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Synthesis and electrochemical study of 2-carbamoyl-4,5-dihydro-1,3,4-thiadiazole-containing ligands and their complexes with Cu^{II}, Co^{II} and Ni^{II}

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NMR spectra were recorded in deuterated solvents using a Bruker Avance 300 NMR spectrometer at working frequencies of 300.13 MHz for ^{1}H and 75.77 MHz for ^{13}C. High resolution mass spectra (HRMS) were obtained using electrospray ionization (ESI) in acetonitrile using a Bruker MicroTOF instrument. Elemental analysis was performed using a Eurovector EA 3000 automatic analyzer. IR spectra were recorded in KBr on a Bruker ALPHA spectrometer. UV measurements were performed in 1 cm quartz cells, in 10^{-4} *M* DMSO solutions, using a Fluorat-02-Panorama spectrofluorimeter.

Electrochemical studies were performed using a PI-50-1.1 potentiostat controlled by a PR-8 programmer. A glass carbon disc (d = 2 mm) as the working electrode, 0.05 *M* solution of Bu_4NClO_4 in DMF as the supporting electrolyte, an Ag/AgCl/KCl(sat.) reference electrode, and a platinum plate as the auxiliary electrode were used. The potential sweep rate was 200 mV sec^{-1} in CVA studies or 20 mV sec^{-1} in rotating disc electrode studies. Potentials were reported with *iR* compensation taken into account. All measurements were performed in dry argon atmosphere. The solvent was pre-deaerated before samples were dissolved. “Pure” grade DMF was purified by stirring for 4 days with freshly calcined K_2CO_3 followed by distillation *in vacuo* first over P_2O_5 and then over anhydrous $CuSO_4$. During the second distillation, the first 20% of the distillate containing amine admixtures was discarded. Distillation was performed at a temperature no higher than 45°C.

Quantum chemical calculations were performed on a PC using HyperChem software by PM3 method. A gradient smaller than 0.01 kcal mol^{-1} was considered as the convergence criterion in the optimization of molecule geometry.

2-[*N*-(3-Ethoxycarbonyl-5-ethylthiophen-2-yl)carbamoyl]-5-(4-oxo-4*H*-chromen-3-yl)-4,5-dihydro-1,2,4-thiadiazole 3a

Yellow crystals (0.22 g, 49%). M.p. 243-244°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.17 (s, 1H, NH), 9.55 (s, 1H, NH), 9.00 (s, 1H, H^2), 8.24 (d, J = 8.1 Hz, 1H, Ar), 7.92 (t, J = 7.5 Hz, 1H, Ar), 7.80 (d, J = 8.5 Hz, 1H, Ar), 7.63 (t, J = 7.5 Hz, 1H, Ar), 6.94 (m, 2H, thiophen+H^{10}), 4.37 (dd, J = 14.3, 7.2 Hz, 2H, CH_2), 2.76 (d, J = 14.8, 7.4 Hz, 2H, CH_2), 1.43 – 1.09 (m, 6H, CH_3). ^{13}C NMR (75 MHz, DMSO-d_6) δ 175.4, 164.7, 156.6, 156.2, 155.0, 145.5, 137.5, 137.0, 135.1, 126.3, 125.4, 123.6, 123.5, 119.8, 119.0, 112.6, 68.1, 61.0, 22.4, 15.8, 14.6. IR, ν/cm^{-1} :3198 (NH), 2966 (NH), 1672 (C=O), 1636 (C=N), 1527 (C-N), 1027 (N-N). UV–Vis, λ_{max}, nm (ε, Lmol^{-1} cm^{-1}) (DMSO): 263 (17100), 310 (19500), 369 (19900). HRMS (ESI) Calc. for $[C_{21}H_{19}N_3O_5S_2 + H]^+$: 458.0839; Found: 458.0831.

5-(6-Bromo-7-hydroxy-4-oxo-4*H*-chromen-3-yl)-2-[*N*-(3-ethoxycarbonyl-5-ethylthiophen-2-yl)carbamoyl]-4,5-dihydro-1,2,4-thiadiazole 3b.

