Synthesis and coordinating properties of 5-phenyl- and 5-pyridylmethylidene-substituted 2-selenohydantoines and 2-selenoimidazol-4-ones

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2-Selenoimidazolidin-4-ones and 2-selenoimidazol-4-ones containing phenyl- or pyridylmethylidene substituent at position 5 were synthesized. The structure of 3-benzyl-2-selenohydantoine was confirmed by X-ray crystallography. A series of 2-(methylseleno)imidazol-4ones was obtained by alkylation of 3,5-disubstituted selenohydantoines with methyl iodide. The synthesized selenohydantoines and 3-benzyl-5-pyridylmethylidene-2-(methylseleno)imidazol-4-ones were examined in the complexation reactions with CoCl₂, NiCl₂, CuCl₂, and Cu^I(CH₃CN)₄ClO₄; electrochemical investigations showed that reduced forms of the coppercontaining complexes were stable

Key words: 2-selenohydantoines substituted at position 5, 2-selenoimidazol-4-ones substituted at position 5, N,Se-containing ligands, transition metal complexes, electrochemistry.

Organoselenium compounds are important intermediates in organic synthesis and convenient models for the investigation of reaction mechanisms in organic and bioorganic chemistry. A wide application of organoselenium compounds in the synthesis is determined by their easy incorporation into organic molecules and subsequent removal after performing all the necessary synthetic transformations, which was used in the preparation of a number of complicated natural compounds.¹

High biological activity of organoselenium compounds is yet another reason for their active studies. Selenium deficiency in human body was found to increase the probability of cardio-vascular pathologies, cancer, and arthritis. It is known that the process of peroxide oxidation of lipids is one of the main reasons of human organism ageing. A selenium-containing enzyme glutathioneperoxidase catalyzing reactions of peroxides with mercapto groups of glutathione can inhibit this process in the organism.²

Development of chemistry of selenium-containing compounds received a powerful impulse by the studies directed on the preparation of conducting materials based on the charge-transfer selenium-containing complexes and radical ion salts. An important field of their practical application is the preparation of semiconductor materials, films, and coatings.³

As to the present moment, coordination compounds of metals with selenium-containing ligands are studied poorly. 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.⁴ The latest studies on intramolecular stabilization of organoselenium compounds showed that the intramolecular interactions Se…N play an important role in the antioxidant activity of these compounds.⁵

The Ni atom in the active site of the [FeNiSe] hydrogenase enzyme is coordinated with the selenium atom of selenocysteine.⁶ The catalytic properties of this enzyme considerably differ from the properties of the sulfur-containing analog, [FeNi] hydrogenase.⁷ The molybdenumcontaining enzyme formate dehydrogenase H, besides the molybdenum—sulfur bonds, contains the molybdenum—selenium bond (selenocysteine), which is required for the catalytic activity.⁸ Comparison of complex compounds simulating these active centers and containing S and Se atoms allows one to better understand the nature of the catalytic activity of these enzymes.

The present work was devoted to the development of methods for the preparation of new Se,N-containing ligands of the 2-selenoimidazolidin-4-one and 2-selenoimidazol-4-one series, including those containing donating pyridylmethylene substituents at position 5 of the five-membered heterocycle and studies of a pos-

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sibility of their complexation with Cu^{II} , Co^{II} , Ni^{II} , and Cu^{I} salts.

Results and Discussion

A two-step procedure for the preparation of seleniumcontaining analog from the corresponding thiohydantoine described in the literature⁹ (Scheme 1) turned out to be applicable only to the synthesis of 5-phenylmethylidenesubstituted selenohydantoine 3 in a moderate yield; the preparation of 5-pyridylmethylidene-substituted selenohydantoines by this method failed.



5-Pyridylmethylidene-substituted selenohydantoines were synthesized by an alternative procedure starting from 3-*N*-benzyl-substituted selenohydantoine **4**. Compound **4** was obtained using two methods: the reaction of benzyl isoselenocyanate with ethyl glycinate¹⁰ or with the potassium salt of the same amino acid with subsequent acidifying of the reaction mixture and cyclization of the thus formed selenourea according to the modified by us literature procedure by reflux in a mixture of HCl/EtOH (Scheme 2). The latter method allowed us to achieve a 45% yield of the target product, while in the first method it did not exceed 20%.

