Electronic supplementary materials *Mendeleev Commun.*, 2019, **29**, 444–446

Binuclear copper(II) complex with 2-imidazolylbenzothiazole and bridged chloride ligands

Elena S. Barskaya, Artem V. Rzheutskiy, Anna A. Moiseeva, Victor A. Tafeenko, Nikolay V. Zyk and Elena K. Beloglazkina

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

Compounds **1**, **3a**,**b** and **6b** were synthesized as reported [S1-S4].

Reaction of 2-hetarylbenzothiazoles with copper(II) chloride dihydrate.

Di-μ-chloro-bis[{2-(1*H*-Imidazol-4-yl)-1,3-benzothiazole}chloro-copper(II)] (2).

2-(1*H*-Imidazol-4-yl)-1,3-benzothiazole **1** (0.2 g, 1 mmol) was dissolved in ethanol (10 ml), then $CuCl_2$*$2H_2O$ (0.17 g, 1 mmol) was added, and the mixture was boiled for 1.5 hours. The precipitate formed during cooling was filtered and dried *in vacuo* to afford 0.27 g (74%) of compound **2** as a green powder. IR, ν/cm^{-1}: 3205 (NH), 1604 (C=C), 1437 и 1408 (C=N), 759 (C-S). Found (%): C, 60.31; H, 4.03; N, 18.72; S, 14.57. $C_{10}H_7N_3SCuCl_2$. Calculated (%): C, 60.36; H, 4.33; N, 19.2; S, 14.65. UV/Vis (DMF), λ_{max}/nm (ε): 290 (49600), 309 (71200), 445 (2670), 533 (1000), 599 (800).

[2-(1-Methyl-1*H*-imidazol-2-yl)-1,3-benzothiazole]copper(II) chloride (4).

2-(1-Methyl-1*H*-imidazol-2-yl)-1,3-benzothiazole **3** (0.15 g, 0.5 mmol) was dissolved in ethanol (10 ml), then $CuCl_2$*$2H_2O$ (0.08 g, 0.465 mmol) was added, and the mixture was boiled for 1.5 hours. The precipitate formed on cooling was filtered and dried *in vacuo* to afford 0.164 g (68%) of compound **4** as a green powder. IR, ν/cm^{-1}: 3421 (H_2O), 1567 (C=C), 1469 и 1442 (C=N), 1400 (N-CH_3), 765 (C-S). Found (%): C, 35.93; H, 2.73; N, 10.81; S, 8.81. $C_{11}H_9N_3SCuCl_2 \cdot H_2O$. Calculated (%): C, 35.93; H, 3.01; N, 11.43; S, 8.72. UV/Vis (DMF), λ_{max}/nm (ε): 313 (4890), 325 (5870), 338 (4500), 371 (70).

[2-(Pyridin-2-yl)-1,3-benzothiazol-6-ol]copper(II) chloride (6a). 2-(Pyridin-2-yl)-1,3-benzothiazol-6-ol **5a** (0.05 g, 0.2193 mmol) was dissolved in ethanol (10 ml), then $CuCl_2*2H_2O$ (0.0375 g, 0.2193 mmol) was added, and the mixture was boiled for 1.5 hours. The precipitate formed during cooling was filtered and dried *in vacuo* to afford 0.032 g (41%) of compound **6a** as a green powder. IR, ν/cm^{-1}: 3399 and 3149 (OH), 1560 (C=C), 1423 (C=N), 777 (C-S). Found (%): C, 39.31; H, 2.03; N, 7.38; S, 8.46. $C_{12}H_8Cl_2CuN_2OS$. Calculated (%): C, 39.74; H, 2.22; N, 7.72; S, 8.84. UV/Vis (DMF), λ_{max}/nm (ε): 337 (18520).

[6-(2-Ethoxy-2-oxoethoxy)-2-(pyridin-2-yl)-1,3-benzothiazole]copper(II) chloride 6c. Step 1. *Ethyl 2-[(2-(pyridin-2-yl)benzothiazol-6-yloxy]acetate* **5c**. 6-Hydroxy-2-(pyridin-2-yl)-1,3-benzothiazole **5a** (270 mg, 1.184 mmol), K_2CO_3 (245 mg, 1.776 mmol) and ethyl bromoacetate (297 mg, 1.776 mmol, 197 μl) were suspended in anhydrous acetone (5 ml). The mixture was stirred under heating for 6 hours. At the end of the reaction, the solvent was removed under reduced pressure, water was added, and the product was extracted with ethyl acetate (3*20 ml), the extract was washed with 10% KOH (3×10 ml), then H_2O (3×30 ml). The organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Yield 372 mg (73%). NMR ^{1}H ($CDCl_3$): 8.68 (d, 1H, *J*= 4.8 Hz, Py), 8.32 (d, 1H, *J* = 7.9 Hz, Py), 7.99 (d, 1H, *J* = 9.0 Hz, Ar), 7.84 (td, 1H J_1 = 7.7 Hz, J_2 = 1.7 Hz, Py), 7.33 – 7.44 (m, 2H, Ar+Py), 7.17 (dd, 1H, J_1 = 9.0 Hz, J_2 = 2.6 Hz, Ar), 4.72 (s, 2H, CH_2), 4.31 (q, 2H, *J* = 7.1 Hz, O**C**$\mathbf{H_2}$$CH_3$), 1.32 (t, 3H, *J* = 7.1 Hz, OCH_2**C**$\mathbf{H_3}$). NMR ^{13}C ($CDCl_3$): 168.63 ($SC_{ar}N$), 167.57 (C=O), 156.35 (**C**OCH_2COOEt), 151.44 (NC_{ar}), 149.60 (CN_{pyr}), 149.57 (CH_{pyr}), 137.51 (CH_{pyr}), 136.98 (CS_{ar}), 124.99 (CH_{ar}), 124.34 (CH_{pyr}), 120.48 (CH_{pyr}), 116.25 (CH_{ar}), 105.69 (CH_{ar}), 66.01 (**C**$\mathbf{H_2}$$COOCH_2CH_3$), 61.52 (O**C**$\mathbf{H_2}$$CH_3$), 14.17 ($OCH_2$**C**$\mathbf{H_3}$). IR, ν/sm^{-1}: 1726 (C=O), 1222 (CO-O). Found (%): C% 59.76, H% 4.49, N% 8.59, S% 9.39. $C_{16}H_{14}N_2SO_{3*}0.3H_2O$. Calculated (%): C% 59.99, H% 4.61, N% 8.74, S% 10.01.

