Polyhedron 50 (2013) 425–433

Contents lists available at SciVerse ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Novel copper(II) and cobalt(II) complexes with selenium substituted imidazolyl imines. The molecular and crystal structure of [*N*-(2-(phenylseleno)ethyl)-*N*-(imidazol-2-ylmethylene)amine]copper(II) dichloride

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ARTICLE INFO

Article history:
Received 15 October 2012
Accepted 29 November 2012
Available online 8 December 2012

Keywords:
Copper(II) and cobalt(II) complexes
X-ray crystal structure
Cyclic voltammetry
Semi-empirical calculations

ABSTRACT

A series of copper(II) and cobalt(II) complexes with novel selenium containing Schiff base ligands obtained from 2- or 3-aminoalkyl phenyl selenides and imidazole carbaldehydes have been synthesized by the interaction of corresponding organic ligands with $MCl_2 \cdot 6H_2O$ (M = Cu, Co). The crystal structure of a copper(II) complex with *N*-(2-(phenylseleno)ethyl)-*N*-(imidazolyl-2-ylmethylene)amine has been solved by a single-crystal X-ray diffraction method. The copper(II) ions are coordinated by the imine and imidazole nitrogen atoms of organic ligands and two chloride anions in a distorted square planar geometry. The electrochemical investigations of the synthesized ligands and complexes have been made by cyclic voltammetry method. It is established that the first stage of complexes reduction takes place to metal and the reduced forms of complexes are stable in the solution.

1. Introduction

Organoselenium compounds represent an important class of biologically active compounds. Selenium deficiency in human body was found to increase the probability of cardio-vascular pathologies, cancer, and arthritis [1–3]. The occurrence of selenium as an integral component of a few redox-type enzymes in prokaryotes has been known for several years, but until recently the only known example in eukaryotes was glutathione peroxidase [4] which can effectively reduce organic peroxides and thus protect cells from damage due to reactive oxygen species. The ability of this peroxidase to provided an explanation at the biochemical level for the requirement of selenium as an essential trace element in mammals and birds. The discovery during the past year provides examples of an even more ubiquitous role of the element, namely in growth and developmental processes of diverse animal species including amphibian, and the plasma selenoprotein P with the fundamental physiological importance [5–8].

High biological activity made selenium-containing organic compounds an attractive class of ligands for studying of coordination properties in the reactions with transition metals. Low-molecular organic ligands containing both selenium and nitrogen atoms are of special interest, since the presence of a powerful electron-donating nitrogen atom and weakly donating selenium atom gives them a possibility to coordinate metals of various nature and oxidation state or to accomplish competing coordination of a certain metal atom. Such complexes can be used as cytostatic agents [9]. It is shown that intramolecular interactions Se–N play an important role in the antioxidant activity of these compounds [10]. In view of the recent increased interest in effects of selenium as well as exciting new developments at the basic biochemical level, rapid expansion of our understanding of the roles of this trace element in biology can be expected [5].

In recent publications we have described a series of new sulfur- and seleno-substituted Schiff base ligands derived from 2- or 3-aminoalkyl phenyl selenides and 2-pyridine carbaldehyde [11] and their coordination compound with Co(II) and Cu(II) [12]. In this work we describe the synthesis of novel selenium containing organic ligands *N*-(ω-phenylseleno)ethyl)-*N*-(imidazolylmethylene)amines, and the results of their reactions with copper(II) and cobalt(II) chloride.

2. Experimental

2.1. General

Diphenyl diselenide and imidazole carbaldehydes were obtained from commercial sources and used as received. 2-(Phenylseleno)ethyl amine hydrochloride (**1**) and 3-(Phenylseleno)propyl amine hydrochloride (**2**) were obtained according to the procedures described earlier [13]. The melting points are uncorrected. ^{1}H NMR spectra were recorded on a Varian-XR-400 recorder (400 MHz for

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http://dx.doi.org/10.1016/j.poly.2012.11.039

^{1}H and 100 MHz for ^{13}C). The IR spectra in Nujol (for solids) or film (for oils) were recorded on a Perkin-Elmer 1430 spectrophotometer. Electronic spectra in 10^{-3} mol L^{-1} CH_3CN solution were obtained on a Perkin–Elmer Lambda 35 UV–Vis spectrophotometer. Mass spectra with laser ionization were recorded on a Autoflex II Bruker mass-spectrometer (resolution FWHM 18000, nitrogen laser with λ = 337 nm, time-of-flight mass-spectrometer, potential accelerating 20 kV, recording of spectra in positive ions mode; the samples were applied to polished steel plate; the resulting spectra were the sum of 300 spectra, obtaining in different regions of a sample). Electrochemical studies were carried out on a PI-50-1.1 potentiostat. Glassy-carbon disk (2 mm in diameter) was used as the working electrodes; a 0.05 M Bu_4NClO_4 solution in DMF served as the supporting electrolyte; Ag/AgCl/KCl(sat.) was used as the reference electrode. All measurements were carried out under argon; the samples were dissolved in the pre-deaerated solvent. Dimethylformamide (high-purity grade) was purified by successive refluxing and vacuum distillation over anhydrous $CuSO_4$ and P_2O_5.

PM3 calculation were performed by use the HYPERCHEM software on PC. Geometry optimization of the molecules was carried out with a gradient less than 0.01 kcal/mol as the convergence criterion.

2.2. Synthesis of organic ligands

2.2.1. Selenium-substituted imines **3**–**10** (typical procedure)

Solution of KOH (0.09 g, 1.7 mmol) in minimal amount of EtOH was added to an equimolar amount of the stirred solution of compound **1** or **2** in 5 ml of EtOH. After a complete precipitation of white flakes of KCl the solid was filtered off and equimolar amount of aldehyde in EtOH was added to the resulting solution. The mixture was boiled for 7 h, then the solvent was removed in reduced pressure and the resulting solid or oil was recrystallized from EtOH of purified by flash chromatography (SiO_2, ligroin).

2.2.2. N-(2-(Phenylseleno)ethyl)-N-(imidazol-2-ylmethylene)amine (**3**)

Brown powder (0.283 g, 60%). M.p. 149–150 °C. ^{1}H NMR ($CDCl_3$): 8.19 (s, 1H, HC═N), 7.53 (m, 2H, Ph), 7.27 (m, 3H, Ph), 7.08 (b.s., 2H, Im), 3.92 (t, 2H, CH_2N, J = 6.8 Hz), 3.21 (t, 2H, CH_2Se, J = 6.8 Hz). ^{13}C NMR ($CDCl_3$): 153.6, 143.9, 131.8, 129.7, 129.6, 129.8, 127.0, 125.4, 60.3, 28.0. IR, ν/cm^{-1}: 2940, 1650, 1500, 1520. MS (m/z): 279 (M^+).

