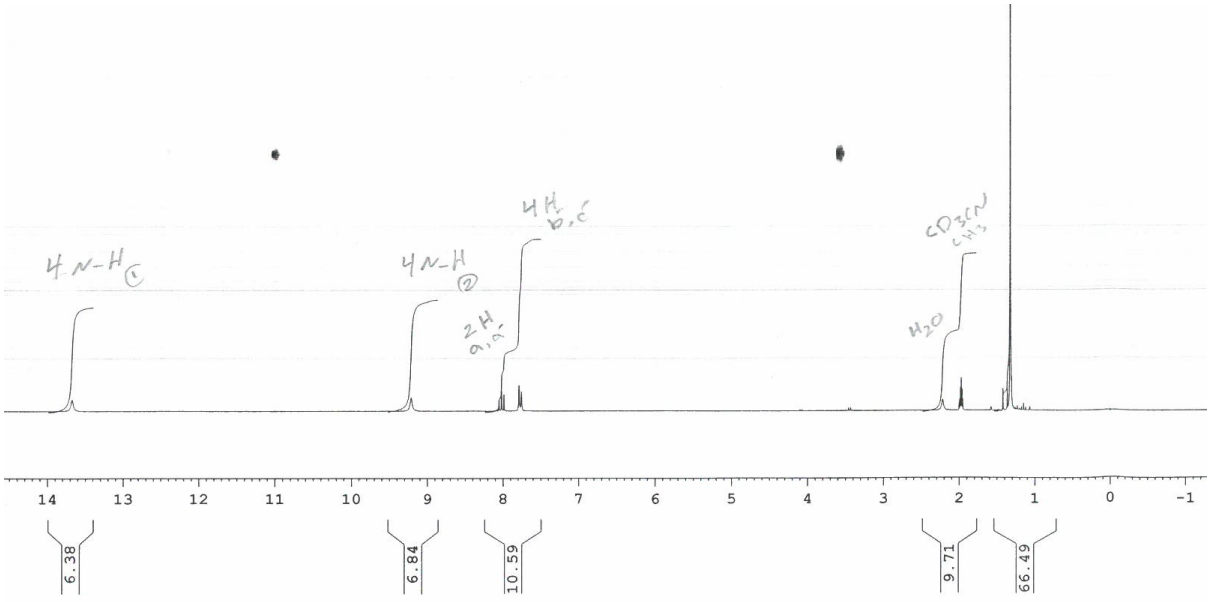

Figure S8. ^{1}H NMR spectrum of complex **22**.