Step 2. **Complex 6c.** Ligand **5c** (0.05 g, 0.16 mmol) was dissolved in ethanol (10 ml), then $CuCl_2*2H_2O$ (0.0274 g, 0.16 mmol) was added, and the mixture was boiled for 1.5 hours. The precipitate formed during cooling was filtered and dried *in vacuo* to afford 0.0817g (36%) of compound **6c** as a green powder. IR, ν/cm^{-1}: 3000 (H_2O), 1758 (C=O) and 1195 ($COOCH_2CH_3$). Found (%): C, 41.03; H, 3.29; N, 6.06; S, 7.28. $C_{16}H_{14}N_2O_3S\cdot CuCl_2\cdot H_2O$. Calculated (%): C, 41.17; H, 3.45; N, 6.00; S, 6.87. UV/Vis (DMF), λ_{max}/nm (ε): 333 (8730), 346 (6200).

X-ray. The data for **2** were collected by using STOE diffractometer Pilatus100K detector, focusing mirror collimation Cu Kα (1.54086 Å) radiation, rotation method mode. STOE X-AREA software was used for cells refinement and data reduction. Data collection and image processing was performed with X-Area 1.67 (STOE & Cie GmbH, Darmstadt, Germany, 2013). Intensity data were scaled with LANA (part of X-Area) in order to minimize differences of intensities of symmetry-equivalent reflections (multi-scan method).

Crystal class is monoclinic, space group C2/c.

The structures were solved and refined with SHELX [S5] program. The non-hydrogen atoms were refined by using the anisotropic full matrix least-square procedure. All hydrogen atoms were placed in the calculated positions and allowed to ride on their parent atoms [C-H 0.93-0.98; Uiso 1.2 Ueq(parent atom)]. Molecular geometry calculations were performed with the SHELX program, and the molecular graphics were prepared by using DIAMOND [S6] software.

Table S1. Crystal data and structure refinement for **2.**

Identification code	av003
Empirical formula	C10 H7 Cl2 Cu N3 S
Formula weight	335.69
Temperature	295(2) K
Wavelength	1.54086 Å
Crystal system	Monoclinic
Space group	C 2/c
Unit cell dimensions	a = 7.4839(2) Å α= 90°.
	b = 15.0351(4) Å β= 94.060(3)°.
	c = 20.8944(5) Å γ = 90°.
Volume	2345.16(11) Å3
Z	8
Density (calculated)	1.902 Mg m^{-3}
Absorption coefficient	8.304 mm^{-1}
F(000)	1336
Crystal size	0.19x 0.16 x 0.14 mm^3
Theta range for data collection	4.240 to 72.697°.
Reflections collected	2267
Independent reflections	1867 [R(int) = 0.08]
Completeness to theta = 67.595°	98.9 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2267 / 0 / 154
Goodness-of-fit on F^2	1.086
Final R indices [I>2sigma(I)]	R1 = 0.0684, wR2 = 0.2183
R indices (all data)	R1 = 0.0770, wR2 = 0.2250
Largest diff. peak and hole	0.853 and -0.451 e.$Å^{-3}$

Table S2. Selected bond lengths [Å] and angles [°] for **2.**

Cu(1)-N(2)	1.997(5)
Cu(1)-N(1)	2.089(5)
Cu(1)-Cl(1)	2.2444(19)
Cu(1)-Cl(2)	2.3014(19)
Cu(1)-Cl(2)#1	2.678(2)
N(2)-Cu(1)-N(1)	80.1(2)
N(2)-Cu(1)-Cl(1)	154.53(19)
N(1)-Cu(1)-Cl(1)	96.80(15)
N(2)-Cu(1)-Cl(2)	89.79(17)
N(1)-Cu(1)-Cl(2)	169.01(15)
Cl(1)-Cu(1)-Cl(2)	94.18(7)
N(2)-Cu(1)-Cl(2)#1	102.60(18)
N(1)-Cu(1)-Cl(2)#1	88.26(16)
Cl(1)-Cu(1)-Cl(2)#1	102.56(8)
Cl(2)-Cu(1)-Cl(2)#1	89.85(7)
Cu(1)-Cl(2)-Cu(1)#1	88.87(7)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+1/2

Electrochemistry. Cyclic voltammetric experiments were carried out using a IPC Pro M potentiostat. The system consists of three-electrode assembly, glassy carbon (GC) electrode (working electrode, disk d 2 mm), Ag/AgCl/KCl (aq.satur.) (reference electrode) and platinum electrode (counter electrode). Tetrabutylammonium perchlorate (TBP) (Fluka) 0.1 M, was used as received in MeCN or DMF. The anhydrous solvent had electronic grade purity. Compound concentration: 0.5 mM. The cyclic voltammetric experiments were carried out after de-aerating the experimental solutions by purging pure argon gas. All the measurements were carried out at 22 ^{o}C. Scan rate: 100 mV sec^{-1}.