2.2.3. N-(3-(Phenylseleno)propyl)-N-(imidazol-2-ylmethylene)amine (**4**)

Light-brown oil (0.471 g, 95%). ^{1}H NMR ($CDCl_3$): 8.16 (s, 1H, HC═N), 7.53 (d, 2H, Ph, J = 7.3 Hz), 7.24 (m, 4H, Im + Ph), 6.80 (b.s., 1H, Im), 3.68 (t, 2H, CH_2N, J = 6.3 Hz), 2.94 (t, 2H, CH_2Se, J = 6.3 Hz), 2.12 (m, 2H,CH_2). ^{13}C NMR ($CDCl_3$): 153.3, 143.0, 133.5, 130.6, 129.8, 129.6, 127.7, 125.8, 60.3, 31.1, 22.2. IR, ν/cm^{-1}: 2980, 1655, 1585, 1495. MS (m/z): 293 (M^+).

2.2.4. N-(2-(Phenylseleno)ethyl)-N-(1-methyl-imidazol-2-ylmethylene) amine (**5**)

Yellow oil (0.446 g, 90%). ^{1}H NMR ($CDCl_3$): 8.17 (s, 1H, HC═N), 7.55 (m, 2H, Ph), 7.32 (м, 3H, P), 7.12 (b.s., 1H, Im), 6.94 (b.s., 1H, Im), 3.43 (m, 2H, NCH_2), 3.64 (s, 3H, CH_3), 3.01 (m, 2H, $SeCH_2$). ^{13}C NMR ($CDCl_3$): 154.1, 142.8, 132.8, 129.9, 129.2, 129.0, 126.8, 124.8, 61.5, 35.3, 28.7. IR, ν/cm^{-1}: 1655, 1580, 1490. MS (m/z): 293 (M^+).

2.2.5. N-(3-(Phenylseleno)propyl)-N-(1-methyl-imidazol-2-ylmethylene) amine (**6**)

Yellow oil (0.448 g, 90%). ^{1}H NMR ($CDCl_3$): 8,32 (s, 1H, HC═N), 7.51 (m, 2H, Ph), 7.23 (m, 3H, Ph), 7.11 (b.s., 1H, Im), 6.92 (b.s., 1H, Im), 3.9 (s, 3H, CH_3), 3.67 (t, 2H, CH_2N, J = 7.3 Hz), 3.00 (t, 2H, CH_2Se, J = 7.3 Hz), 2.07 (m, 2H, CH_2). ^{13}C NMR ($CDCl_3$): 153.6, 143.0, 132.5, 130.2, 129.1, 126.7, 124.7, 61.1, 35.3, 31.3, 25.4. IR, ν/cm^{-1}: 1655, 1580, 1490. MS (m/z): 308 (M^+).

2.2.6. N-(2-(Phenylseleno)ethyl)-N-(imidazol-4-ylmethylene)amine (**7**)

Brown powder (0.283 g, 60%). M.p. 146–147 °C. ^{1}H NMR ($CDCl_3$): 8.12 (s, 1H, HC═N), 7.86 (m, 2H, Ph), 7.74(b.s., 2H, Im), 7.48 (м, 3H, Pn) 3.92 (m, 2H, CH_2N), 3.26 (m, 2H, CH_2Se). ^{13}C NMR ($CDCl_3$): 154.0, 137.5, 134.4, 132.7, 129.7, 129.1, 127.0, 125.7, 60.7, 28.4. IR, ν/cm^{-1}: 1650, 1580, 2970. MS (m/z): 279 (M^+).

2.2.7. N-(3-(Phenylseleno)propyl)-N-(imidazol-4-ylmethylene)amine (8)

Brown oil (0.300 g, 62%). ^{1}H NMR ($CDCl_3$): 8.25 (s, 1H, HC═N), 7.73 (b.s., 2H, Im), 7.48 (d, J = 7.3 Гц, 2H, Ph), 7.24 (m, 3H, Ph), 3.72 (m, 2H, CH_2N), 2.94 (m, 2H, CH_2Se), 2.06 (m, 2H, CH_2). ^{13}C NMR ($CDCl_3$): 152.1, 139.5, 137.5, 132.7, 129.1, 129.9, 126.9, 127.2, 59.8, 31.0, 25.2. IR, ν/cm^{-1}: 1655, 1580, 1480. MS (m/z): 293 (M^+).

2.2.8. N-(2-(Phenylseleno)ethyl)-N-(5-methyl-imidazol-4-ylmethyl ene)amine (9)

Yellow oil (0.421 g, 85%). ^{1}H NMR ($CDCl_3$): 8.10 (s, 1H, HC═N), 7.63 (s, 1H, Im), 7.52 (m, 3H, Ph) 7.29 (m, 2H, Ph), 3.9 (t, 2H, CH_2N, J = 6.7 Hz), 3.23 (t, 2H, CH_2Se, J = 6.7 Hz), 2.41 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): 154.1, 142.2, 132.0, 129.9, 129.6, 126.3, 122.5, 61.1, 28.2, 20.5. IR, ν/cm^{-1}: 1640, 1580, 2990. MS (m/z): 293 (M^+).

2.2.9. N-(3-(Phenylseleno)propyl)-N-(5-methyl-imidazol-4-ylmethyl ene)amine (**10**)

Yellow-orange oil (0.283 g, 60%). ^{1}H NMR ($CDCl_3$): 8.20 (s, 1H, HC═N), 7.59 (s, 1H, Im), 7.46 (m, 2H, Ph), 7.22 (dd, 3H, Ar, J_1 = 1.6 Hz, J_2 = 7.4 Hz), 3.68 (m, 2H, CH_2N), 2.95 (m, 2H, CH_2Se), 2.37 (s, 3H, CH_3), 2.05 (m, 2H, CH_2). ^{13}C NMR ($CDCl_3$): 151.2, 149.2, 138.5, 132.8, 130.9, 129.1, 127.1, 59.3, 50.0, 28.0, 12.6. IR, ν/cm^{-1}: 1655, 1585, 1455. MS (m/z): 307 (M^+).

2.3. Synthesis of copper(II) and cobalt(II) complexes

2.3.1. Synthesis of coordination compounds **11**–**26** (typical procedure)

Concentrated solutions of ligand **3**–**10** (0.05 g) in 1–2 ml of CH_2Cl_2 and equimolar amount of $MCl_2{\cdot}6H_2O$ (M = Cu, Co) in 1–2 ml of EtOH were mixed at room temperature and stand to the complex precipitation. The forming solid was filtered off, washed by small portions of Et_2O and dried in air.

