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A convenient synthesis of copper(II) bis[5-(pyridin-2-ylmethyidlene)-2-thiohydantoin] complexes

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Experimental

All common reagents were purchased from commercial suppliers and used as received. The melting points are uncorrected. ^{1}H NMR spectra were recorded on a Bruker Avance recorder (400 MHz for ^{1}H) in DMSO-d_6. Chemical shifts are reported in ppm relative to the solvent signal. Electronic spectra in 10^{-3} *M* DMF solution were obtained on a U2900 Hitachi UV–Vis spectrophotometer.

Synthesis of 3-substituted 2-thioxoimidazolidin-4-ones (2) or thioureas (3) (typical procedure). Benzylic amine **1a-g** (2-3 mmol) was dissolved in absolute diethyl ether (5 ml per 1 mmol of amine), and ethyl isothiocyanatoacetate was added. The mixture was stirred for 2 h. The resulting precipitated solid was filtered off, dried in air and used without additional purification.

Ethyl *N*-[(benzylamino)carbonothioyl]glycinate (3a) was obtained from benzylamine **1a** (0.3 g, 2.8 mmol) and ethyl isothiocyanatoacetate (0.41 g, 2.8 mmol), white solid. Yield 0.55 g (86%). mp 160-162 ºC. ^{1}H NMR spectrum, δ, ppm (J, Hz): 8.23 (1H, s, Ar-N<u>H</u>-CS-); 7.76 (1H, s, -CS-N<u>H</u>-CH_2-); 7.47 (2H, t, J = 7.4, H_3-,H_5-Ar); 7.41 (1H, t, J = 7.3, H_4-Ar); 7.27 (2H, d, J =7.1, H_2-, H_6-Ar); 4,66 (2H, br., s, -NH-C<u>H</u>$_2$-Ar); 4.21 (2H, br., s,-NH-C<u>H</u>$_2$-C(O)-); 4.09 (2H, q, J_3=7.35, C<u>H</u>$_2$-CH_3), 1.18 (3H, t, J=6.68, CH_2-C<u>H</u>$_3$).

3-(2-Chlorobenzyl)-2-thioxoimidazolidin-4-one (2b) was obtained from 2-chlorobenzyl-amine **1b** (0.3 g, 2.1 mmol) and ethyl isothiocyanatoacetate (0.31 g, 2.1 mmol), white solid. Yield 0.46 g (96%). mp 158-160ºC. ^{1}H NMR spectrum, δ, ppm (J, Hz): 7.48 (2H, d, J =7.62, H_3-, H_5-Ar); 7.15 (1H, t, J =7.64, H_4-Ar); 7.08 (1H, s, H_6-Ar); 4.90 (2H, s, =N-C<u>H</u>$_2$-Ar); 4.28 (2H, s, -NH-C<u>H</u>$_2$-C(O)-).

Ethyl *N*-[(3-chlorobenzylamino)carbonothioyl]glycinate (3c) was obtained from 3-chloro-benzylamine **1c** (0.3 g, 2.1 mmol) and ethyl isothiocyanatoacetate (0.31 g, 2.1 mmol), white solid. Yield 0.41 g (86%). mp 118-119 ºC**.** ^{1}H NMR spectrum, δ, ppm (J, Hz): 8.27 (1H, s, Ar-N<u>H</u>-CS-); 7.81 (1H, s, -CS-N<u>H</u>-CH_2-); 7.45 (1H, d, J =7.60, H_5-Ar); 7.28 (2H, d, J = 7.75, H_2-,H_6-Ar); 7.05 (1H, d, J =7.60, H_4-Ar); 4.66 (2H, br., s, -NH-C<u>H</u>$_2$-Ar); 4.21 (2H, br., s,-NH-C<u>H</u>$_2$-C(O)-); 4.09 (2H, q, J=7.35, C<u>H</u>$_2$-CH_3); 1.18 (3H, t, J=6.68, CH_2-C<u>H</u>$_3$).

Ethyl *N*-[(4-chlorobenzylamino)carbonothioyl]glycinate (3d) was obtained from 4-chlorobenzylamine **1d** (0.3 g, 2.1 mmol) and ethyl isothiocyanatoacetate (0.31 g, 2.1 mmol), white solid. Yield 0.40 g (85%). mp 120-122 °C. ^{1}H NMR spectrum, δ, ppm (J, Hz): 8.23 (1H, s, Ar-NH-CS-); 7.76 (1H, s, -CS-NH-CH$_2$-); 7.37 (2H, d, J = 8.28, H$_3$-,H$_5$-Ar); 7.29 (2H, d, J =8.31, H$_2$-, H$_6$-Ar); 4.66 (2H, br., s, -NH-CH$_2$-Ar); 4.21 (2H, br., s,-NH-CH$_2$-C(O)-); 4.09 (2H, q, J$_3$=7.35, CH$_2$-CH$_3$), 1.18 (3H, t, J$_3$=6.68, CH$_2$-CH$_3$).

3-(2-Bromobenzyl)-2-thioxoimidazolidin-4-one (2e) was obtained from 2-bromobenzylamine **1e** (0.3 g, 1.61 mmol) and ethyl isothiocyanatoacetate (0.23 g, 1.61 mmol), white solid. Yield 0.41 g (95%). mp 171-173 °C. ^{1}H NMR spectrum, δ, ppm (J, Hz): 7.54 (2H, d, J =7.68, H$_3$, H$_5$-Ar); 7.18 (1H, t, J =7.60, H$_4$-Ar); 7.05 (1H, s, H$_6$-Ar); 4.94 (2H, s, =N-CH$_2$-Ar); 4.32 (2H, s, -NH-CH$_2$-C(O)-).