Table S3. The electrochemical potentials (vs. Ag/AgCl/KCl (aq.,sat.)) of the compounds **1**-**6** in DMF in the presence of 0.1 M Bu_4NClO_4 at GC electrode; potential scan rate 100 mV sec^{-1}.

Compound	**E_{pc}, mV**	**$E_{1/2}^{Red}$, mV**	**E_{pa}, mV**	**$E_{1/2}^{Ox}$, mV**
1	2120/-130	-2100	1650	1580
2	400/510; 280/510; -2070; -2190; -2330	450; 280; -1620 -1920	1180; 1640	1160; 1630
3	2060/-1990	-2040	1640	1590
4	400/490; -1970; -2060	450; 2030	1190	1140
5a	-1710; -1830; -2190/-2110	-1800; -2200	1170; 1360; 1520	1180
6a	350/530; -1790; -2170	410; -1790; -2180	1170; 1270	1160
5b	-1840/-1780; -2410		1690	1620
6b	320/500; -1830; -2320		1110; 1650	
5c	-1800/-1740; -2280; -2490	-1760; -2330	1740	1740
6c	320/510; -1800; -2330	430; -1780	1130	1080

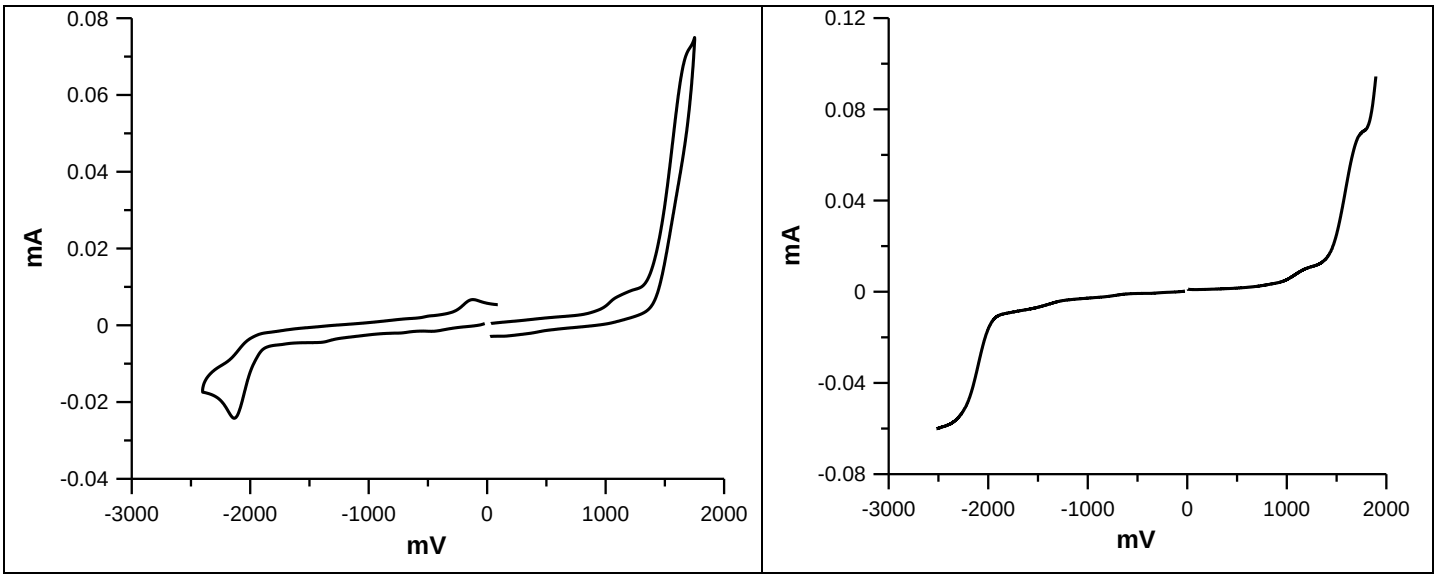

Figure S1. CVA (*left*) and RDE (*right*) for ligand **1** (DMF, Bu_4NClO_4, GC electrode).