2.3.2. [N-(2-(Phenylseleno)ethyl)-N-(imidazol-2-ylmethylene) amine]copper(II) dichloride (**11**)

Dark-green powder (0.040 g, 55%). M.p. 168–169 °C. IR, ν/cm^{-1}: 1640, 1585, 1470. MS (m/z): 377 ([M−Cl]$^+$). *Anal.* Calc. for $C_{12}H_{13}Cl_2CuN_3Se$: C, 34.93; H, 3.18; N, 10.18. Found: C, 34.70; H, 3.33; N, 10.56%.

2.3.3. [N-(2-(Phenylseleno)ethyl)-N-(imidazol-2-ylmethylene) amine]cobalt(II) dichloride (**12**)

Dark-blue powder (0.029 g, 40%). M.p. 110–111 °C. IR, ν/cm^{-1}: 1600, 1520, 1470. UV–Vis, λ_{max}, nm (ε, L mol^{-1} cm^{-1}) (CH_3CN): 344 (5020), 718 (115). MS (m/z): 408 (M^+). *Anal.* Calc. for $C_{12}H_{13}Cl_2CoN_3Se$: C, 35.32; H, 3.21; N, 10.30. Found: C, 34.90; H, 3.08; N, 9.97%.

2.3.4. [N-(3-(Phenylseleno)propyl)-N-(imidazol-2-ylmethylene)amine] copper(II) dichloride (**13**)

Dark-green powder (0.043 g, 59%). M.p. 121–122 °C. IR, ν/cm^{-1}: 1644, 1580, 1473. MS (m/z): 391 ([M−Cl]$^+$). *Anal.* Calc. for $C_{13}H_{15}$-

Cl_2CuN_3Se: C, 36.59; H, 3.54; N, 9.85. Found: C, 35.99; H, 3.51; N, 9.49%.

*2.3.5. [N-(3-(Phenylseleno)propyl)-N-(imidazol-2-ylmethylene) amine]cobalt(II) dichloride (**14**)*

Dark-green powder (0.039 g, 55%). M.p. 170–171 °C. IR, ν/cm^{-1}: 1650, 1610, 1635. UV–Vis, λ_{max}, nm (ε, L mol^{-1} cm^{-1}) (CH_3CN): 244 (2630), 620 (120). MS (*m*/*z*): 387 ([M−Cl]$^+$). *Anal.* Calc. for $C_{13}H_{15}Cl_2CoN_3Se$: C, 36.99; H, 3.58; N, 9.96. Found: C, 36.92; H, 3.50; N, 9.89%.

*2.3.6. [N-(2-(Phenylseleno)ethyl)-N-(1-methyl-imidazol-2-ylmethylene)amine]copper(II) dichloride (**15**)*

Light-green powder (0.039 g, 55%). M.p. 146–147 °C. IR, ν/cm^{-1}: 1625, 1580, 1545. UV–Vis, λ_{max}, nm (ε, L mol^{-1} cm^{-1}) (CH_3CN): 344.0 (14 315), 398.0 (15 030), 736.0 (600). MS (*m*/*z*): 391 ([M−Cl]$^+$). *Anal.* Calc. for $C_{13}H_{15}Cl_2CuN_3Se$: C, 36.59; H, 3.54; N, 9.85. Found: C, 36.80; H, 3.66; N, 10.00%.

2.3.7. [N-(2-(Phenylseleno)ethyl)-N-(1-methyl-imidazol-2-ylmethylene)amine]cobalt(II) dichloride (16)

Dark-green powder (0.032 g, 45%). M.p. 111–112 °C. IR, ν/cm^{-1}: 1620, 1580, 1472. UV–Vis, λ_{max}, nm (ε, L mol^{-1} cm^{-1}) (CH_3CN): 288 (1325), 570 (150). MS (*m*/*z*): 387 ([M−Cl]$^+$). *Anal.* Calc. for $C_{13}H_{15}Cl_2CoN_3Se$: C, 36.99; H, 3.58; N, 9.96. Found: C, 36.77; H, 3.80; N, 9.70%.

2.3.8. [N-(3-(Phenylseleno)propyl)-N-(1-methyl-imidazol-2-ylmethylene)amine]copper(II) dichloride (17)

Green powder (0.031 g, 43%). M.p. 165 °C. IR, ν/cm^{-1}: 1642, 1520, 1475. UV–Vis, λ_{max}, nm (ε, L mol^{-1} cm^{-1}) (CH_3CN): 204 (1585), 264 (980), 300 (905), 743 (200). MS (*m*/*z*): 405 ([M−Cl]$^+$).

*2.3.9. [N-(3-(Phenylseleno)propyl)-N-(1-methyl-imidazol-2-ylmethylene)amine]cobalt(II) dichloride (**18**)*

Green powder (0.017 g, 25%). M.p. 99–100 °C. IR, ν/cm^{-1}: 1650, 1585, 1490. UV–Vis, λ_{max}, nm (ε, L mol^{-1} cm^{-1}) (CH_3CN): 230 (1120), 523 (150). MS (*m*/*z*): 401 ([M−Cl]$^+$). *Anal.* Calc. for $C_{14}H_{17}Cl_2CoN_3Se$: C, 38.56; H, 3.93; N, 9.64. Found: C, 38.38; H, 3.52; N, 9.38%.

*2.3.10. [N-(2-(Phenylseleno)ethyl)-N-(imidazol-4-ylmethylene) amine]copper(II) dichloride (**19**)*

Light-blue powder (0.035 g, 48%). M.p. 140–141 °C. IR, ν/cm^{-1}: 1679, 1640, 1580. UV–Vis, λ_{max}, nm (ε, L·mol^{-1}·cm^{-1}) (CH_3CN): 262 (5540), 707(140). MS (*m*/*z*): 377 ([M−Cl]$^+$). *Anal.* Calc. for $C_{12}H_{13}Cl_2CuN_3Se$: C, 34.93; H, 3.18; N, 10.18. Found: C, 34.85; H, 3.12; N, 10.39%.

*2.3.11. [N-(2-(Phenylseleno)ethyl)-N-(imidazol-4-ylmethylene) amine]cobalt(II) dichloride (**20**)*

Green powder (0.036 g, 50%). M.p. 178–180 °C. IR, ν/cm^{-1}: 1640, 1587, 1575. UV–Vis, λ_{max}, nm (ε, L mol^{-1} cm^{-1}) (CH_3CN): 344 (14 314), 398 (15 031), 736 (600). MS (*m*/*z*): 373 ([M−Cl]$^+$). *Anal.* Calc. for $C_{12}H_{13}Cl_2CoN_3Se$: C, 35.32; H, 3.21; N, 10.30. Found: C, 34.96; H, 3.18; N, 10.08%.