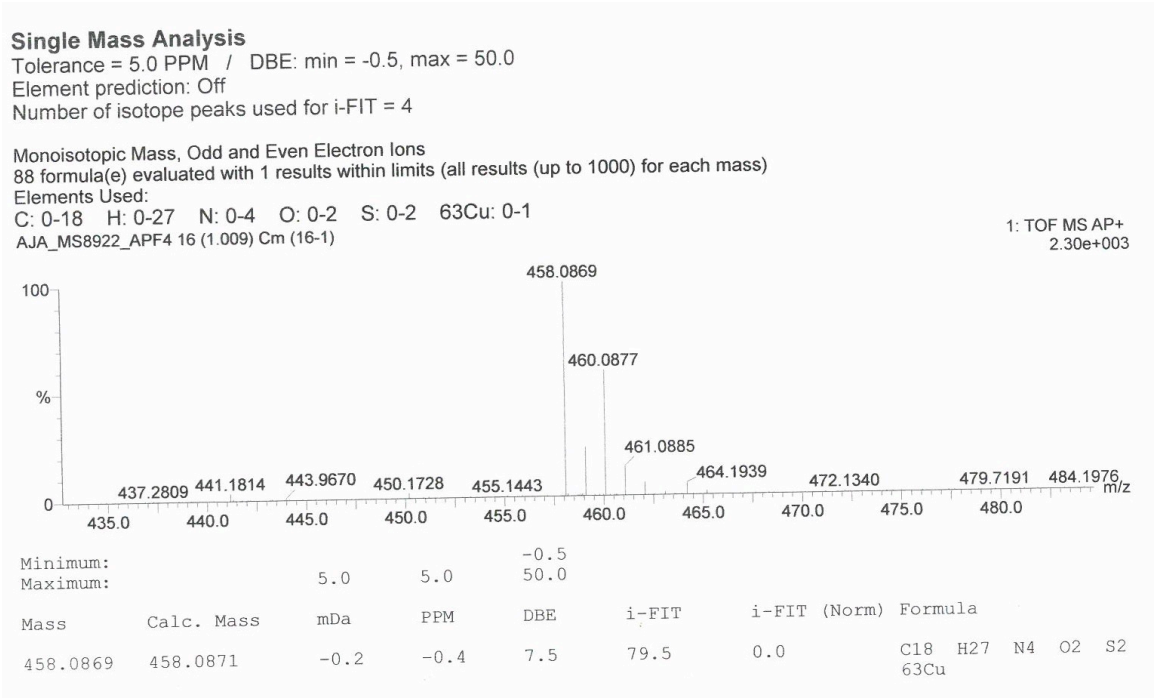

Figure S9. HRMS of complex **21**.

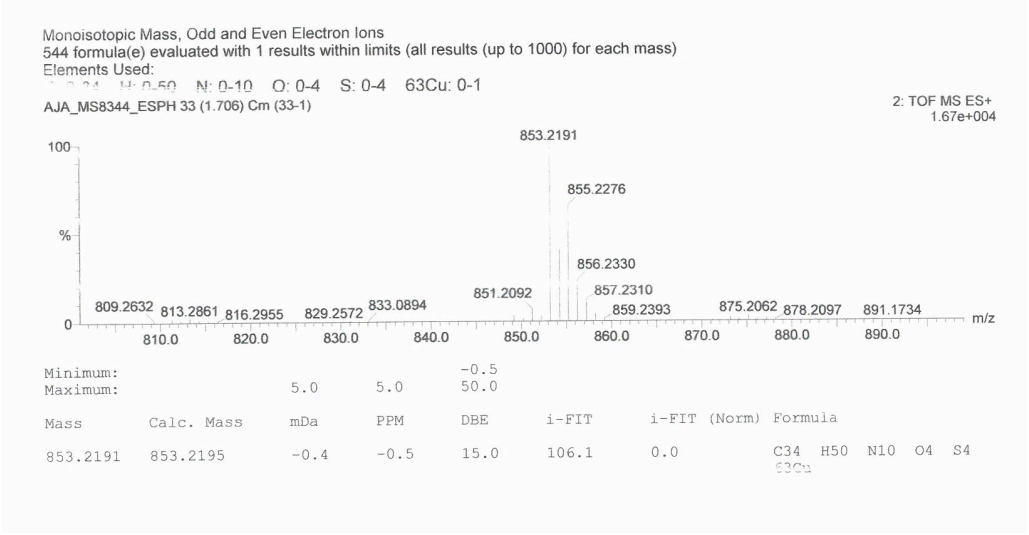

Figure S10. HRMS of complex **22**.

Table S2: Redox potential for the Cu complexes

Complex	Complex	E_P/V vs Ag^+/ AgCl	E_P/V vs Fc^+/Fc
L^1Cu	**1**	+0.922, +0.043 -0.216	+0.541, -0.337 -0.596
L^2Cu	**6**	+0.929, +0.110, -1.346	+0.474, -0.345, -1.801
L_3Cu	**11**	+0.461, -0.547	-0.029, -1.033
L_3Cu	**12**	-0.575	-1.072
$L^{1b}Cu$	**15**	-0.281	-0.733
$L^{1b}CuCl$	**16**	+1.159, +0.662, +0.086, -0.122	+0.634, 0.137, -0.437, -0.648
$L_{2b}Cu$	**18**	-0.640, -0.222	-1.144, -0.726
$L_{3b}Cu$	**21**	+0.186, -0.257, -0.778, -1.385	-0.167, -0.610, -1.130, -1.738
$L_{3b}Cu$	**22**	+0.017, -1.181	-0.358, -1.555