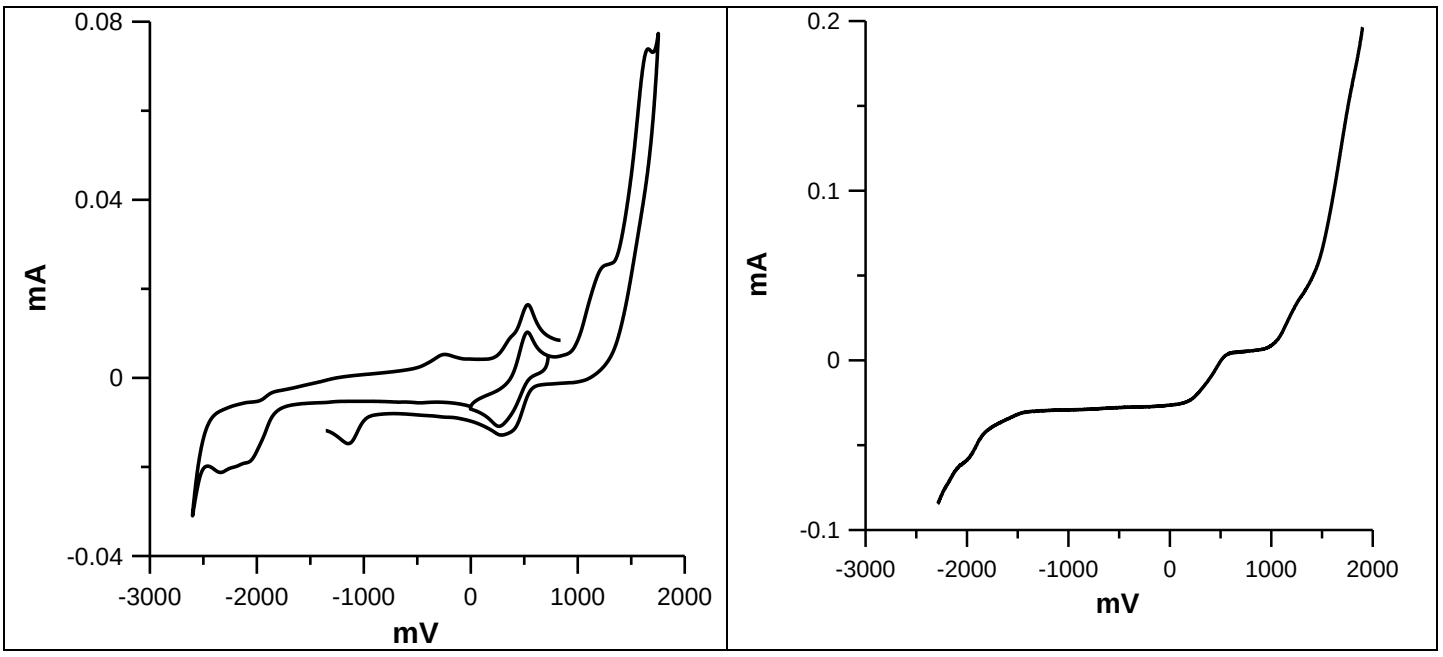

Figure S2. CVA (*left*) and RDE (*right*) for complex **2** (DMF, Bu_4NClO_4, GC electrode).

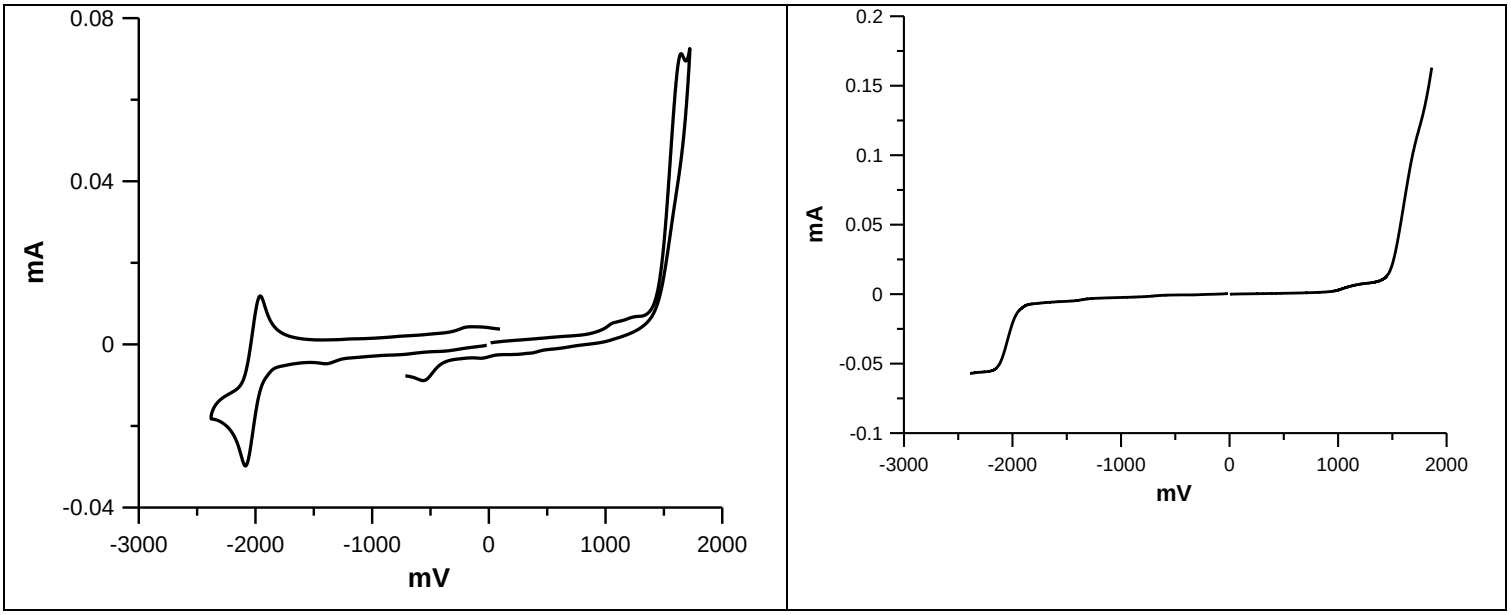

Figure S3. CVA (*left*) and RDE (*right*) for ligand **3** (DMF, Bu_4NClO_4, GC electrode).