Ethyl *N*-[(3-bromobenzylamino)carbonothioyl]glycinate (3f) was obtained from 3-bromobenzylamine **1f** (0.3 g, 1.61 mmol) and ethyl isothiocyanatoacetate (0.23 g, 1.61 mmol), white solid. Yield 0.40 g (93%). mp 122-123 °C**.** ^{1}H NMR spectrum, δ, ppm (J, Hz): 8.21 (1H, s, Ar-NH-CS-); 7.71 (1H, s, -CS-NH-CH$_2$-); 7.35 (1H, d, J =7.60, H$_5$-Ar); 7.24 (2H, d, J = 7.75, H$_2$-,H$_6$-Ar); 7.01 (1H, d, J =7.60, H$_4$-Ar); 4.66 (2H, br., s, -NH-CH$_2$-Ar); 4.21 (2H, br., s,-NH-CH$_2$-C(O)-); 4.09 (2H, q, J$_3$=7.35, CH$_2$-CH$_3$); 1.18 (3H, t, J$_3$=6.68, CH$_2$-CH$_3$).

Ethyl *N*-[(4-bromobenzylamino)carbonothioyl]glycinate (3g) was obtained from 4-bromobenzylamine **1g** (0.3 g, 1.61 mmol) and ethyl isothiocyanatoacetate (0.23 g, 1.61 mmol), white solid. Yield 0.37 g (86%). mp 125-126 °C. ^{1}H NMR spectrum, δ, ppm (J, Hz): 8.23 (1H, s, Ar-NH-CS-); 7.76 (1H, s, -CS-NH-CH$_2$-); 7.37 (2H, d, J = 8.28, H$_3$-,H$_5$-Ar); 7.29 (2H, d, J =8.31, H$_2$-, H$_6$-Ar); 4.66 (2H, br., s, -NH-CH$_2$-Ar); 4.21 (2H, br., s,-NH-CH$_2$-C(O)-); 4.09 (2H, q, J=7.35, CH$_2$-CH$_3$), 1.18 (3H, t, J=6.68, CH$_2$-CH$_3$).

Synthesis of 3-substituted Z-5-(pyridin-2-ylmethylidene)-2-thioxoimidazolidin-4-ones 4 (typical procedure). 2-Thiohydantoins **2** or thioureas **3** (0.3 g; 1.05 or 1.24 mmol) were dissolved in ethanolic KOH solution (2%, 6 ml) with stirring. After complete dissolution, pyridine-2-carbaldehyde (0.13-0.167 g, 1.24-1.45 mmol) was added dropwise. The mixture was stirred for 1.5 h. Dilute hydrochloric acid (~10%) was added to the resulting mixture with vigorous stirring to reach pH = 7. The formed precipitate was filtered off, washed with ethyl alcohol and then with diethyl ether, and dried in air.

***Z*-3-Benzyl-5-(pyridin-2-ylmethylidene)-2-thioxoimidazolidin-4-one (4a)** was obtained from compound **3a** (0.3 g, 1.56 mmol) and pyridine-2-carbaldehyde (0.167 g, 1.45 mmol), orange solid. Yield 0.41 g (93%). mp 190-191 °C. ^{1}H NMR spectrum, δ, ppm (J, Hz): 11.88 (br., 1H, s, -NH); 8.77 (1H, d, J=4,5, H$_6$-Py); 7.91 (1H, t, J=7.7, H$_4$-Py); 7.77 (1H, d, J=7.7, H$_3$-Py); 7.44-7.54 (3H, m.); 7.35-7.44 (3H, m.); 6.81 (1H, s, -CH=). Found, %: C 66.10; H 4.77; N 13.76; S 10.56. $C_{17}H_{15}N_3OS$. Calculated, %: C 66.00; H 4.89; N 13.58; S 10.36.

***Z*-3-(2-Chlorobenzyl)-5-(pyridin-2-ylmethylidene)-2-thioxoimidazolidin-4-one (4b)** was obtained from compound **2b** (0.3 g, 1.24 mmol) and pyridine-2-carbaldehyde (0.13 g, 1.24 mmol), orange solid. Yield 0.34 g (82%). mp 194-195 °C. ^{1}H NMR spectrum, δ, ppm (J, Hz): 11.92 (br., 1H, s, -NH); 8.78 (1H, d, J=4.1, H_3-Py); 7.90 (1H, t, J=7.7, H_4-Py); 7.77 (1H, d, J=7.8, H_6-Py); 7.49 (1H, d, J=7.8, H-Ar); 7.41 (1H, t, J=6.1, H_5-Py); 7.25-7.33 (2H, m, H-Ar); 7.07 (1H, d, J = 6.6, H-Ar); 6.82 (1H, s, -CH=); 5.05 (2H, s, -CH_2-Ar). Found, %: C 58.18; H 3.77; N 12.76; S 9.56. $C_{16}H_{12}ClN_3OS$. Calculated, %: C 58.27; H 3.67; N 12.74; S 9.72.