Yellowish-red crystals (0.41 g, 74%). M.p. 260-262°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.66 (s, 1H, NH), 9.36 (s, 1H, NH), 8.35 (s, 1H, H^5), 8.05 – 7.62 (m, 3H, Ar), 6.90 (s, 1H, thiophen), 6.67 (s, 1H, H^{10}), 4.30 (d, *J* = 8.2 Hz, 2H, CH_2), 2.71 (d, *J* = 7.4 Hz, 2H, CH_2), 1.47 – 1.02 (m, 6H, CH_3). ^{13}C NMR low solubility. IR, ν/cm^{-1} : 3384 (NH), 3320 (OH), 3282 (NH), 1667 (C=O), 1636 (C=N), 1528 (C_{11}-N_2), 1077 (N-N). UV–Vis, λ max, nm (ε, Lmol^{-1} cm^{-1}) (DMSO): 267 (71000), 298 (9800), 432 (2800). HRMS (ESI). Calculated for $[C_{21}H_{18}BrN_3O_6S_2+H]^+$: 551.9893; Found: 551.9903.

5-(2-Amino-4-oxo-4*H*-chromen-3-yl)-2-[*N*-(3-ethoxycarbonyl-5-ethylthiophen-2-yl)carbamoyl]-4,5-dihydro-1,2,4-thiadiazole 3c.

Yellow crystals (0.3 g, 64%). M.p. 194-197°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 14.26 (s, 1H, NH), 12.59 (s, 1H, NH), 9.96 (s, 1H, NH_2), 9.63 (s, 1H, NH_2), 9.41 (s, 1H, H^{10}), 8.02 (d, *J* = 7.5 Hz, 1H, Ar), 7.72 (t, *J* = 7.8 Hz, 1H, Ar), 7.44 (m, 2H, Ar), 6.99 (s, 1H, thiophen), 4.34 (d, *J* = 6.9 Hz, 2H, CH_2), 2.77 (d, *J* = 11.9 Hz, 2H, CH_2), 1.56 – 1.02 (m, 6H, CH_3). ^{13}C NMR (75 MHz, DMSO-d_6) δ 176.2, 168.9, 166.2, 164.3, 156.0, 153.1, 138.2, 134.9, 134.16, 126.2, 125.6, 120.5, 119.3, 117.4, 117.2, 112.2, 93.6, 61.3, 22.5, 15.8, 14.6. IR , ν/cm^{-1} : 3383 (NH_2), 3164 (NH), 3109 (NH), 1669 (C=O), 1609 (C=N), 1558 (C-N), 1037 (N-N). UV–Vis, λ max, nm (ε, Lmol^{-1} cm^{-1}) (DMSO): 261 (11000), 283 (13300), 399 (20700). HRMS (ESI) Calc. for $[C_{21}H_{20}N_4O_5S_2 + H]^+$: 473.0948; Found: 473.0936.

2-[*N*-(3-Ethoxycarbonyl-5-ethylthiophen-2-yl)carbamoyl]-5-(6-fluoro-4-oxo-4*H*-chromen-3-yl)-4,5-dihydro-1,2,4-thiadiazole 3d

White crystals (0.25 g, 59%). M.p. 235-237°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.66 (s, 1H, NH), 9.36 (s, 1H, NH), 8.35 (s, 1H, H^2), 7.90 – 7.68 (m, *J* = 6.9 Hz, 3H, Ar), 6.90 (s, 1H, thiophen), 6.66 (s, 1H, H^{10}), 4.29 (dd, *J* = 15.3, 8.2 Hz, 2H, CH_2), 2.71 (dd, *J* = 15.1, 7.7 Hz, 2H, CH_2), 1.30 (t, *J* = 7.1 Hz, 3H. CH_3), 1.20 (t, *J* = 7.5 Hz, 3H, CH_3). ^{13}C NMR low solubility. IR, ν/cm^{-1} : 3190 (NH), 3161 (NH), 1670 (C=O), 1635 (C=N), 1557 (C-N), 1035 (N-N). UV–Vis, λ max, nm (ε, Lmol^{-1} cm^{-1}) (DMSO): 267 (4000), 318 (6300), 369 (5500). HRMS (ESI) Calculated for $[C_{21}H_{18}FN_3O_5S_2 + H]^+$: 476.0735; Found: 476.0745.

Di-μ-dichloro-bis[2-(3-ethoxycarbonyl-5-ethylthiophene-2-ylamino)-(*Z*)-1-{(*E*)-[(4-oxo-4*H*-chromen-3-yl)methylidene]hydrazono}-2-oxoethyl)thio]dicopper(II) 4a

Green powder (0.01 g, 60%). M.p. 255-257°C. IR, ν/cm^{-1} : 3525 (NH), 1672 (C=O), 1616 (C=N), 1525 (C-N), 1027 (N-N). UV–Vis, λ max, nm (ε, Lmol^{-1} cm^{-1}) (DMSO): 267 (20600), 293 (22900), 357 (23100), (28700). Calculated for $C_{42}H_{36}Cl_2Cu_2N_6O_{10}S_4$ (%): C, 45.40; H, 3.27; N, 7.56; Found: C, 45.15; H, 3.45; N, 7.73.