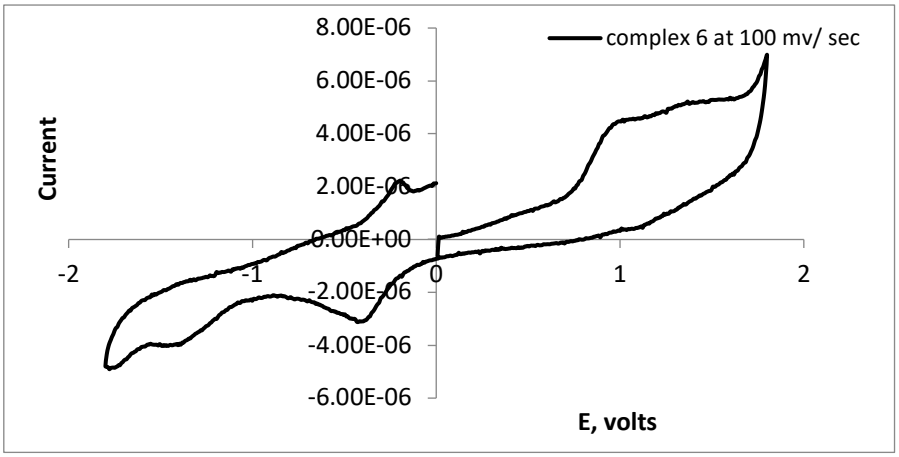

Figure S11. Cyclic voltammogram of complex **6**.

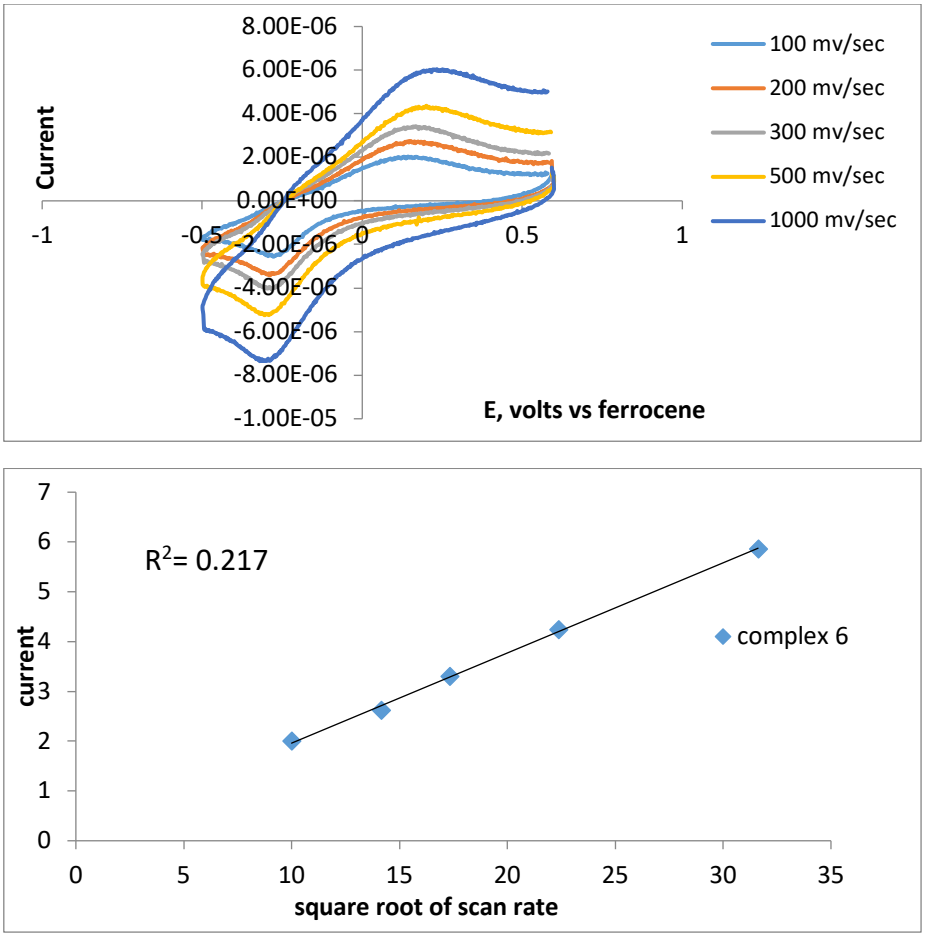

Figure S12. Cyclic voltammogram of complex **6** at varying scan rates along with a plot of current vs square root of the scan rate.