***Z*-3-(3-Chlorobenzyl)-5-(pyridin-2-ylmethylidene)-2-thioxoimidazolidin-4-one (4c)** was obtained from compound **3c** (0.3 g, 1.24 mmol) and pyridine-2-carbaldehyde (0.13 g, 1.24 mmol), orange solid. Yield 0.36 g (87%). mp 193-194 °C. ^{1}H NMR spectrum, δ, ppm (J, Hz): 11.86 (br., 1H, s, -NH); 8.77 (1H, d, J=4.5, H_3-Py); 7.89 (1H, t, J=7.7, H_4-Py); 7.73 (1H, d, J=7.5, H_6-Py); 7.25-7.42 (3H, m, H_5-Py, 4H-Ar); 6.79 (1H, s, -CH=); 5.01 (2H, s, -N-CH_2-) Found, %: C 58.28; H 3.84; N 12.82; S 9.54. $C_{16}H_{12}ClN_3OS$. Calculated, %: C 58.27; H 3.67; N 12.74; S 9.72.

***Z*-3-(4-Chlorobenzyl)-5-(pyridin-2-ylmethylidene)-2-thioxoimidazolidin-4-one (4b)** was obtained from compound **3d** (0.3 g, 1.24 mmol) and pyridine-2-carbaldehyde (0.13 g, 1.24 mmol), orange solid. Yield 0.34 g (84%). mp 190-192 °C. ^{1}H NMR spectrum, δ, ppm (J, Hz): 11.88 (br., 1H, s, -NH); 8.75 (1H , d, J=4.5, H_6-Py); 7.89 (1H, t, J=7.36, H_4-Py); 7.75 (1H, d, J=7.89, H_3-Py); 7.33-7.40 (3H, m.); 7.35-7.44 (3H, m.); 6.78 (1H, s, -CH=). Found, %: C 58.32; H 3.64; N 12.92; S 9.32. $C_{16}H_{12}ClN_3OS$. Calculated, %: C 58.27; H 3.67; N 12.74; S 9.72.

***Z*-3-(2-Bromobenzyl)-5-(pyridin-2-ylmethylidene)-2-thioxoimidazolidin-4-one (4e)** was obtained from compound **2e** (0.3 g, 1.05 mmol) and pyridine-2-carbaldehyde (0.11 g, 1.24 mmol), orange solid. Yield 0.30 g (76%). ^{1}H NMR spectrum, δ, ppm (J, Hz): 11.88 (br., 1H, s, -NH); 8.77 (1H, d, H_6-Py); 7.91 (1H, t, H_4-Py); 7.77 (1H, d, H_3-Py); 7.44-7.54 (3H, m); 7.35-7.44 (3H, m); 6.81 (1H, s, -CH=). Found, %: C 51.32; H 3.34; N 11.62; S 8.32. $C_{16}H_{12}BrN_3OS$. Calculated, %: C 51.35; H 3.23; N 11.23; S 8.57.

***Z*-3-(3-Bromobenzyl)-5-(pyridin-2-ylmethylidene)-2-thioxoimidazolidin-4-one (4f)** was obtained from compound **3f** (0.3 g, 1.05 mmol) and pyridine-2-carbaldehyde (0.11 g, 1.24 mmol), orange solid. Yield 0.33 g (84%). ^{1}H NMR spectrum, δ, ppm (J, Hz): 11.88 (br., 1H, s, -NH); 8.77 (1H, d, H_6-Py); 7.91 (1H, t, H_4-Py); 7.77 (1H, d, H_3-Py); 7.44-7.54 (3H, m); 7.35-7.44 (3H, m); 6.81 (1H, s, -CH=). Found, %: C 51.34; H 3.26; N 11.21; S 8.42. $C_{16}H_{12}BrN_3OS$. Calculated, %: C 51.35; H 3.23; N 11.23; S 8.57.

***Z*-3-(4-Bromobenzyl)-5-(pyridin-2-ylmethylidene)-2-thioxoimidazolidin-4-one (4g)** was obtained from compound **3g** (0.3 g, 1.05 mmol) and pyridine-2-carbaldehyde (0.11 g, 1.24 mmol), orange solid. Yield 0.31 g (80%). ^{1}H NMR spectrum, δ, ppm (J, Hz): 11.88 (br., 1H, s, -NH); 8.77 (1H, d, H_6-Py); 7.91 (1H, t, H_4-Py); 7.77 (1H, d, H_3-Py); 7.44-7.54 (3H, m); 7.35-7.44

(3H, m); 6.81 (1H, s, -CH=). Found, %: C 51.46; H 3.29; N 11.25; S 8.64. $C_{16}H_{12}BrN_3OS$. Calculated, %: C 51.35; H 3.23; N 11.23; S 8.57.

Synthesis of coordination compounds 5 (typical procedure). Ligand **4** (0.02 g) was dissolved in dichloromethane (4 ml). Copper(II) acetylacetonate (1 equiv.) was dissolved in dichloromethane (4 ml). A solution of $Cu(acac)_2$ was slowly added to a ligand solution, avoiding rapid precipitation. The reaction vessel was tightly closed and allowed to settle to a crystalline precipitate at a temperature of 0 °C. If the precipitate was not formed within 48 hours, precipitation was achieved by slow diffusion of diethyl ether vapors into the reaction mixture.