Di-μ-dichloro-bis[2-(3-ethoxycarbonyl-5-ethylthiophene-2-ylamino)-(*Z*)-1-{(*E*)-[(4-oxo-4*H*-chromen-3-yl)methylidene]hydrazono}-2-oxoethyl)thio]dicobalt(II) 4b

Dark-red powder (0.01 g, 59%). M.p. 222-225°C. IR, ν/cm^{-1} : 3246 (NH), 1671 (C=O), 1624 (C=N), 1559 (C-N), 1032 (N-N). UV–Vis, λ max, nm (ε, Lmol^{-1} cm^{-1}) (DMSO): 265 (40600), 286 (36900), 334 (31700), 496 (21200). Calculated for $C_{42}H_{36}Cl_2Co_2N_6O_{10}S_4$ (%): C, 45.78; H, 3.29; N, 7.63; Found: C, 45.95; H, 3.45; N, 7.53.

Di-μ-dichloro-bis[2-(3-ethoxycarbonyl-5-ethylthiophene-2-ylamino)-(*Z*)-1-{(*E*)-[(6-bromo-7-hydroxy-4-oxo-4*H*-chromen-3-yl)methylidene]hydrazono}-2-oxoethyl)thio]dicopper(II) 4c

Green powder (0.01 g, 78%). M.p.>300°C. IR, ν/cm^{-1} : 3442 (OH), 3324 (NH), 1665 (C=O), 1628 (C=N), 1510 (C-N), 1072 (N-N). UV–Vis, λ max, nm (ε, Lmol^{-1} cm^{-1}) (DMSO): 261 (14600), 309 (26900), 436 (8700). Calculated for $C_{42}H_{32}Br_2Cl_2Cu_2N_6O_{12}S_4$ (%): C, 38.78; H, 2.63; N, 6.46; Found: C, 38.70; H, 2.55; N, 6.51.

Di-μ-dichloro-bis[2-(3-ethoxycarbonyl-5-ethylthiophene-2-ylamino)-(*Z*)-1-{(*E*)-[(6-bromo-7-hydroxy-4-oxo-4*H*-chromen-3-yl)methylidene]hydrazono}-2-oxoethyl)thio]dicobalt(II) 4d

Dark red powder (0.01 g, 76%). m.p. >300°C. IR, ν/cm^{-1} : 3422 (OH), 3320 (NH), 1666 (C=O), 1597 (C=N), 1527 (C-N), 1074 (N-N). UV–Vis, λ max, nm (ε, Lmol^{-1} cm^{-1}) (DMSO): 265 (17800), 319 (29200), 446 (7800). Calculated for $C_{42}H_{32}Br_2Cl_2Co_2N_6O_{12}S_4$ (%): C, 39.06; H, 2.65; N, 6.61; Found: C, 39.12; H, 2.55; N, 6.81.

Di-μ-dichloro-bis[2-(3-ethoxycarbonyl-5-ethylthiophene-2-ylamino)-(*Z*)-1-{(*E*)-[(2-amino-4-oxo-4*H*-chromen-3-yl)methylidene]hydrazono}-2-oxoethyl)thio]dicopper(II) 4e

Green powder (0.01 g, 71%). M.p. 220-222°C. IR, ν/cm^{-1} : 3547 (NH), 3436 (NH), 1654 (C=O), 1602 (C=N), 1560 (C-N), 1078 (N-N). UV–Vis, λ max, nm (ε, Lmol^{-1} cm^{-1}) (DMSO): 262 (12400), 343 (16000), 427 (11700). Calculated for $C_{42}H_{38}Cl_2Cu_2N_8O_{10}S_4$ (%): C, 44.21; H, 3.36; N, 9.82; Found: C, 44.32; H, 3.55; N, 9.70.