*2.3.12. [N-(3-(Phenylseleno)propyl)-N-(imidazol-4-ylmethylene) amine]copper(II) dichloride (**21**)*

Dark-green powder (0.021 g, 30%). M.p. 170 °C. IR, ν/cm^{-1}: 1640, 1475. UV–Vis, λ_{max}, nm (ε, L mol^{-1} cm^{-1}) (CH_3CN): 209 (1820), 734 (150). MS (*m*/*z*): 391 ([M−Cl]$^+$). *Anal.* Calc. for $C_{13}H_{15}Cl_2CuN_3Se$: C, 36.59; H, 3.54; N, 9.85. Found: C, 36.28; H, 3.41; N, 9.55%.

*2.3.13. [N-(3-(Phenylseleno)propyl)-N-(imidazol-4-ylmethylene) amine]cobalt(II) dichloride (**22**)*

Dark-green powder (0.037 g, 52%). M.p. 178–180 °C. IR, ν/cm^{-1}: 1640, 1587, 1575. UV–Vis, λ_{max}, nm (ε, L mol^{-1} cm^{-1}) (CH_3CN): 280 (1080), 743 (600). MS (*m*/*z*): 387 ([M−Cl]$^+$).]$^+$). *Anal.* Calc. for $C_{13}H_{15}Cl_2CoN_3Se$: C, 36.99; H, 3.58; N, 9.96. Found: C, 36.79; H, 3.47; N, 9.71%.

*2.3.14. [N-(2-(Phenylseleno)ethyl)-N-(5-methyl-imidazol-4-ylmethylene)amine]copper(II) dichloride (**23**)*

Green powder (0.044 g, 61%). M.p. 170–171 °C. IR, ν/cm^{-1}: 1678, 1600, 1554. UV–Vis, λ_{max}, nm (ε, L mol^{-1} cm^{-1}) (CH_3CN): 269 (3990), 700 (100). MS (*m*/*z*): 391 ([M−Cl]$^+$). *Anal.* Calc. for $C_{13}H_{15}Cl_2CuN_3Se$: C, 36.59; H, 3.54; N, 9.85. Found: C, 36.52; H, 3.43; N, 9.75%.

*2.3.15. [N-(2-(Phenylseleno)ethyl)-N-(5-methyl-imidazol-4-ylmethylene)amine]cobalt(II) dichloride (**24**)*

Green powder (0.035 g, 49%). M.p. 165 °C. IR, ν/cm^{-1}: 1622, 1580. UV–Vis, λ_{max}, nm (ε, L mol^{-1} cm^{-1}) (CH_3CN): 261 (447), 298 (3260), 755 (150). MS (*m*/*z*): 387 ([M−Cl]$^+$).]$^+$). *Anal.* Calc. for $C_{13}H_{15}Cl_2CoN_3Se$: C, 36.99; H, 3.58; N, 9.96. Found: C, 36.63; H, 3.41; N, 9.79%.

*2.3.16. [N-(3-(Phenylseleno)propyl)-N-(5-methyl-imidazol-4-ylmethylene)amine]copper(II) dichloride **(25)***

Dark-green powder (0.047 g, 65%). M.p. 115–116 °C. IR, ν/cm^{-1}: 1635, 1588, 1475. UV–Vis, λ_{max}, nm (ε, L mol^{-1} cm^{-1}) (CH_3CN): 250 (8700), 701 (100). MS (*m*/*z*): 405 ([M−Cl]$^+$). *Anal.* Calc. for $C_{14}H_{17}Cl_2CuN_3Se$: C, 38.15; H, 3.89; N, 9.53. Found: C, 37.96; H, 3.85; N, 9.50%.

*2.3.17. [N-(3-(Phenylseleno)propyl)-N-(5-methyl-imidazol-4-ylmethylene)amine]cobalt(II) dichloride **(26)***

Green powder (0.035 g, 49%). M.p. 149–150 °C. IR, ν/cm^{-1}: 1635, 1610, 1470. UV–Vis, λ_{max}, nm (ε, L·mol^{-1} cm^{-1}) (CH_3CN): 234 (9920), 720 (120). MS (*m*/*z*): 401 ([M−Cl]$^+$). *Anal.* Calc. for $C_{14}H_{17}Cl_2CoN_3Se$: C, 38.56; H, 3.93; N, 9.64. Found: C, 38.19; H, 3.44; N, 9.41%.

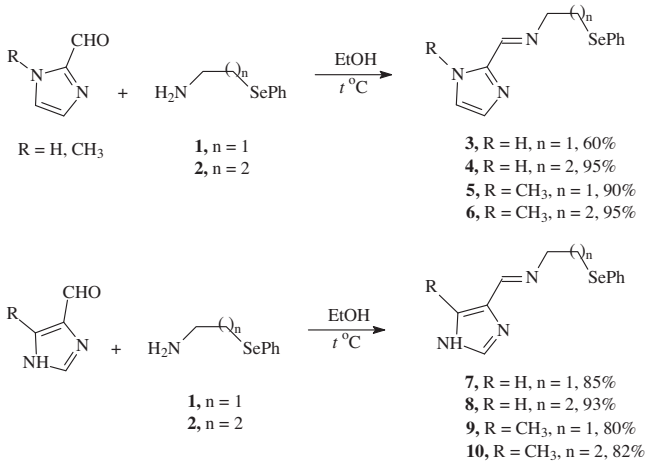
*2.3.18. [N-(2-(Phenylseleno)ethyl)-N-(imidazol-2-ylmethylene)amine] copper(I) chloride **(27)***

A solution of $Cu(MeCN)_4ClO_4$ (0.058 g, 0.1 mmol) and benzyl triethyl ammonium chloride (0.022 g, 0.1 mmol) in 3 ml of CH_3CN was slowly added to the solution of ligand **11** (0.028 g, 0.1 mmol) in 3 ml of CH_3Cl, and the reaction mixture, placed in an open test-tube, was left at room temperature at a tightly capped vessel containing 10 ml of diethyl ether. After three days the forming solid of compound **27** was separated by centrifugation and dried in air. Olive green powder (0.012 g, 30%). M.p. 160–161 °C. MS (*m*/*z*): 342 ([M−Cl]$^+$).

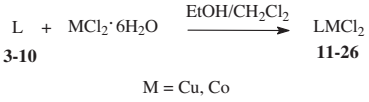
3. Results and discussion

3.1. Synthesis of ligand and complexes

Selenium-substituted imines **3–10** were synthesized by the condensation reactions of 2- or 4-imidazole carbaldehydes with amino selenides **1** or **2** in EtOH (Scheme 1). According to NMR spectra data, all Schiff bases **3–10** were isolated as single geometric isomers, which were identified as the *anti*-isomers basing on the results of NOE experiment performed on the example of compound **5** (NOE with the 1.5% intensity is observed for the protons of CH_2N groups (3.43 ppm) under the irradiation of HC=N protons



Scheme 1. Synthesis of ligands **3–10**.