Bis[*Z*-3-benzyl-4-oxo-5-(pyridin-2-ylmethylidene)-2-thioxoimidazolidin-1-yl]copper(II) 5a. Black spiky prisms (0.007 g; 20%), were obtained from ligand **4a** (0.02 g, $10.4•10^{-2}$ mmol) and $Cu(acac)_2$ (0.027 g, $10.4•10^{-2}$ mmol). Found, %: C 58.49%; H 3.64%; N 13.05%. $C_{32}H_{24}CuN_6O_2S_2$. Calculated, %: C 58.93%; H 3.71%; N 12.88%.

Bis[*Z*-3-(2-chlorobenzyl)-4-oxo-5-(pyridin-2-ylmethylidene)-2-thioxoimidazolidin-1-yl]copper(II) 5b. Black spiky prisms (0.0062 g; 56%), were obtained from ligand **4b** (0.02 g, $6.06•10^{-2}$ mmol) and $Cu(acac)_2$ (0.010 g, $6.06•10^{-2}$ mmol). Found, %: C 53.49%; H 3.17%; N 11.65%. $C_{32}H_{24}ClCuN_6O_2S_2$. Calculated, %: C 53.30%; H 3.07%; N 11.65%.

Bis[*Z*-3-(3-chlorobenzyl)-4-oxo-5-(pyridin-2-ylmethylidene)-2-thioxoimidazolidin-1-yl]copper(II) 5c. Black spiky prisms (0.005 g; 46%), were obtained from ligand **4c** (0.02 g, $6.06•10^{-2}$ mmol) and $Cu(acac)_2$ (0.010 g, $6.06•10^{-2}$ mmol). Found, %: C 52.98%; H 3.34%; N 11.71%. $C_{32}H_{24}Cl_2CuN_6O_2S_2$. Calculated, %: C 53.30%; H 3.07%; N 11.65%.

Bis[*Z*-3-(4-chlorobenzyl)-4-oxo-5-(pyridin-2-ylmethylidene)-2-thioxoimidazolidin-1-yl]copper(II) 5d. Black spiky prisms (0.006 g; 54%), were obtained from ligand **4d** (0.02 g, $6.06•10^{-2}$ mmol) and $Cu(acac)_2$ (0.010 g, $6.06•10^{-2}$ mmol). Found, %: C 53.62%; H 3.35%; N 11.46%. $C_{32}H_{24}Cl_2CuN_6O_2S_2$. Calculated, %: C 53.30%; H 3.07%; N 11.65%.

Bis[*Z*-3-(2-bromobenzyl)-4-oxo-5-(pyridin-2-ylmethylidene)-2-thioxoimidazolidin-1-yl]copper(II) 5e. Black spiky prisms (0.005 g; 20%), were obtained from ligand **4e** (0.02 g, $5.83•10^{-2}$ mmol) and $Cu(acac)_2$ (0.015 g, $5.83•10^{-2}$ mmol). Found, %: C 47.49%; H 2.64%; N 10.54%. $C_{32}H_{24}Br_2CuN_6O_2S_2$. Calculated, %: C 47.45%; H 2.74%; N 10.37%.

Bis[*Z*-3-(3-bromobenzyl)-4-oxo-5-(pyridin-2-ylmethylidene)-2-thioxoimidazolidin-1-yl]copper(II) 5f. Black spiky prisms (0.006 g; 24%), were obtained from ligand **4f** (0.02 g, $5.83•10^{-2}$ mmol) and $Cu(acac)_2$ (0.015 g, $5.83•10^{-2}$ mmol). Found, %: C 47.69%; H 2.44%; N 10.35%. $C_{32}H_{24}Br_2CuN_6O_2S_2$. Calculated, %: C 47.45%; H 2.74%; N 10.37%.

Bis[*Z*-3-(4-bromobenzyl)-4-oxo-5-(pyridin-2-ylmethylidene)-2-thioxoimidazolidin-1-yl]copper(II) 5g. Black spiky prisms (0.005 g; 20%), were obtained from ligand **4g** (0.02 g, $5.83•10^{-2}$ mmol) and $Cu(acac)_2$ (0.015 g, $5.83•10^{-2}$ mmol). Found, %: C 47.10%; H 2.89%; N 10.34%. $C_{32}H_{24}Br_2CuN_6O_2S_2$. Calculated, %: C 47.45%; H 2.74%; N 10.37%.

X-Ray Study

Table S1 Summary of Crystallographic Information for $C_{32}H_{24}Br_2CuN_6O_2S_2*CH_2Cl_2$.

Crystal data

Chemical Formula	$C_{33}H_{24}Br_2CuN_6O_2S_2*CH_2Cl_2$*
Molecular weight	895
Crystal system	Tetragonal
Space group	P*4/n*
Cell constants (Å)	*a* = 31.6531(6) *c* = 7.7612(7)
Volume (Å^3)	7776.1(7)
Z	8
D_{calc}, g·cm^{-3}	1.528
Radiation	CuKα
Wavelenghth (Å)	1.54178
Diffraction pattern	Single crystal
θ range	3.95 – 74.80
Linear absorption coefficient (cm^{-1})	57.73
Temperature (K)	295
Diffractometer	STOE STADI VARI PILATUS-100K

Refinement

Program package	
Solution	SIR2002
Refinement	JANA2000, SHELX-2014
Refinement on	F, F^2
R/R_{wp}	0.059/0.077
Goodness of fit	1.151
No. of observed reflections	4034
No. of refined parameters	434
Residual density, *e*/Å^3	+0.72 / –0.51

*The structure contains additional strongly disordered molecule of a solvent.