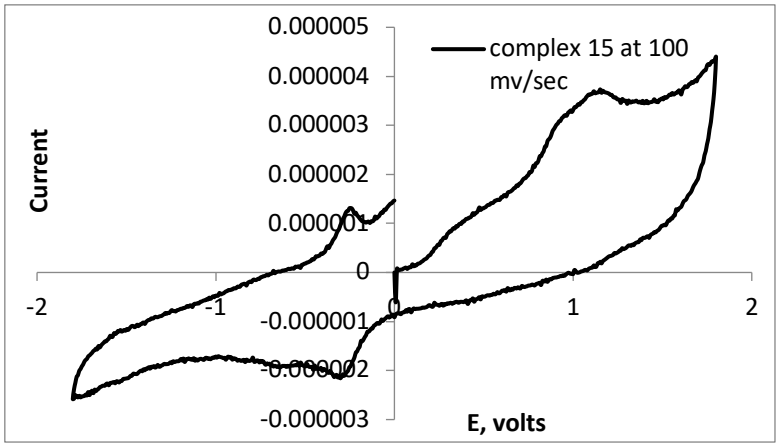

Figure S13. Cyclic voltammogram of complex **15**.

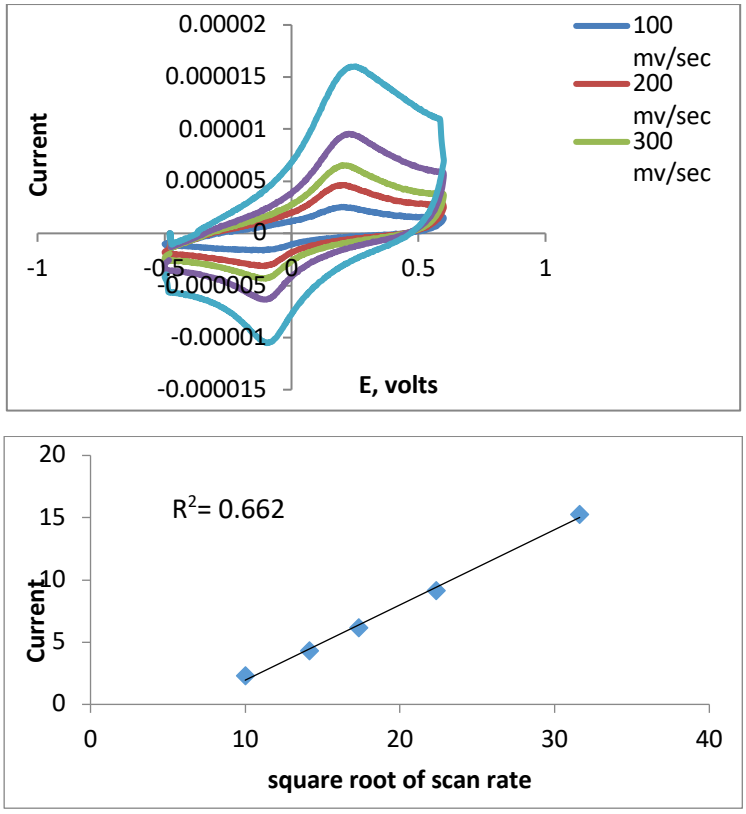

Figure S14. Cyclic voltammogram of complex **15** at varying scan rates along with a plot of current vs square root of the scan rate.

Table S3. Redox potential for Ni complexes

Complex	Complex	E_P/V vs Ag^+/AgCl	E_P/V vs Fc^+/Fc
$L^{1a/c}Ni$	**2**	-0.569, -1.332	-1.1447, -1.908
$L^{1a}Ni$	**3**	-0.446, -1.346	-1.022, -1.922
$L^{2c}Ni$	**7**	-0.641, -1.044	-1.267, -1.670
$L^{2a}Ni$	**8**	-0.785, -1.138	-1.332, -1.685
$L^{3a}Ni$	**13**	-0.706, -1.224	-1.112, -1.631
$L^{1b}Ni$	**17**	-0.576, -1.044	-1.150, -1.618
$L^{2b}Ni$	**20**	-0.641	-1.253
$L^{3b}Ni$	**23**	-0.648, -1.354	-1.058, -1.764