Scheme 2. Synthesis of complexes **11–26**.

(8.17 ppm)). *Anti*-configuration of ligand **3** was also confirmed by the X-ray data for its copper complex **11** (see below).

IR spectra of all synthesized ligands display C=N and C=C absorption bands in the region of 1450–1660 cm^{-1}. IR spectra of ligands **3**, **4**, **7**, **8** show broad low-intensive band at 2900–3000 cm^{-1} indicating the existence of hydrogen bond H–N, either intramolecular (between imidazole NH protone and imino nitrogen atoms) or intermolecular.

To obtain the coordination compounds, the ligand **3–10** solutions in CH_2Cl_2 were mixed with eqimolar amount of $CuCl_2·6H_2O$ or $CoCl_2·6H_2O$ solution in EtOH and the resulting mixture standing to the solid precipitation. Complexes **11–26** (Scheme 2) with composition $L·MCl_2$ (M = Cu, Co) were obtained in all cases (the collective designation «**L**» for organic ligands **3–10** will use below). All complexes are reasonably soluble in CH_3CN, DMF or DMSO.

IR spectra of complexes **11–26** show the shift of C=N and C=C groups absorption bands at 1470–1680 cm^{-1} compare to initial ligands which confirms the coordination of the metal ions with the C=N nitrogen atoms.

The electronic absorption spectra of complexes **11–26** display weak *d–d* transition bands in the visible region at 520–755 nm with ε = 100–600 L mol^{-1} cm^{-1}. According to literature, the square planar compounds of Cu(II) possess a broad band in the 550–750 nm region [14,15], which shows bathochromic shift upon tetrahedral distortion [16]. The square planar cobalt complexes normally have only one band in the visible region whereas three bands at this area are commonly appeared for tetrahedral complexes of Co(II) [17]. Thus, an observed pattern of the spectrum and values of the molar absorption coefficient are typical for the coordination compounds with the square planar or slightly tetrahedrally distorted ligand environment of the central ion Cu^{2+} or Co^{2+}. All complexes also have more strong charge transfer bands in the UV region of their electronic spectra with the maximum at 204–398 nm.

3.1.1. Molecular and crystal structure of complex *11*

The structure of complex **11** was established by X-ray diffraction. Single crystal data for **11** were collected on a Bruker APEX2 DUO diffractometer using graphite monochromated Mo Kα radiation (= 0.71 073 Å, ω-scans) at 100 K. The structure was solved by direct method and refined by the full-matrix least-squares against F^2 in anisotropic approximation for non-hydrogen atoms. Hydrogen atoms were placed geometrically and refined in isotropic approximation in riding model. Crystallographic data and refinement parameters for **11** are shown in Table 1, and selected bond lengths are given in Table 2. Molecular structure of compound **11** together with the atom numbering scheme is shown in Fig. 1. The crystals, available for structural investigation, were made by slow diffusion of diethyl ether to ethanolic solution of $CuCl_2·6H_2O$ and ligand **11** (1:1). The coordination geometry of the copper(II) atom is nearly square planar. The metal atom is surrounded by two chloride anions and two nitrogen atoms of imidazole and imine fragments. Selenium atom of ligand does not take part in the coordination of metal. The

Table 1
Crystal data and structure refinement for **11**.[a]

Empirical formula	$C_{12}H_{13}Cl_2CuN_3Se$
Formula weight	412.65
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	*C*2/*c*
Unit cell dimensions	
a (Å)	29.0194(14)
b (Å)	15.8127(8)
c (Å)	7.1159(3)
α (°)	90
β (°)	97.3990(10)
γ (°)	90
Volume (Å3)	3238.1(3)
Z	8
D_{calc} (Mg/m^3)	1.693
Absorption coefficient (mm−1)	3.916
F(000)	1624
Crystal size (mm)	0.25 × 0.20 × 0.05
Theta range for data collection (°)	2.48–28.00
Index ranges	$-38 \leqslant h \leqslant 38$, $0 \leqslant k \leqslant 20$, $0 \leqslant l \leqslant 9$
Reflections collected	3873
Independent reflections	3873 [R_{int} = 0.0000]
Completeness to theta = 28.00° (%)	98.8
Absorption correction	semi-empirical from equivalents
Maximum and minimum transmissions	0.823 and 0.440
Refinement method	full-matrix least-squares on *F*2
Data/restraints/parameters	3873/0/176
Goodness-of-fit on *F*2	1.037
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0441, wR_2 = 0.1317
R indices (all data)	R_1 = 0.0587, wR_2 = 0.1390
Largest difference in peak and hole (e Å−3)	1.126 and −0.897

[a] The solvent molecule (which is a superpositon of dichloromethane, ethanol and diethyl ether) is disordered around an inversion center. Thereby, the contribution of the solvent was removed from overall scattering by using PLATON/SQUEEZE program [18].

Table 2
Selected bond lengths (Å) and angles (°) for **11**.

Bond lengths	*d* (Å)	Bond angles	ω (°)
Cu(1)–N(1)	1.973(3)	N(1)–Cu(1)–N(3)	80.32(12)
Cu(1)–N(3)	2.090(3)	N(1)–Cu(1)–Cl(1)	91.18(9)
Cu(1)–Cl(1)	2.2915(9)	N(3)–Cu(1)–Cl(1)	170.49(9)
Cu(1)–Cl(2)	2.2583(9)	N(1)–Cu(1)–Cl(2)	171.58(8)
N(3)–C(4)	1.278(5)	N(3)–Cu(1)–Cl(2)	93.61(9)
C(1)–C(4)	1.442(5)	Cl(2)–Cu(1)–Cl(1)	95.27(3)
N(1)–C(1)	1.321(4)	C(4)–N(3)–Cu(1)	112.4(2)
N(1)–C(3)	1.380(5)	C(1)–N(1)–Cu(1)	113.2(2)
C(2)–C(3)	1.373(5)	N(1)–C(1)–C(4)	118.3(3)
N(2)–C(2)	1.359(5)	C(4)–N(3)–C(5)	120.0(3)
N(2)–C(1)	1.343(5)	C(1)–N(1)–C(3)	106.6(3)

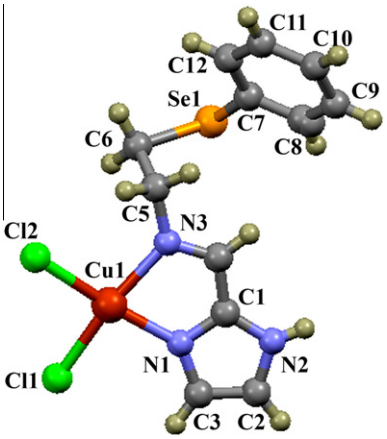


Fig. 1. Molecular structure of complex **11**. The minor component of the disordered Se-Ph fragment (with the occupancy ratio 0.559(8):0.441(8)) is not shown.