Table S2 Selected interatomic distances in $C_{32}H_{24}Br_2CuN_6O_2S_2*CH_2Cl_2$.

Atoms	Distance, Å	Atoms	Distance (Range), Å
Cu1 – N1	2.147(4)	N2 – C10	1.553(9)
Cu1 – N3	1.942(4)	C10 – C11	1.521(8)
Cu1 – N4	2.088(4)	C21 – C22	1.444(6)
Cu1 – N6	1.898(4)	C22 – C23	1.334(7)
C5 – C6	1.497(9)	N5 – C26	1.473(5)
C6 – C7	1.376(9)	C26 – C27	1.595(8)

Electrochemistry

Electrochemical measurements were performed on a IPC Pro M potentiostate. Glassy-carbon (GC) disks (d = 2 mm) were used as the working electrodes, a 0.1 *M* Bu_4NClO_4 solution in DMF served as the supporting electrolyte, and Ag/AgCl/KCl(satur.) was used as the reference electrode. The potential scan rates were 100 mV s^{-1} All measurements were carried out under argon. The samples were dissolved in the pre-deaerated solvent. Dimethylformamide (high purity grade) was purified by refluxing followed by successive vacuum distillation over anhydrous $CuSO_4$ and P_2O_5.

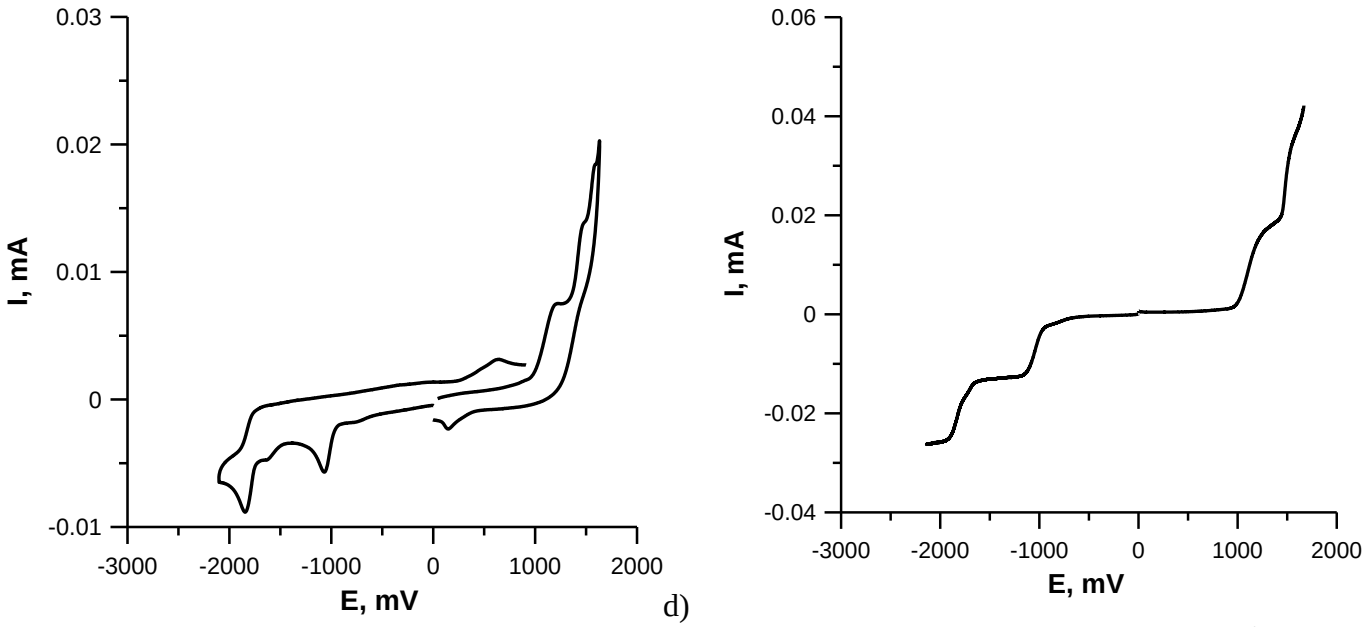

Figure S1. Cyclic voltammograms and RDE curves for ligand **4b**. GC electrode, DMF, $5 \cdot 10^{-4}$ M, Bu_4NClO_4.