Di-μ-dichloro-bis[2-(3-ethoxycarbonyl-5-ethylthiophene-2-ylamino)-(*Z*)-1-{(*E*)-[(2-amino-4-oxo-4*H*-chromen-3-yl)methylidene]hydrazono}-2-oxoethyl)thio]dicobalt(II) 4f

Dark red powder (0.01 g, 69%). M.p. 215-216°C. IR, ν/cm^{-1} : w 3432 (NH), 3161 (NH), 1676 (C=O), 1602 (C=N), 1560 (C-N), 1064 (N-N). UV–Vis, λ max, nm (ε, Lmol^{-1} cm^{-1}) (DMSO): 263 (14600), 301 (16900), 429 (28700). Calculated for $C_{42}H_{38}Cl_2Co_2N_8O_{10}S_4$ (%):C, 44.57; H, 3.38; N, 9.90; Found: C, 44.62; H, 3.45; N, 9.73.

Di-μ-dichloro-bis[2-(3-ethoxycarbonyl-5-ethylthiophene-2-ylamino)-(*Z*)-1-{(*E*)-[(2-amino-4-oxo-4*H*-chromen-3-yl)methylidene]hydrazono}-2-oxoethyl)thio]dinickel(II) 4g

Yellowish-brown powder (0.01 g, 58%). M.p. 211-212°C. IR, ν/cm^{-1}: 3560 (NH), 3441 (NH), 1672 (C=O), 1607 (C=O), 1558 (C-N), 1030 (N-N). UV–Vis, λ max, nm (ε, Lmol^{-1} cm^{-1}) (DMSO): 261 (4900), 300 (8300), 362 (4900), 436 (9300). Calculated for $C_{42}H_{38}Cl_2Ni_2N_8O_{10}S_4$ (%):C, 44.59; H, 3.39; N, 9.90; Found: C, 44.64; H, 3.46; N, 9.70.

Di-μ-dichloro-bis[2-(3-ethoxycarbonyl-5-ethylthiophene-2-ylamino)-(*Z*)-1-{(*E*)-[(6-fluoro-4-oxo-4*H*-chromen-3-yl)methylidene]hydrazono}-2-oxoethyl)thio]dicopper(II) 4h

Green powder (0.01 g, 59%). M.p. 228-230°C. IR, ν/cm^{-1} : 3468 (NH), 1673 (C=O), 1626 (C=N), 1560 (C-N), 1022 (N-N). UV–Vis, λ max, nm (ε, Lmol^{-1} cm^{-1}) (DMSO): 261 (10600), 301 (16900), 436 (10900). Calculated for $C_{42}H_{32}Cl_2Cu_2F_2N_6O_{10}S_4$ (%): C, 43.98; H, 2.99; N, 7.33; Found: C, 43.95; H, 3.15; N, 7.13.

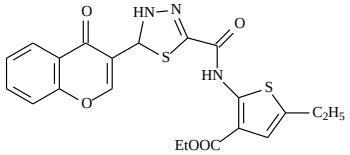
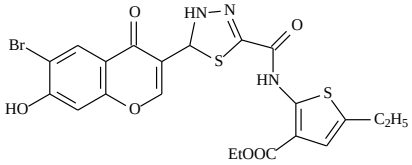
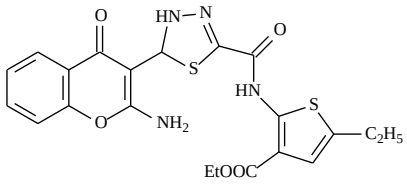
Di-μ-dichloro-bis[2-(3-ethoxycarbonyl-5-ethylthiophene-2-ylamino)-(*Z*)-1-{(*E*)-[(6-fluoro-4-oxo-4*H*-chromen-3-yl)methylidene]hydrazono}-2-oxoethyl)thio]dicobalt(II) 4i

Reddish-brown powder (0.01 g, 69%). M.p. 241-242°C. IR, ν/cm^{-1} : 3441 (NH), 1672 (C=O), 1624 (C=N), 1561 (C-N), 1067 (N-N). UV–Vis, λ max, nm (ε, $Lmol^{-1}$ cm^{-1}) (DMSO): 261 (12000), 300 (10900), 460 (8700). Calculated for $C_{42}H_{32}Cl_2Co_2F_2N_6O_{10}S_4$ (%): C, 44.34; H, 3.01; N, 7.39; Found: C, 44.37; H, 3.25; N, 7.53.