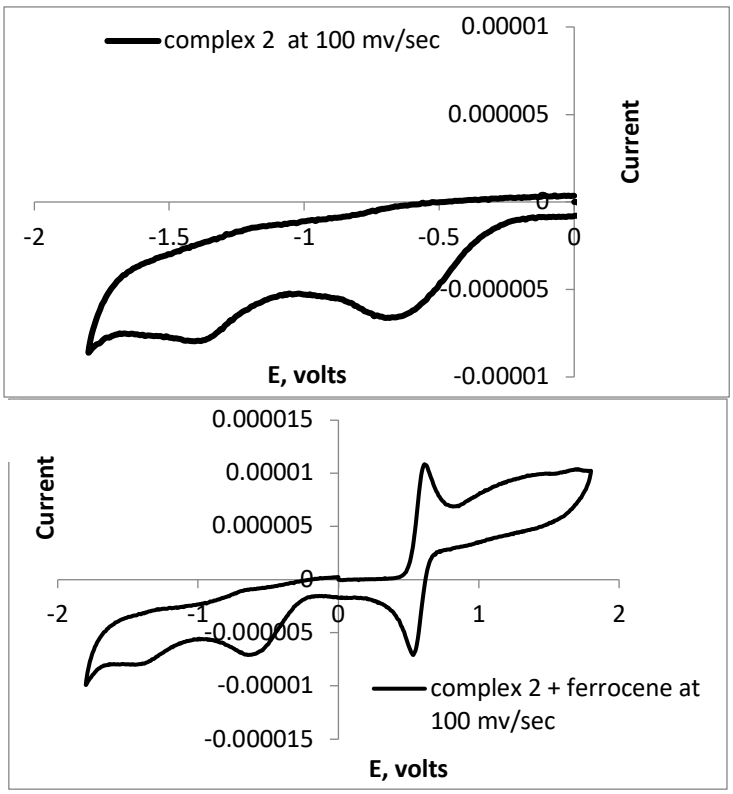

Figure S15. Cyclic voltammogram of complex **2** (top) and complex **2** + ferrocene (bottom).

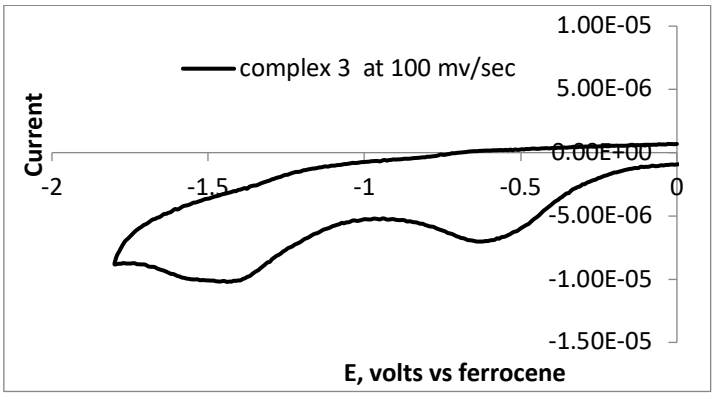

Figure S16. Cyclic voltammogram of complex **3**.

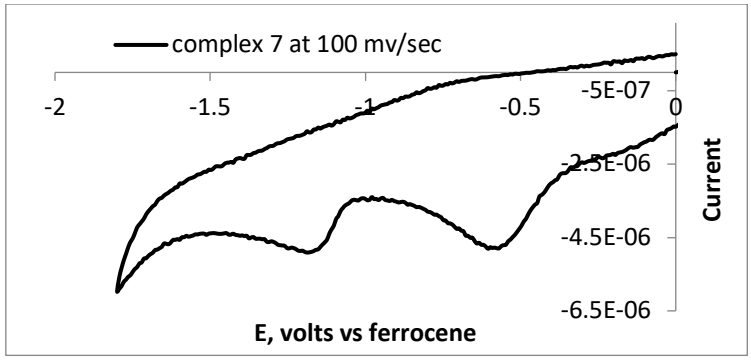

Figure S17. Cyclic voltammogram of complex **7**.