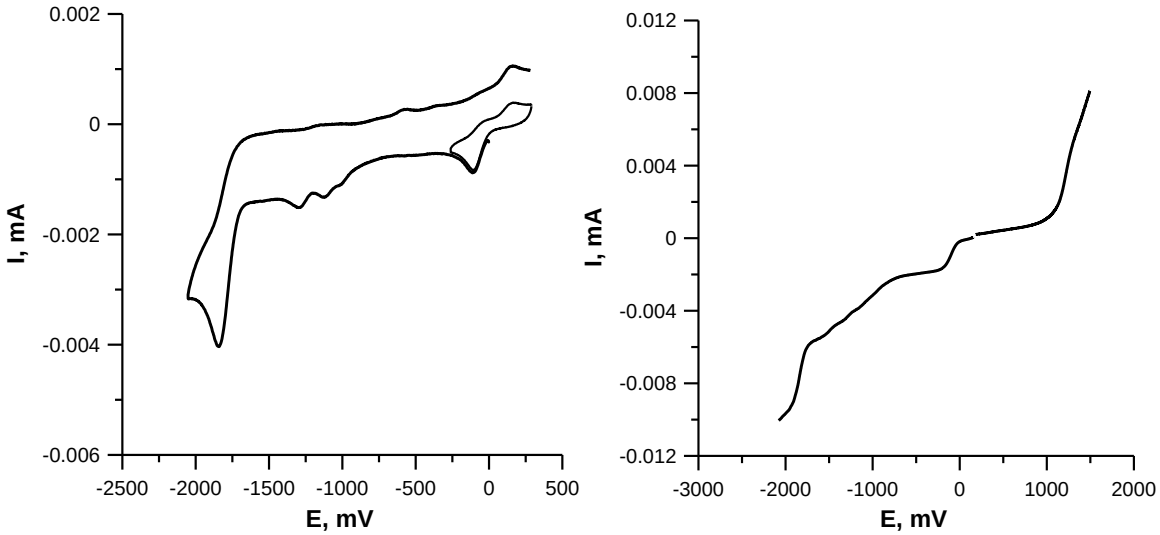

Figure S2. Cyclic voltammograms and RDE curves for complex **5b**. GC electrode, DMF, $5 \cdot 10^{-4}$ *M*, Bu_4NClO_4.

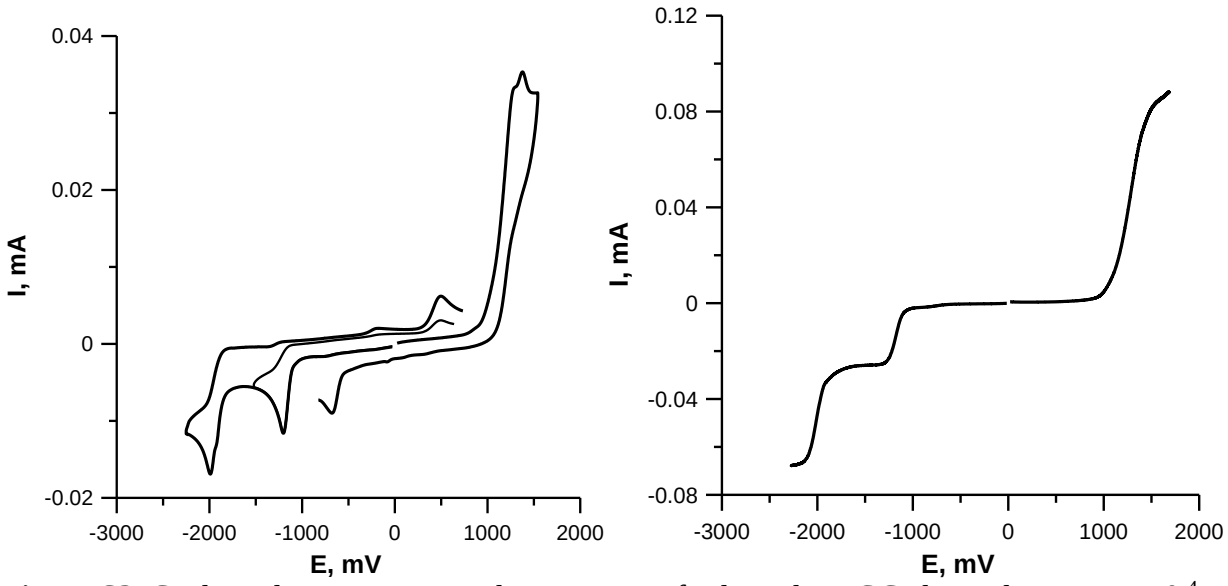

Figure S3. Cyclic voltammograms and RDE curves for ligand **4c**. GC electrode, DMF, $5 \cdot 10^{-4}$ *M*, Bu_4NClO_4.