Di-μ-dichloro-bis[2-(3-ethoxycarbonyl-5-ethylthiophene-2-ylamino)-(*Z*)-1-{(*E*)-[(6-fluoro-4-oxo-4*H*-chromen-3-yl)methylidene]hydrazono}-2-oxoethyl)thio]dinickel(II) 4j

Yellowish-brown powder (0.01 g, 54%). M.p. 230-232°C. IR, ν/cm^{-1} 3434 (NH), 1675 (C=O), 1625 (C=N), 1560 (C-N), 1039 (N-N). UV–Vis, λ max, nm (ε, $Lmol^{-1}$ cm^{-1}) (DMSO): 262 (11200), 303 (9800), 464 (9000). Calculated for $C_{42}H_{32}Cl_2F_2Ni_2N_8O_{10}S_4$ (%): C, 44.35; H, 3.01; N, 7.39; Found: C, 44.22; H, 3.15; N, 7.30.

Table S1 Electrochemical reduction (E^{Red}) and oxidation potentials (E^{Ox}) of ligands **3a-d** and their metal-containing coordination compounds **4a-j** measured relative Ag|AgCl|KCl(sat.) by cyclic voltammetry at glassy-carbon electrode (DMF, 0.05 *M* Bu_4NClO_4, 200 mV s^{-1}). The values after the slash show the peak potentials recorded during reverse CV scans.

Compound	E_{pc}^{Red}, **V**	E_{pa}^{Ox}, **V**
 **3a**	-1.60 -1.82 -1.94	0.94 1.29
4a **[(3-H)$_2$Cu$_2$Cl$_2$]**	0.05/0.56 -0.46/-0.28 -1.42 -1.78 -1.97	0.94 1.14 1.34
3b 	-0.93/-0.87 -1.53 -2.04	1.33 1.48
4c **[(4-H)$_2$Cu$_2$Cl$_2$**	- 0.02/0.54 -0.54/-0.44 -1.23/-1.16 -1.78	0.83 1.08 1.23
4d **[(4 -H)$_2$Co$_2$Cl$_2$]**	-1.30/-1.24 -1.82	1.54
3c 	-1.10 -1.65	1.47 1.68
4g **[(5-H)$_2$Ni$_2$Cl$_2$]**	-0.85 -1.18 -1.44 -1.72 -1.95	0.83 0.93 1.14