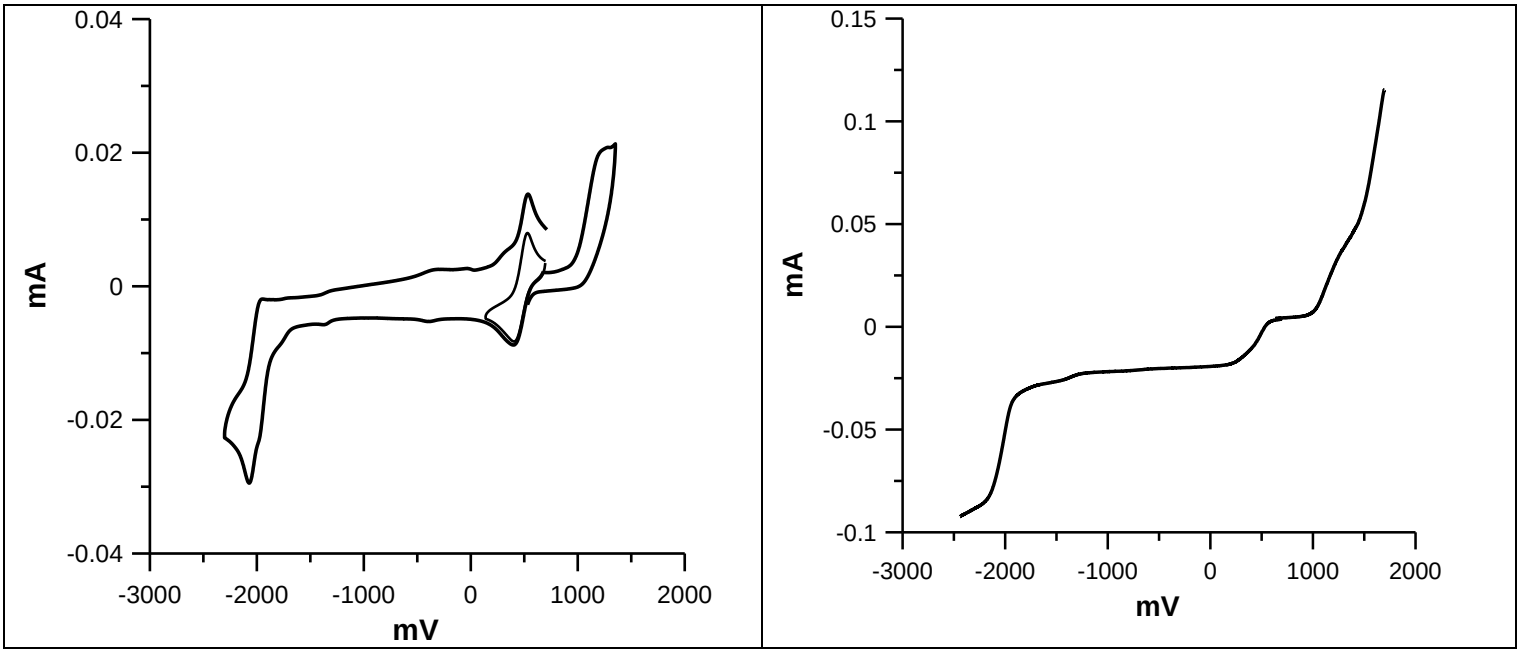

Figure S4. CVA (*left*) and RDE (*right*) for complex **4** (DMF, Bu_4NClO_4, GC electrode).