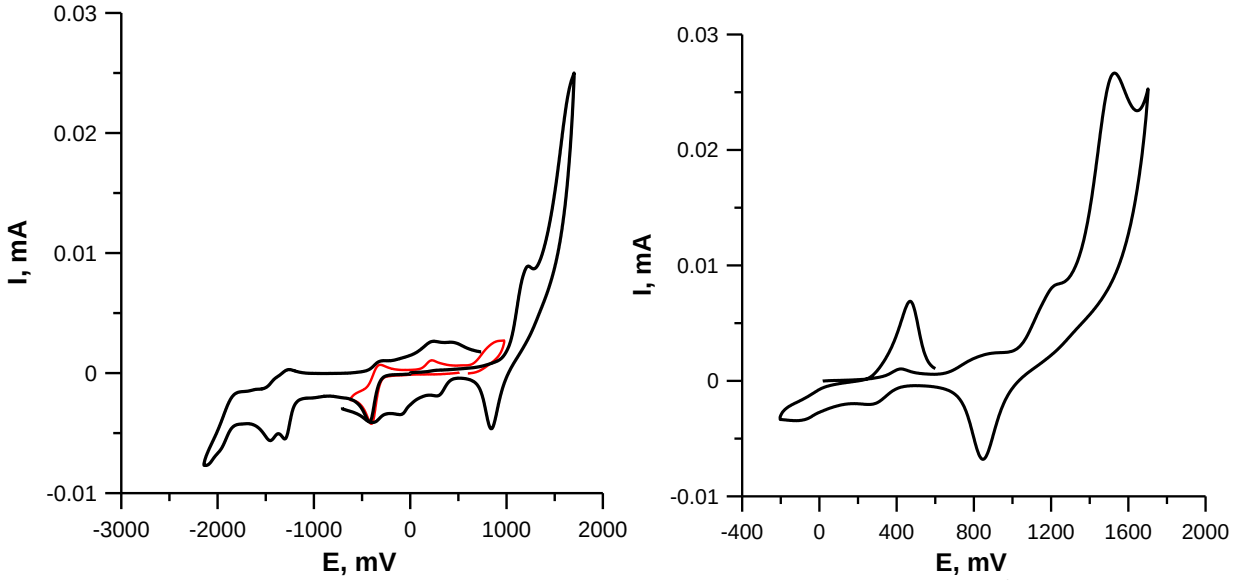

Figure S4. Cyclic voltammograms for complex **5c**. GC electrode, DMF, $5 \cdot 10^{-4}$ *M*, Bu_4NClO_4.

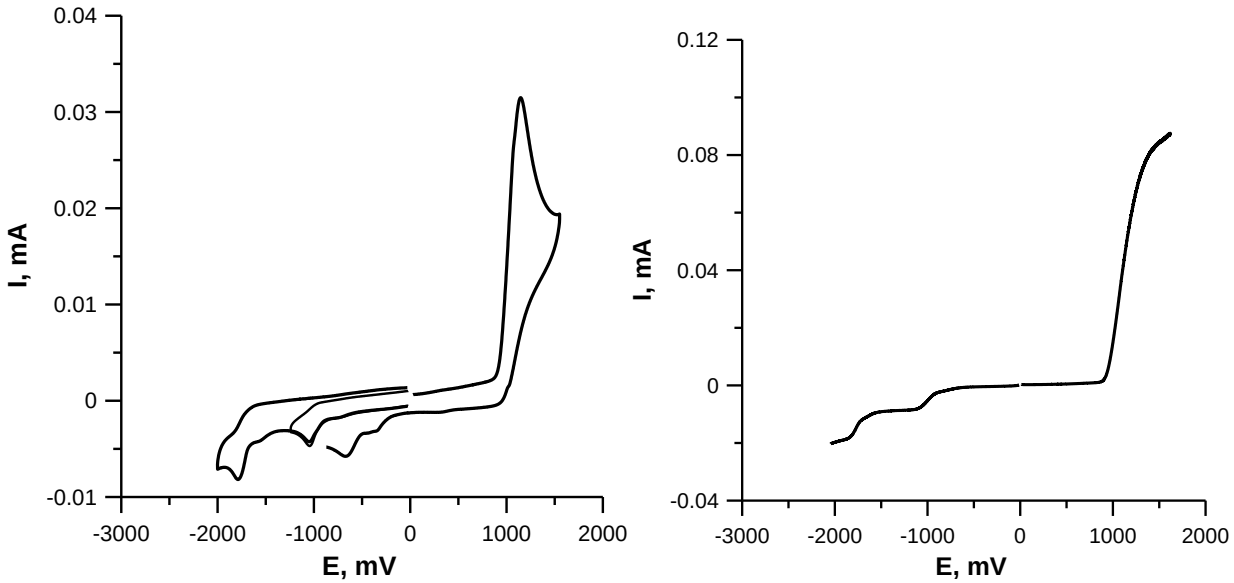

Figure S5. Cyclic voltammograms and RDE curves for ligand **4e**. GC electrode, DMF, $5 \cdot 10^{-4}$ *M*, Bu_4NClO_4.

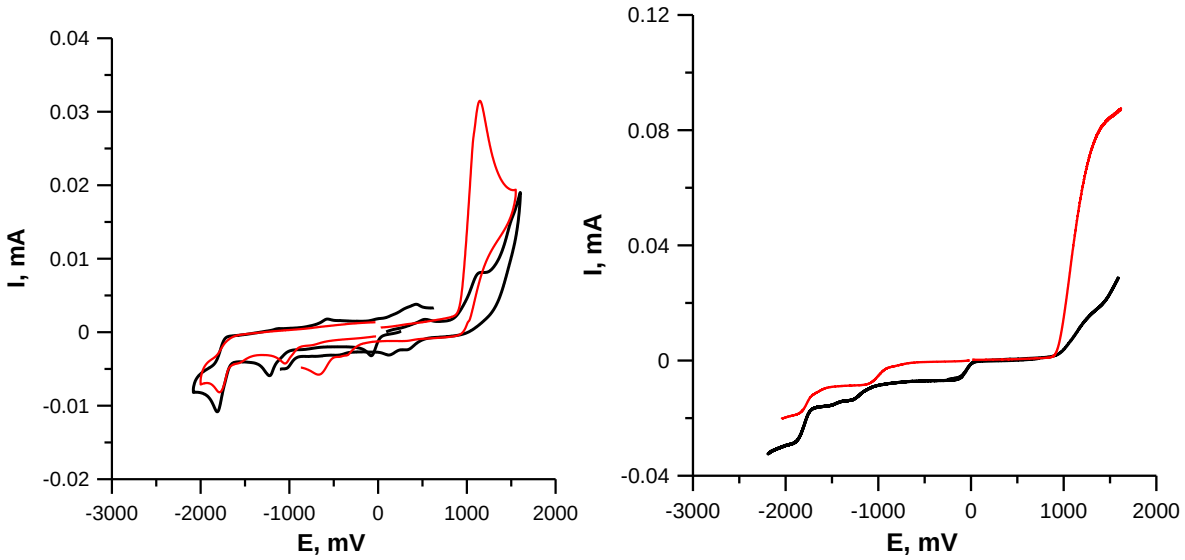

Figure S6. Cyclic voltammograms and RDE curves for complex **5e** (*in black*) and the corresponding ligand **4e** (*in red*). GC electrode, DMF, $5 \cdot 10^{-4}$ *M*, Bu_4NClO_4.