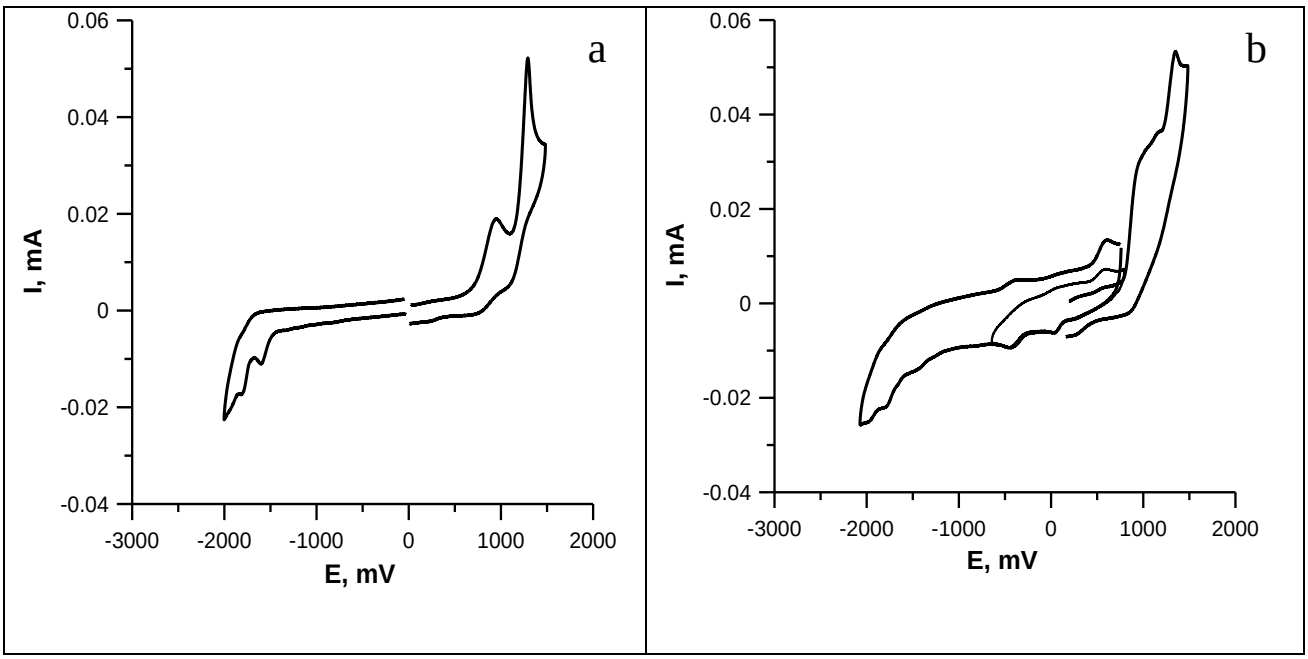


Figure S1 Cyclic voltammograms (GC electrode, DMF, 0.05 M Bu_4NClO_4): a) ligand **3a** (10^{-3} M), b) complex **4a** (10^{-4} M).

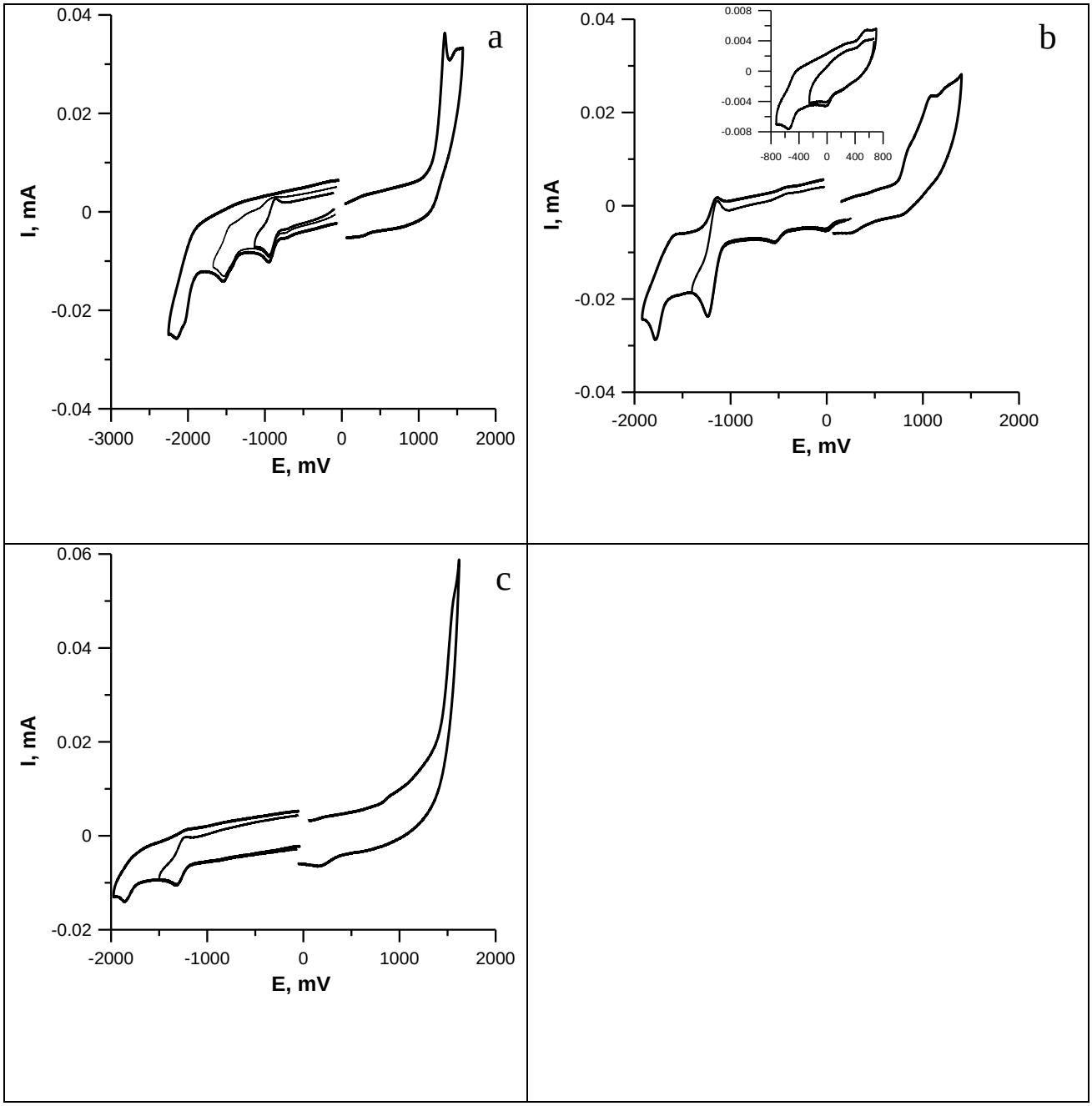


Figure S2 Cyclic voltammograms (DMF, GC electrode, 10^{-3} M concentration, 0.1 *M* Bu_4NClO_4) of ligand **3b** (a) and its coordination compounds **4c** (10^{-4} M) (b) and **4d** (10^{-4} M) (c).