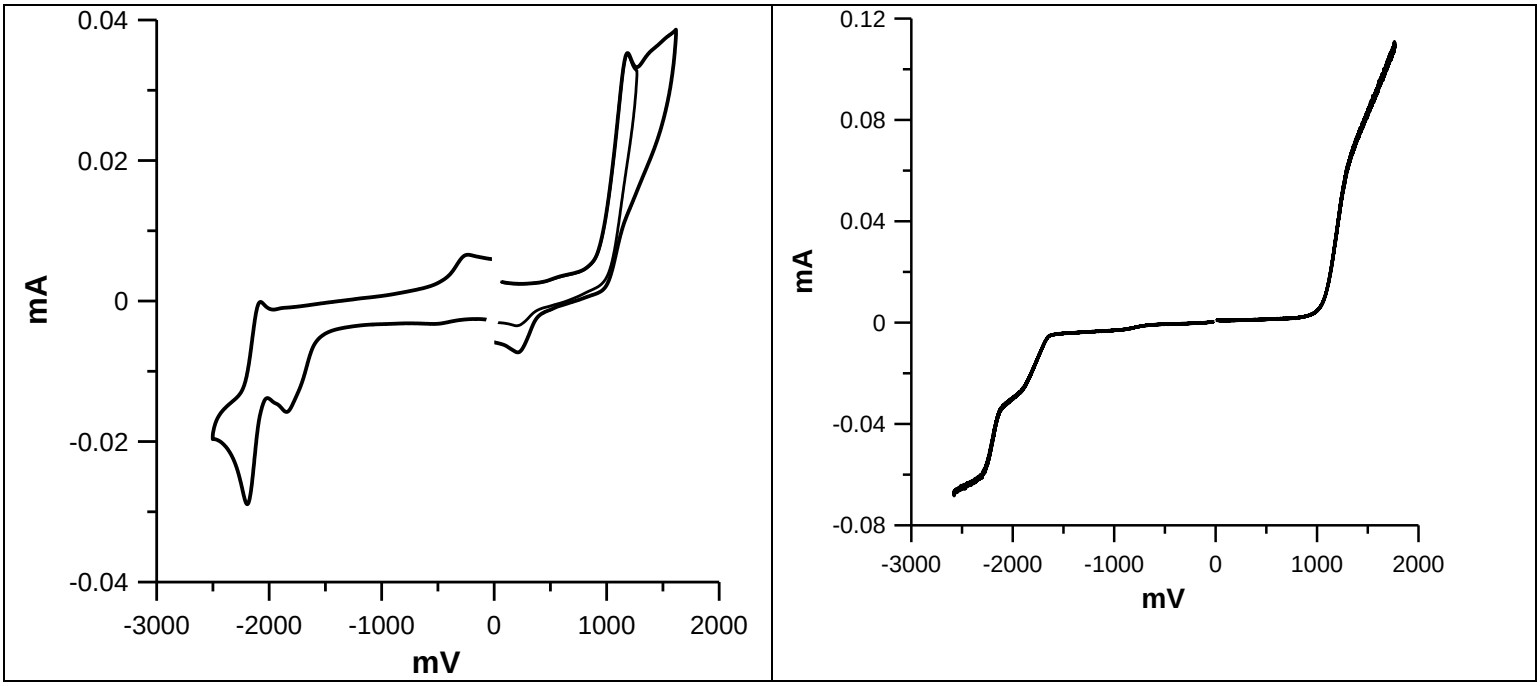

Figure S5. CVA (*left*) and RDE (*right*) for ligand **5a** (DMF, Bu_4NClO_4, GC electrode).

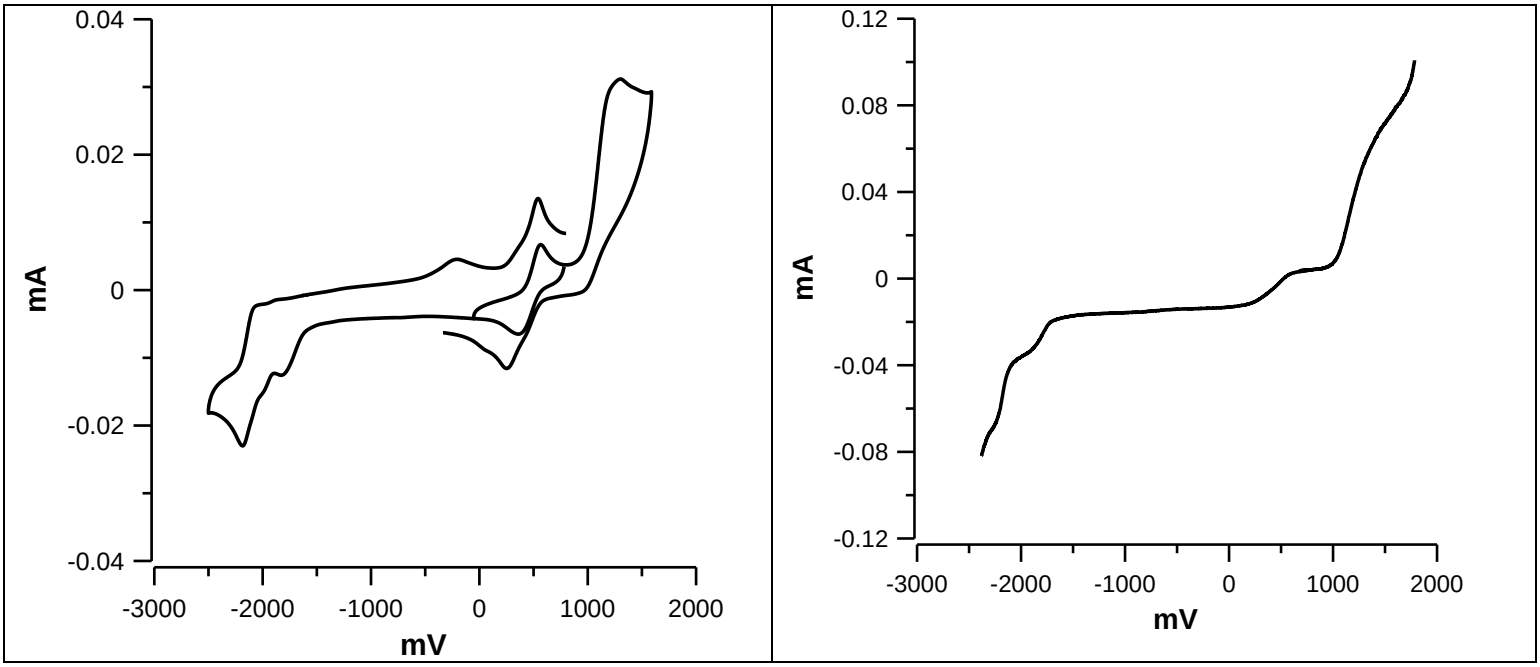

Figure S6. CVA (*left*) and RDE (*right*) for complex **6a** (DMF, Bu_4NClO_4, GC electrode).