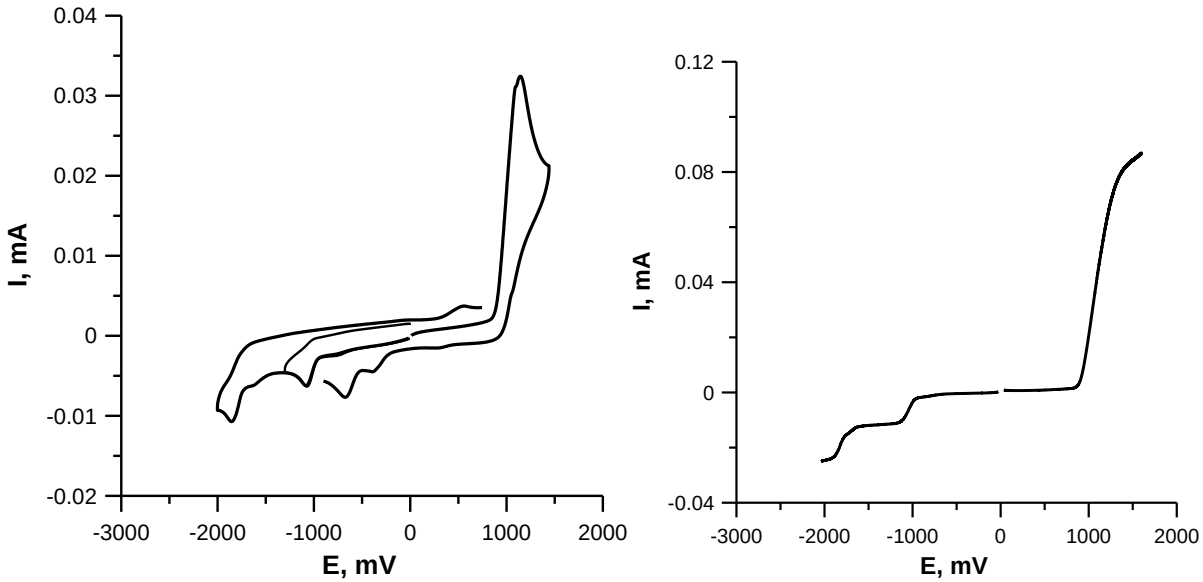

Figure S7. Cyclic voltammograms and RDE curves for ligand **4f**. GC electrode, DMF, $5 \cdot 10^{-4}$ *M*, Bu_4NClO_4.

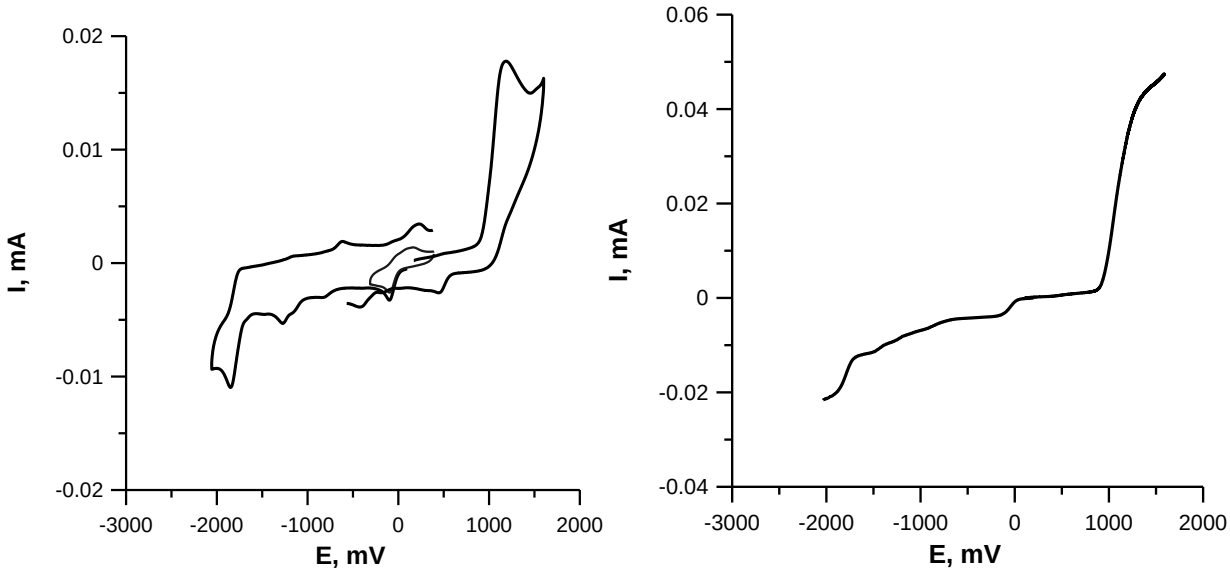

Figure S8. Cyclic voltammograms and RDE curves for complex **5f**. GC electrode, DMF, $5 \cdot 10^{-4}$ *M*, Bu_4NClO_4.