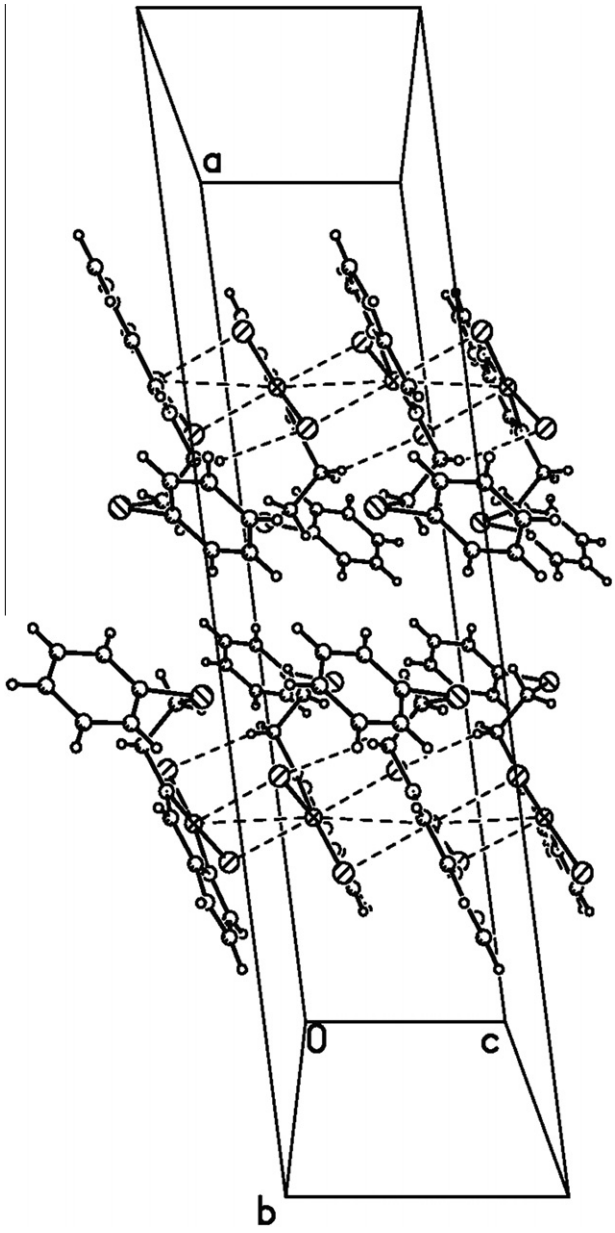


Fig. 2. Fragment of the crystal packing of the compound **11** along the crystallographic axis *c*.

phenyl moiety and the selenium atom it is bound to are severely disordered by two positions. The 5-membered metallacycle Cu(1)–N(3)–C(4)–C(1)–N(1) is practically planar.

In crystal structure of **11**, isolated molecules are packed in layers parallel to each other and oriented toward the space diagonal with respect to the unit cell (Fig. 2). The monomeric units of **11** are arranged in a chain-like fashion such that each copper ion is coordinated additionally as axial ligands by two coordinated chloride of two neighboring monomeric units. These axial bonds are however long (2.933(1) and 2.976(1) Å) and indicate a weak interaction.

3.1.2. Electrochemistry

Some obtained ligands and complexes were studied by cyclic voltammetry (CV) using a glass carbon (GC) electrode in DMF. The electrochemical oxidation and reduction potentials are given in Table 3.

Ligands **3**, **5**, **6**, **7** and **9** undergo a reduction at the potential more negative than −1.7 V (see Table 3 and Fig. 3). Imidazoles **3**, **5**, **6, 7, 9** oxidize irreversible at the potentials 1.08–1.26 V. The additional cathodic peaks at low potentials for complexes CV curves (Figs. 3 and 4) correspond to reduction at the metal; the following cathodic peaks are due to reduction of the organic fragment at more negative potentials that those for the free ligands.

The initial reduction of cobalt complex **12** occurs to metal at −1.46 V. Note, that the reduced form of the complex is stable in the solution which indicated by the absence of zerovalent metal desorption peaks during the reverse anodic scans after the potential of −1.5 V, even when performing the electrolysis within 30 s.

Copper complexes **11**, **15, 17, 19, 23** reduce at first stage quazyreversibly to metal at the anodic potential region (see Table 3 and Figs. 3 and 4). The reduced form of complexes are stable at the time scale of CVA method. The Cu(I) → Cu(0) reductions peaks are observed only for complexes **11**, **17, 23**. These peaks have very low intensity, probably because of poor solubility characteristic for copper(I) complexes [19–21].

It should be especially note, that *two* peaks corresponding to reduction Cu(II) → Cu(I) at anodic potential region are observed on CVA curves of synthesized complexes (Figs. 3 and 4). The intensity of more anodic peak increases for second and the following scans of CVA. These observations indicate the presence in the solution of two different complexes of copper(II) at one time.

This fact may be explained by the equilibrium of isomeric copper complexes with the CuN_2Cl_2 and CuN_2ClSe coordination spheres, analogous to described in [22] for the N,N′,S,S′ scorpionate ligands complexes. The proposed pattern of these equilibriums is shown on Scheme 3. The reduction of original coordination compounds may proceed with the removal of chloride anion resulting in the formation of Cu(I)-containing intermediate **A**. This intermediate, having in the structure more soft copper(I) atom compare to initial copper(II) complex, stabilizes by coordination with soft donor, namely selenium atom of organic ligand, completing of coordination sphere of copper ion with the formation of intermediate **B**. The subsequent oxidation of **B** gives complex **11a**, differing from starting complex. Complex **C** may also be generated directly from initial complex **11** as a result of intramolecular substitution of chloride anion to selenium in copper coordination sphere.

To confirm this hypothesis, semi-empirical PM3 calculation for complex **11**, as well as species **A**, **B** and monocation **11a** were performed. The optimized structures are reported in Figs. 5 and 6. The calculated structure of complex **11** is very much like to X-ray data (square planar environment of copper coordination environment; bond lengths and angles; see Fig. 5). The most significant difference in the experimental and calculated structured of complex **11** is the position of PhSe-groups: a plane of benzene ring in calculated structure is practically perpendicular to imidazole fragment plane

Table 3
Electrochemical reduction potentials (E^{Red}) and oxidation potentials (E^{Ox}) of the ligands **3**, **5**–**7**, **9** and their metal complexes measured relative to Ag|AgCl|KCl(sat.) by the CV methods at a glassy-carbon electrode (DMF, 0.05 M Bu_4NClO_4, 200 mV s−1). The values after the slash marks represent the peak potentials for the reverse CV scans.