The structure of compound **4** was confirmed by X-ray crystallography (Fig. 1). The crystallographic data, experimental details and refinement parameters of the structure are given in Table 1. All the nitrogen and carbon atoms of the five-membered heterocycle lie in one plane; the exocyclic oxygen and selenium atoms are in the same plane. The dihedral angle C(1)-N(1)-C(4)-C(5) is equal to ~84°.

For the introduction of a substituent into position 5 of the selenohydantoine ring, we used two alternative procedures (Scheme 3): a reaction of 2-selenohydantoine **4** and



i. 1) Et₃N/THF, 2) PhCH₂NCSe (20%), Δ; *ii*. 1) KOH/H₂O, 2) PhCH₂NCSe/EtOH, 3) HCl; *iii*. HCl/EtOH (45%), Δ.



5: R = Ph (a), 2-Py (b), 3-Py (c), 4-Py (d)

the corresponding aldehyde in AcOH in the presence of the equimolar amount of AcONa (method *A*) and a two-step *one-pot* synthesis from the same starting compounds (method *B*).

The target products were obtained by both methods, but method A gave higher yields for benzaldehyde and all three pyridinecarbaldehydes (Table 2). In addition, the work-up and the isolation of the final product in this case is experimentally considerably easier.

Note that our attempts to involve benzyl isoselenocyanate into the three-component reaction with glycine and α -, β -, and γ -pyridinecarbaldehydes in glacial acetic acid, analogous to the known procedure for thiohydantoines,¹¹ did not lead to the formation of products **5a**–**d**.

Each of the compounds 3, 5a-d was isolated as a single geometric isomer. We assign them the Z-configuration based on the ¹H NMR data for E- and Z-isomers of

Scheme 2



Fig. 1. Molecular structure of compound 4 (the ellipsoids of atomic displacements are shown with 50% probability). Selected bond distances (Å) and bond angles (deg): Se(1)-C(1) 1.8305(16), N(1)-C(1) 1.380(2), N(1)-C(2) 1.393(2), N(2)-C(1) 1.327(2), N(2)-C(3) 1.455(2); the angle C(1)-N(1)-C(2) 111.42(13), C(1)-N(2)-C(3) 112.63(13), N(2)-C(1)-Se(1) 127.24(12), N(1)-C(1)-Se(1) 124.57(12).

2-thiohydantoine derivatives containing a pyridylmethylidene fragment at position 5, according to which the shifts of the vinylic protons in the spectra of Z- or E- isomers are found in the range of δ 6.40–6.85 and 6.10–6.35, respectively.¹¹

Alkylation of 3,5-disubstituted selenohydantoines **3** and **5b**—**d** with methyl iodide gives rise to 2-(methyl-seleno)imidazolones **6** and **7a**—**c** (Scheme 4). Alkylation with 1,2-dibromoethane and 1,3-dibromopropane leads to the derivatives **8a**,**b** (see Scheme 4), each of which contains two chelating fragments connected by the polymethylene chain with different number of carbon atoms.

The potassium salts of selenohydantoines **3**, **5** and 3-benzyl-2-methylseleno-5-(pyridylmethylene)imidazol-

 Table 1. Crystallographic data, experimental details and parameters of refinement for the structure of compound 4

Parameter	Value
Molecular formula	$C_{10}H_{10}N_2OSe$
Molecular weight	253.16
T/K	120(2)
Wavelength/Å	0.71073
Crystal form	Colorless prisms
Crystal size/mm	0.25×0.15×0.10
Crystal system	Monoclinic
Space group	P21/c
a/Å	13.0120(8)
b/Å	5.6521(4)
c/Å	13.3908(8)
α/deg	90
β/deg	94.1460(10)
γ/deg	90
$V/Å^3$	982.25(11)
Ζ	4
$d_{\rm calc}/{\rm g~cm^{-3}}$	1.712
Absorption coefficient/mm ⁻¹	3.788
<i>F</i> (000)	504
Range of θ/deg	1.57-29.0
Range of reflection indices	$-17 \le h \le 17,$
	$-7 \le k \le 7,$
	$-18 \le l \le 18$
Number of measured/independent	11147/2623
reflections	$(R_{\rm int} = 0.0324)$
Q -Factor on F^2	1.004
<i>R</i> -Factors $(I > 2\sigma(I))$	
R_1	0.0206
wR_2	0.0479
<i>R</i> -Factors (on all the data)	
R_1	0.0276
wR_2	0.0488

4-ones 7 were studied in the complexation reactions with transition metal salts.

