



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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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.

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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. 1H NMR spectra were recorded on a Varian-XR-400 recorder (400 MHz for

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^1H 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 $\lambda = 337$ 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; $\text{Ag}/\text{AgCl}/\text{KCl}(\text{sat.})$ 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 or 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. ^1H 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%). ^1H 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%). ^1H NMR (CDCl_3): 8.17 (s, 1H, HC=N), 7.55 (m, 2H, Ph), 7.32 (m, 3H, Ph), 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%). ^1H 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. ^1H NMR (CDCl_3): 8.12 (s, 1H, HC=N), 7.86 (m, 2H, Ph), 7.74 (b.s., 2H, Im), 7.48 (m, 3H, Ph), 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%). ^1H NMR (CDCl_3): 8.25 (s, 1H, HC=N), 7.73 (b.s., 2H, Im), 7.48 (d, $J = 7.3$ Hz, 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-ylmethylene)amine (**9**)

Yellow oil (0.421 g, 85%). ^1H 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-ylmethylene)amine (**10**)

Yellow-orange oil (0.283 g, 60%). ^1H 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 $\text{MCl}_2 \cdot 6\text{H}_2\text{O}$ ($\text{M} = \text{Cu}, \text{Co}$) 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 ($[\text{M}-\text{Cl}]^+$). Anal. Calc. for $\text{C}_{12}\text{H}_{13}\text{Cl}_2\text{CuN}_3\text{Se}$: 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 , $\text{L mol}^{-1} \text{cm}^{-1}$) (CH_3CN): 344 (5020), 718 (115). MS (m/z): 408 (M^+). Anal. Calc. for $\text{C}_{12}\text{H}_{13}\text{Cl}_2\text{CoN}_3\text{Se}$: 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 ($[\text{M}-\text{Cl}]^+$). Anal. Calc. for $\text{C}_{13}\text{H}_{15}$.

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