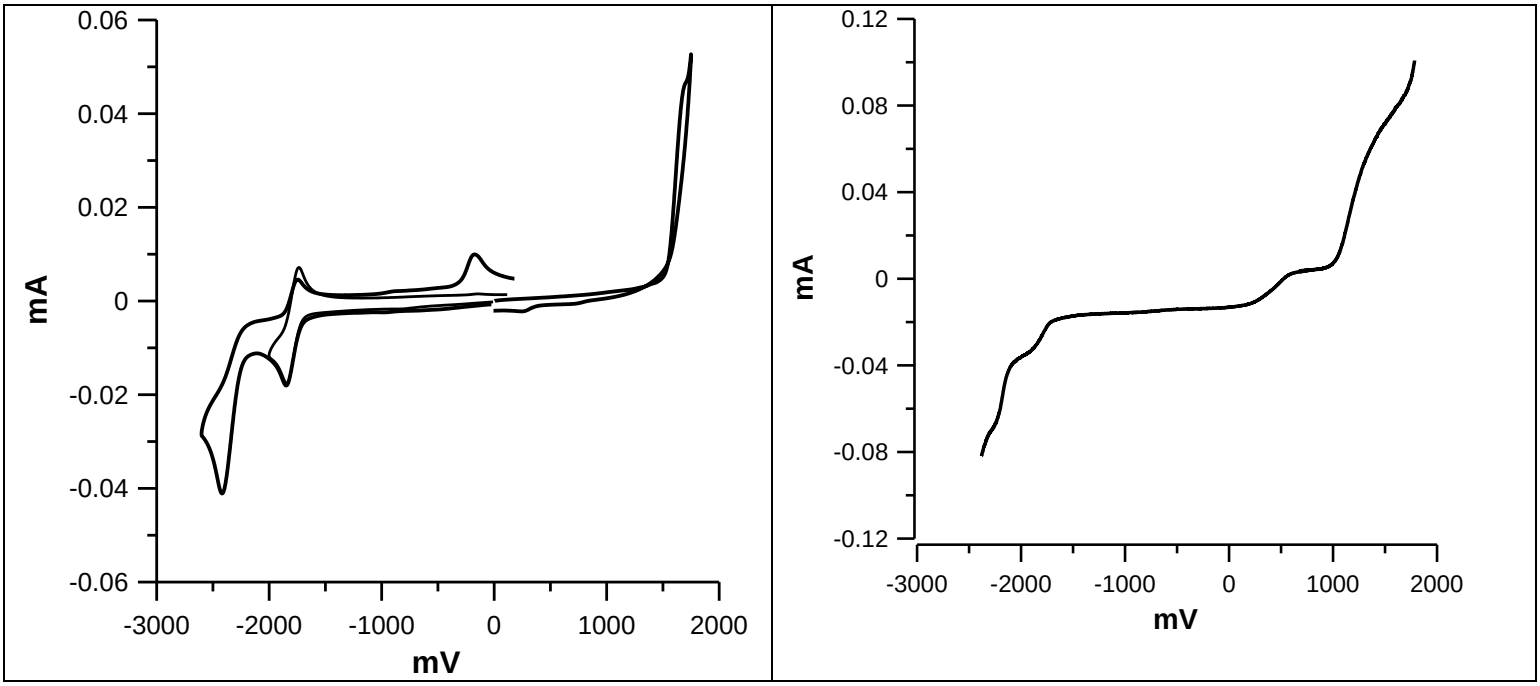

Figure S7. CVA (*left*) and RDE (*right*) for ligand **5b** (DMF, Bu_4NClO_4, GC electrode).

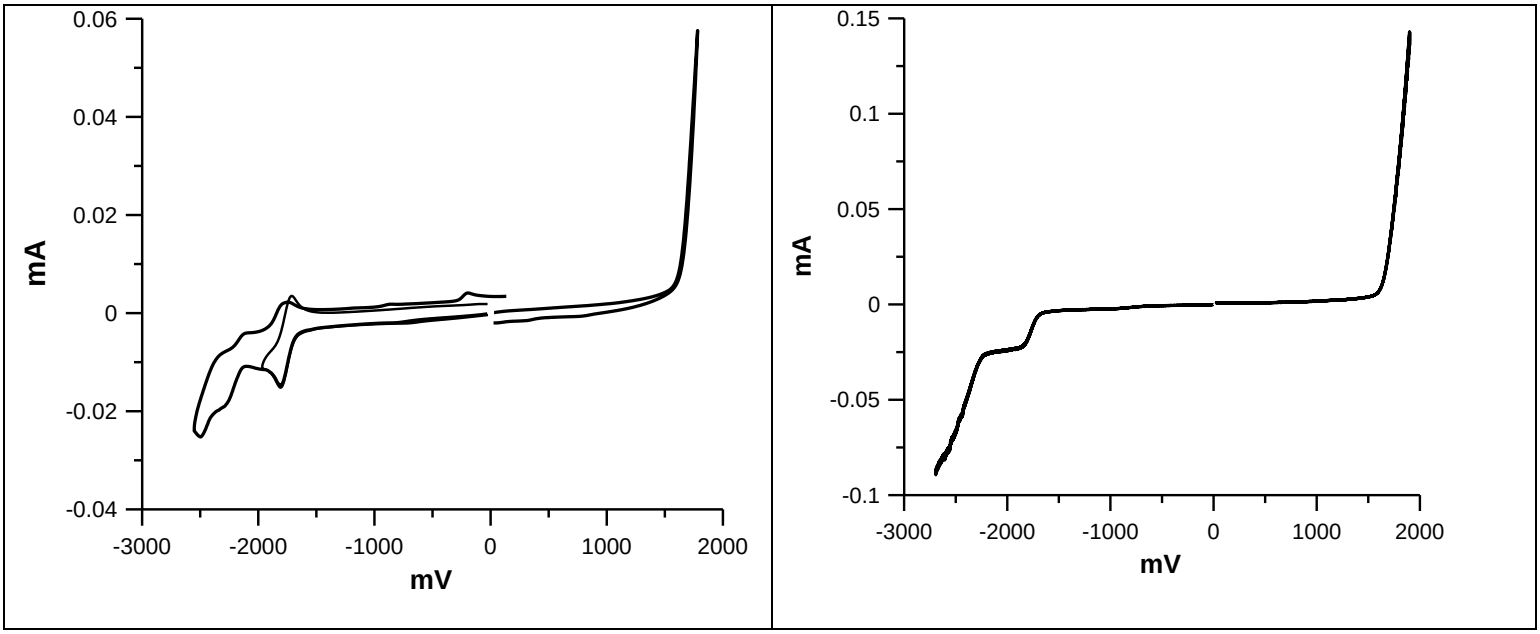

Figure S8. CVA (*left*) and RDE (*right*) for ligand **5c** (DMF, Bu_4NClO_4, GC electrode).