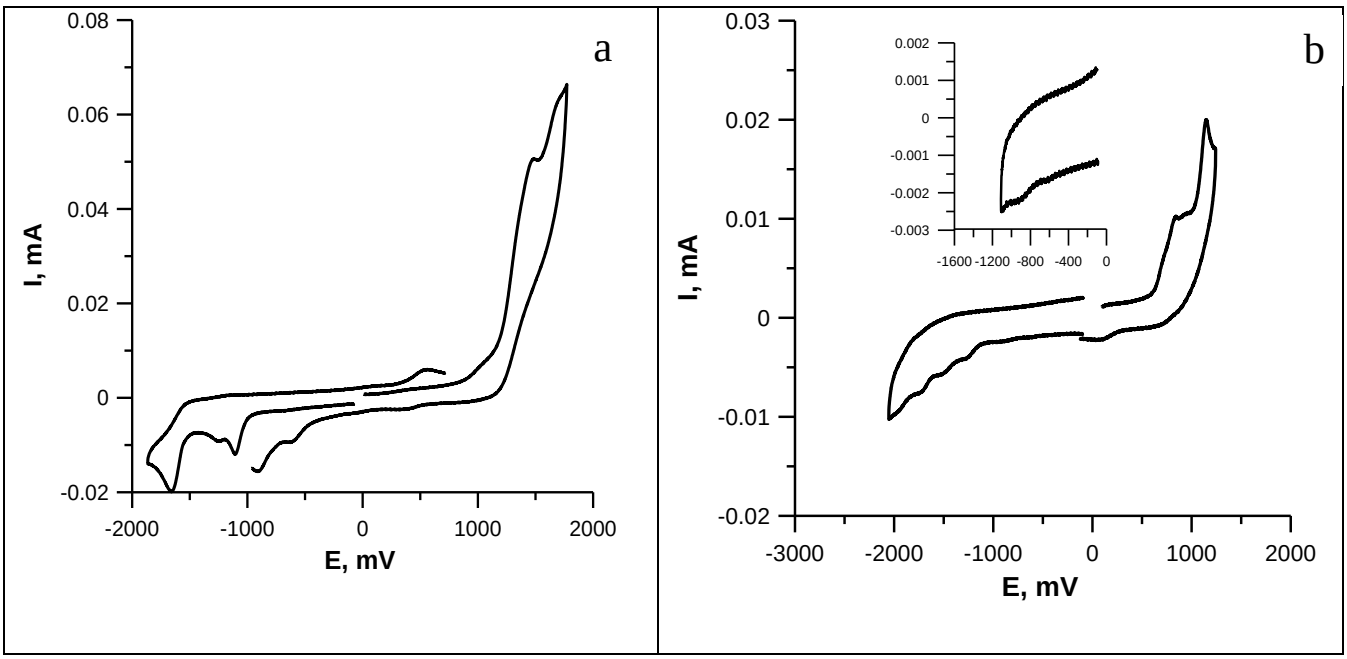


Figure S3 Cyclic voltammograms (DMF, GC electrode, 10^{-3} *M* concentration, 0.1 *M* Bu_4NClO_4) of ligand **3c** (a) and its coordination compound **4g** (10^{-5} M) (b).