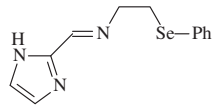
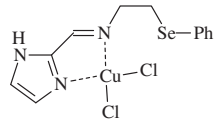
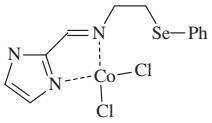
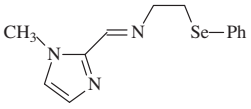
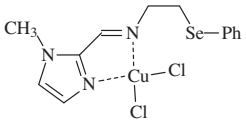
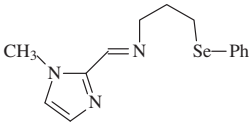
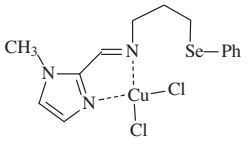
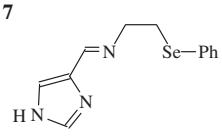
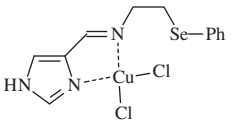
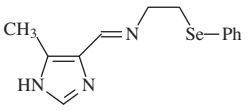
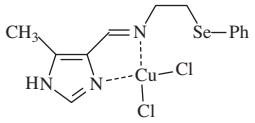
Compound	E_p^{Red}	E_p^{Ox}
3 	−1.77; −2.17; −2.37	1.08; 1.39
11 	+0.40/+0.52; +0.13/+0.52[a]; −0.78[b]; −2.03	1.23[c]
12 	−1.46; −1.77; −2.06	1.16[c]
5 	−1.91; −2.40	1.26; 1.52
15 	+0.44/+0.53; +0.14/+0.48[a]; −2.29	1.28
6 	−2.25; −2.64	1.08; 1.20; 1.39
17	+0.40/+0.50; +0.06/+0.12[a]; −0.78[b]; −1.76; −2.11	1.16
7 	−1.84; −2.38; −2.66	1.17
19 	+0.38/+0.50; +0.10/+0.53[a]; −2.09; −2.48	1.16[c]
9 	−1.88; −2.37	1.14; 1.28
		

Table 3 (*continued*)

Compound	E_p^{Red}	E_p^{Ox}
23 	+0.36/+0.54; −0.09/+0.06[a]; −0.76[b]; −2.16	1.17[c]

[a] The intensity of this peak increases under multiply potential scanning Cu(II) ⇌ Cu(I).
[b] The reverse peak at ~0 V corresponding to the desorption of Cu(0) is detected on CVA.
[c] High-intensive peak corresponding to carrying at least three electrons.

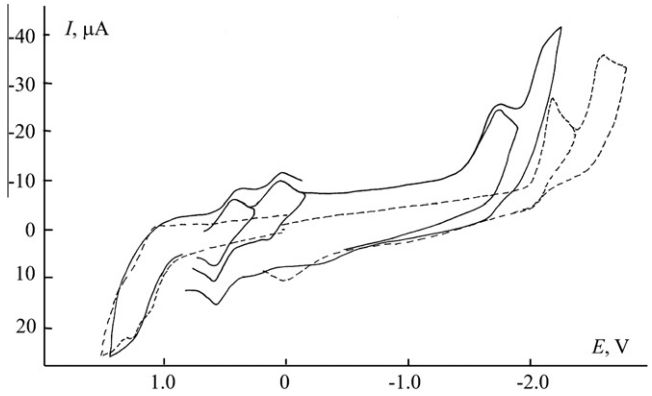


Fig. 3. Cyclic voltammograms of ligand **6** (*dashed line*) and its copper complex **17** (*solid line*). DMF, 0.05 *M* Bu_4NClO_4, 10–3 M.

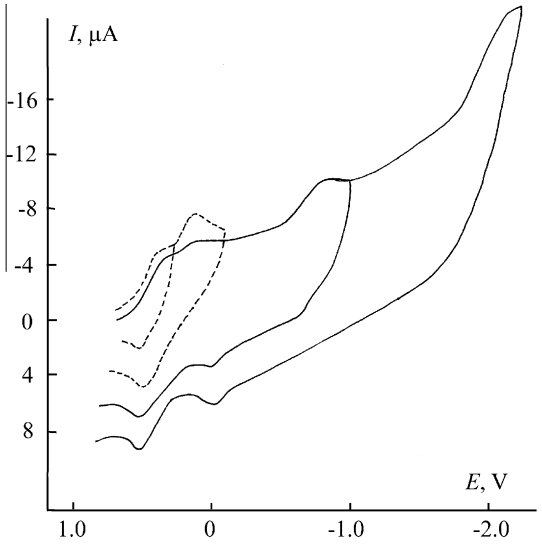
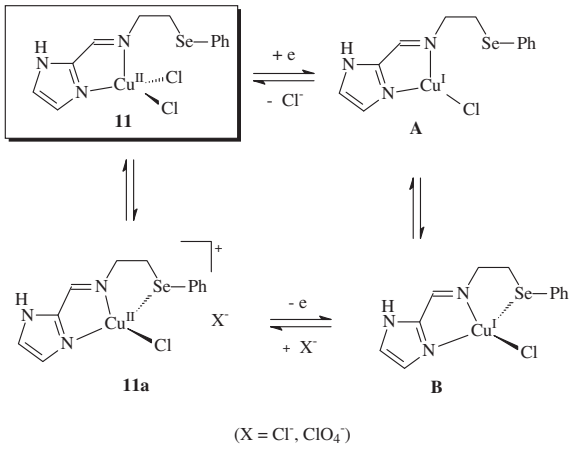


Fig. 4. Cyclic voltammograms of complex **19**: first scan (*solid line*); after the multiply potential cycling Cu(II) ⇌ Cu(I) (*dashed line*).

whereas these cycles in actual structure are near coplanar. This difference is apparently due to the π–π stacking of benzene rings of neighbor ligand molecules in crystal structure, which do not take into account at the calculations process. The similarity of calculated complex **11** structure with X-ray data let we assume that the calculations data are adequate characterize the copper coordination geometry in the complexes under consideration. As to monocation [**11**-Cl]$^+$, in its optimized structure selenium atom takes part in metal coordination with the formation of near square planar copper ion coordination environment.



Scheme 3. The proposed equilibriums between Cu-containing species in the process of reduction and the following oxidation of complex **11**.