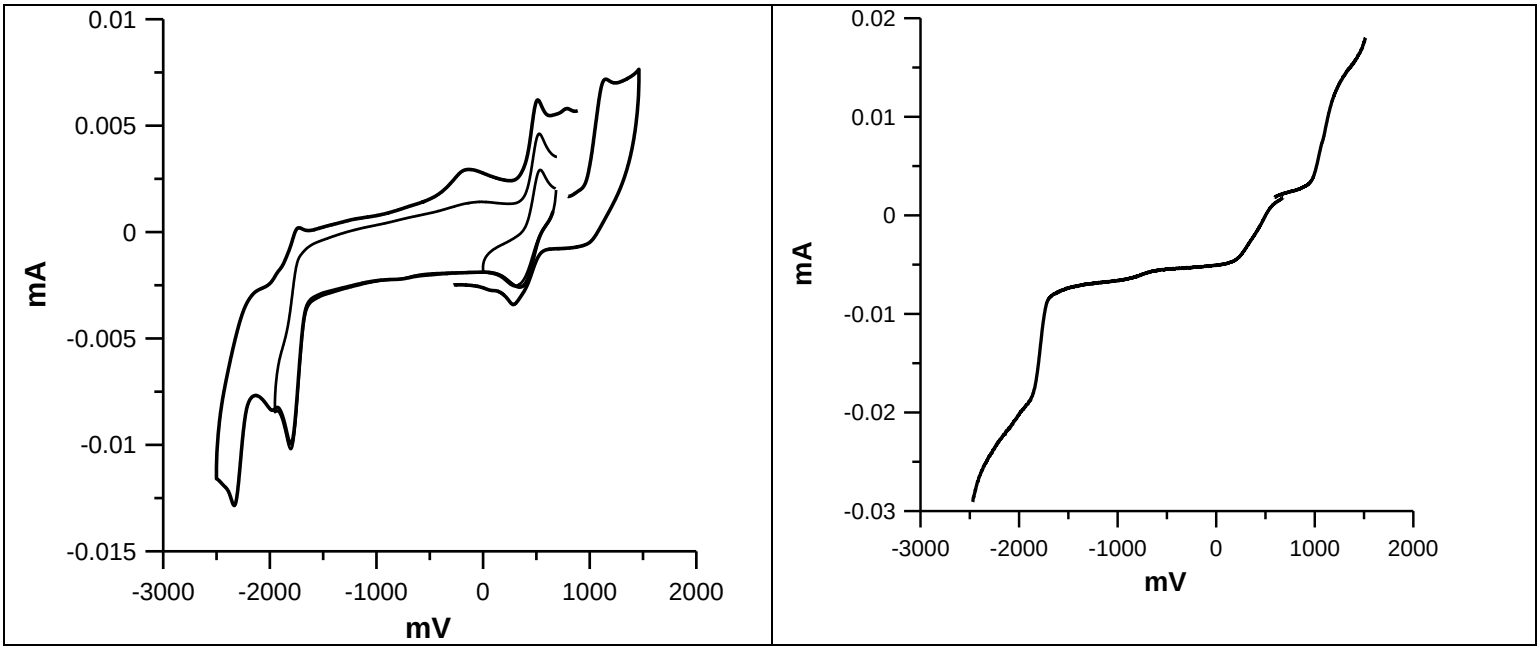

Figure S9. CVA (*left*) and RDE (*right*) for complex **6c** (DMF, Bu_4NClO_4, GC electrode).

References

[S1]. E.K. Beloglazkina, I.V. Yudin, A.G. Majouga, A.A. Moiseeva, A.L. Tursina and N.V. Zyk, *Russ. Chem. Bull., Int. Ed.*, 2006, **55**, 1803 (*Izv. Akad. Nauk, Ser. Khim.*, 2006, 1738).

[S2]. E.K. Beloglazkina, E.S. Barskaya, A.G. Majouga and N.V. Zyk, *Mendeleev Commun.*, 2015, **25**, 1483.

[S3]. E.S. Barskaya, V.V. Shorokhov, A.V. Rzheutsky, A.D. Khudyakov, I.V. Yudin, V.A. Tafeenko, N.V. Zyk and E.K. Beloglazkina, *Russ. Chem. Bull., Int. Ed.*, 2019, **68**, 638 (*Izv. Akad. Nauk, Ser. Khim.*, 2019, 638).

[S4]. E. S. Barskaya, E. K. Beloglazkina, A. G. Mazhuga, I. V. Yudin, and N. V. Zyk, *Russ. Chem. Bull., Int. Ed.*, 2015, **64**, 1975 (*Izv. Akad. Nauk, Ser. Khim.*, 2015, 1975).

[S5]. G. M. Sheldrick, *Acta Crystallogr*., 2008, **A64**, 112.

[S6]. K. Brandenburg, *DIAMOND, Release 2.1d*, Crystal Impact GbR, Bonn, 2000.