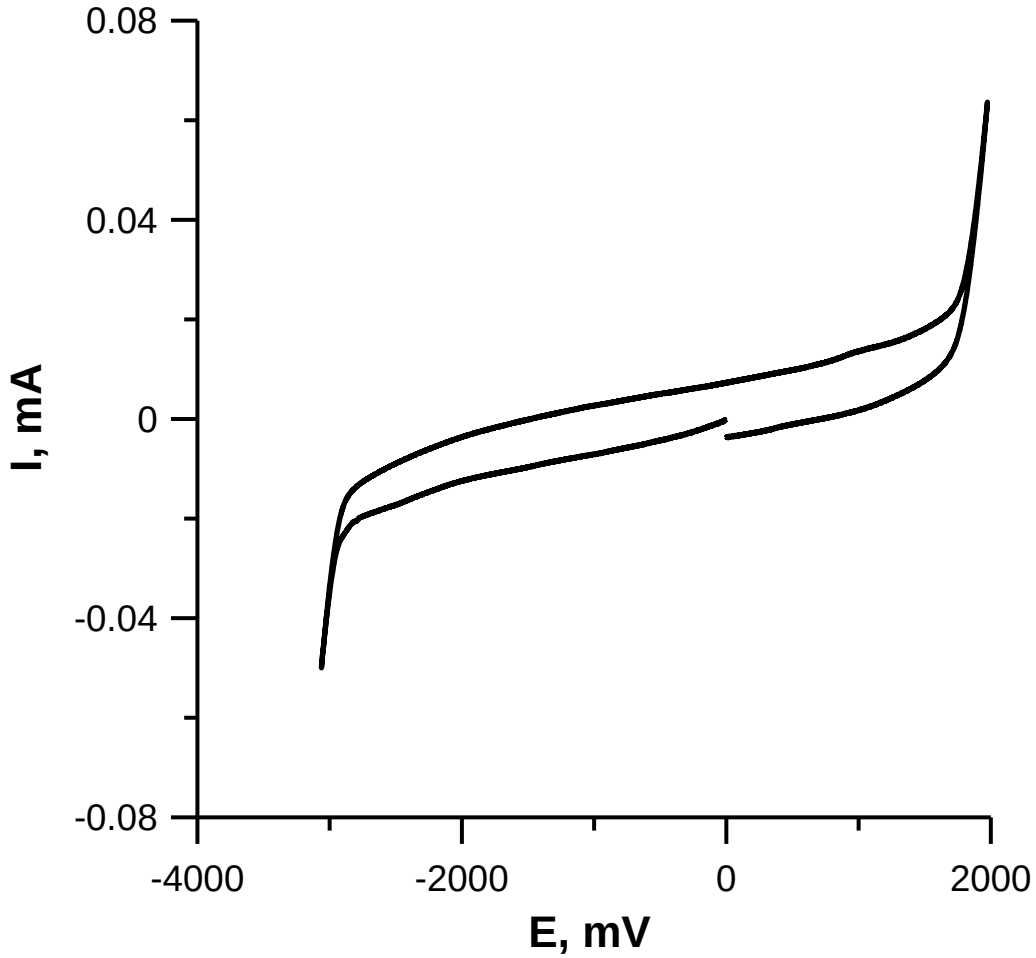


Figure S4 Cyclic voltammograms of DMF(GC electrode 0.05 *M* Bu_4NClO_4)

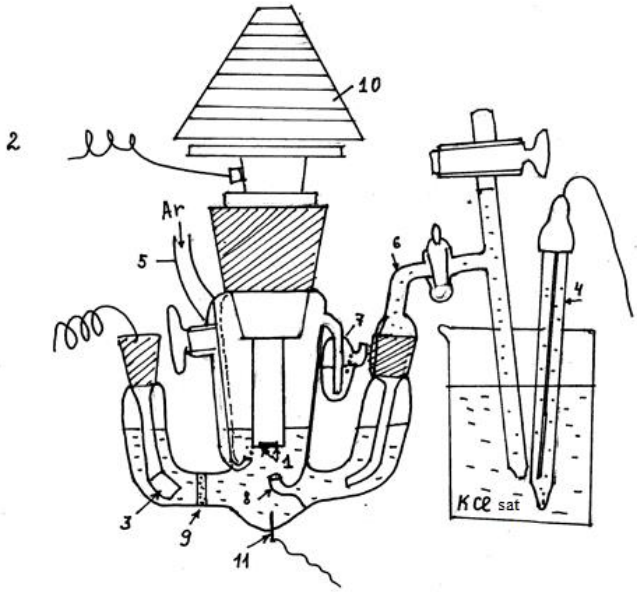


Figure S5 Electrochemical cell: 1 - disk electrode; 2 - graphite brush for contact of working electrode with potentiostat; 3 - auxiliary platinum electrode; 4 - reference electrode; 5 - supply of argon; 6 - electrochemical bridge; 7 - shutter for carrying of argon; 8 - Luggin's capillary; 9 - porous membrane separating the anodic and cathodic spaces (applies only to electrolysis); 10 - installation for rotation of the electrode; 11 - soldered platinum wire.