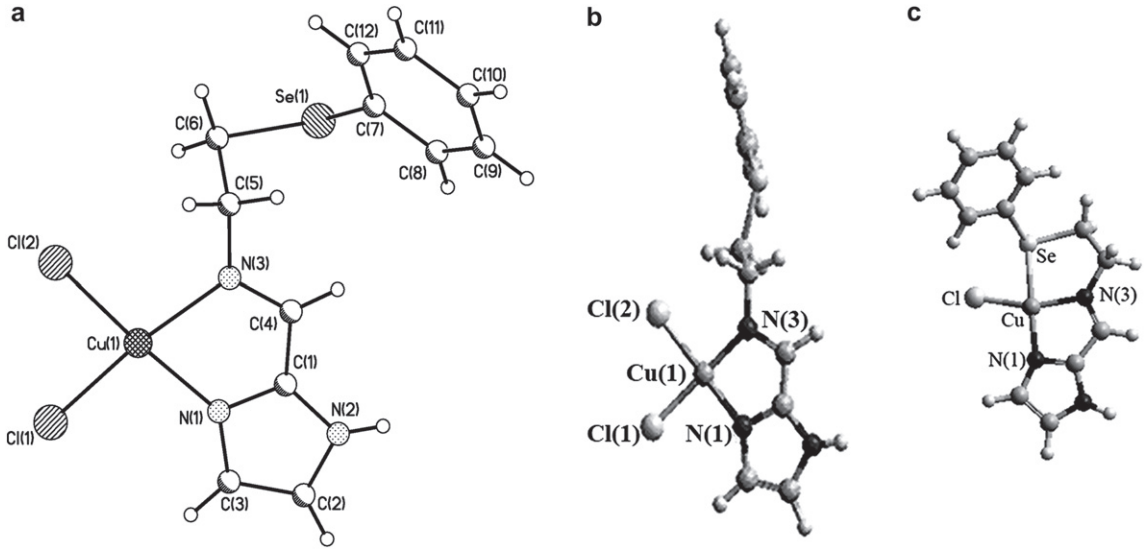
Both structures **A** and **B**, according to calculation results, correspond to the possible reduction intermediates. The calculated heats of formation for species **A** and **B** are −55.52 and −60.11 kcal/mol, respectively. It appears that both **A** and **B** can exist in the solution, but Se-coordinated form **B** is rather more stable.

As additional proof of the predominance of Se-coordinated copper after the reduction of investigated complexes we also synthesized the complex of ligand **11** with copper(I) by the interaction of ligand **11** with $Cu(MeCN)_4ClO_4$ in the presence of equimolar amount of benzyl triethyl ammonium chloride (Scheme 4). To propose a molecular geometry for the complex **27**, PM3 calculation were performed. The optimized structure is given in Fig. 6. In the accordance with calculation results, copper(I) ion in complex **27** is located in a near square planar environment and bound with one chlorine, one selenium and two nitrogen atoms (see Fig. 6).

The oxidation peaks for N-unsubstatued imidazoles complexes **11**, **12**, **19**, **23** are high intensive, which may be explained by contemporary oxidation at the near potentials both organic ligand and chloride anions.

4. Conclusion

In the conclusion, a series of mononuclear copper(II) and cobalt(II) complexes with novel organic ligands, forming as a result of 2- or 3-aminoalkyl phenyl selenides and imidazole carbaldehydes interaction, have been prepared by the reactions of metal chloride with ligand in $EtOH/CH_2Cl_2$ mixture. The complexes have been characterized by IR, UV–vis spectroscopy and cyclic voltammetry. The X-ray analysis of copper complex with 2-(phenylseleno)ethyl)-*N*-(imidazol-4-ylmethylene)amine revealed that the copper(II) ion assumes a tetracoordinated square–planar geometry with an N_2Cl_2 donor set.



Selected bond lendth and angles: Cu(1)-N(1) 1.973Å, Cu(1)-N(3) 2.090Å, Cu(1)-Cl(2) 2.2583Å, Cu(1)-Cl(1) 2.2915Å. Угол N(1)-Cu(1)-N(3) 80.32 °; N(1)-Cu-(Cl1) 91.18 °; N(3)-Cu-(Cl2) 93.61 °; Cl(1)-Cu-(Cl2) 95.27 °.

Selected bond lendth and angles: Cu(1)-N(1) 1.865Å, Cu(1)-N(3) 1.953Å, Cu(1)-Cl(2) 2.191Å, Cu(1)-Cl(1) 2.158Å; N(1)-Cu(1)-N(3) 89.77 °; N(1)-Cu-(Cl1) 90.63 °; N(3)-Cu-(Cl2) 91.19 °; Cl(1)-Cu-(Cl2) 88.68 °.

Fig. 5. Comparison between the Cu(II) experimental geometry (X-ray) of the complex **11** (*a*) with the respective PM3-optimized species **11** (*b*) and monocation **11a** (*c*).

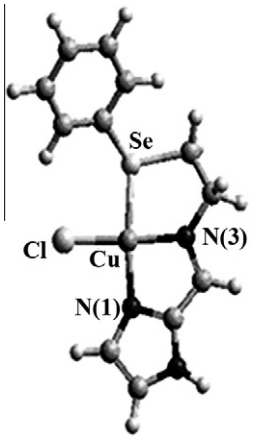
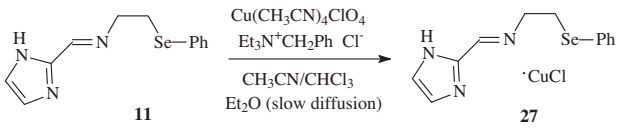


Fig. 6. PM3-optimized structures of complex **27**. *Selected bond lendth and angles*: Cu-N(1) 1.878Å, Cu-N(3) 1.872Å, Cu-Cl 2.153Å, Cu-Se 2.211Å; N(1)-Cu(1)-N(3) 90.88°; N(1)-Cu-Cl 94.81°; N(3)-Cu-Se 83.83°; Cl-Cu-Se 90.41°.



Scheme 4. Synthesis of complex **27**.

Cyclic voltammetry experiments performed in DMF showed a quasi-reversible behavior of the Cu^{II}/Cu^{I} redox couple for all copper containing complexes, whereas the cobalt containing complex is reduced irreversibly. Cyclic voltammogramms of copper complexes exhibit the existence in the solution of two different copper(II) complexes as a result of reduction/re-oxidation or oxidation/re-reduction sequences. These results are interpreted in terms of formation of complexes with different composition and geometry of copper coordination sphere.

Acknowledgment

We are grateful to the Russian Foundation of Basic Research (Project 10-03-00677) for the financial support of this work.

Appendix A. Supplementary material

CCDC 898469 contains the supplementary crystallographic data for complex **11**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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