The reaction of the potassium salt of selenohydantoine **3** with copper(II) chloride in ethanol unexpectedly led to the isolation of a coordination compound **9** of the compo-



Table 2. Yields of selenohydantoines 5a-d obtained by methods *A* and *B*

Com-	Yield (%)		
pound	A	В	
5a	74	19	
5b	91	53	
5c	83	57	
5d	77	59	

sition Cu_2L_2 (Scheme 5), *i.e.* in the course of the reaction copper(11) was reduced to copper(1). We suggested that this reduction can be caused by the solvent (EtOH). To check this hypothesis, the reaction was reproduced in MeCN. In fact, the complex compound **10** of the composition CuL_2 was the product in this case. Thus, coordination compounds of different composition can be obtained by varying solvent in the reaction of ligand **3** with CuCl₂.

Scheme 5



According to the electron spectroscopic data,¹² the copper atoms in the coordination compound **9** are in the trigonal environment. The electron spectroscopy data did not allow us to unambiguously determine coordination environment of the copper atom in compound **10**; however, the IR spectra of the complex compounds **9** and **10** exhibit displacement of the vibration bands of the C=N group to the short-wave region of the spectrum as compared to the spectrum of the starting ligand by 9 and 7 cm⁻¹, respectively, which confirms the coordination of the copper ion with the nitrogen atom. A suggested structure of complex **9** is shown below. In addition to the data of elec-



tron spectroscopy, the results of electrochemical studies also give evidences in favor of the indicated structure (for the details, see below): the presence on the CVA curve of two peaks of the reduction $Cu^{I} \rightarrow Cu^{0}$ at different potentials confirms the presence of two attached to each other copper atoms.

The potassium salts of pyridylmethylidene-substituted selenohydantoines **5b**—**d** were examined in the complexation reactions with nickel, cobalt, and copper(II) chlorides, as well as with $Cu^{I}(MeCN)_{4}ClO_{4}$. The complex compounds of the composition LM or $L_{2}M$ were isolated as the reaction products (Scheme 6).



5: R = 2-Py (**b**[´]), 3-Py (**c**[´]), 4-Py (**d**[´])

Com-	R	М	Com-	R	М
11	4-Py	Cu	12c	2-Py	Cu
12a	2-Py	Co	12d	4-Py	Co
12b	2-Py	Ni	12c	4-Py	Cu

The structures of complexes **11** and **12e** with the deprotonated 4-Py-containing ligand **8**, suggested based on the results of elemental analysis and spectroscopic data, are shown below.

Extremely low solubility of the complexes in all the solvents tried and the electrochemical data evidence in favor of their polymeric structure. The region of the reduction potentials $Cu^{I} \rightarrow Cu^{II}$ for compounds 11 and 12e and the region of the reduction potentials $Cu^{II} \rightarrow Cu^{II}$ for compound 12e have a single peak each, which indicates the absence of the interaction between the copper atoms









and allows us to rule out a binuclear structure with the Cu—Cu bond analogous to that suggested above for the complex **9**. Such a polymeric structure has been described earlier for the structurally similar coordination compounds with the ligands of γ -pyridylmethylidenethiohydantoine series.¹¹

According to the electron spectroscopic data,¹³ the coordination polyhedrons of the metal atoms in complexes **12a** and **12d** are the tetrahedrons. The IR spectra of the complex compounds exhibit a displacement of the vibration band of the C=N group toward the short-wave region of the spectrum by 7–16 cm⁻¹ as compared to the position of this band in the IR spectra of the ligands, which indicates that the metal atoms are bonded to the nitrogen atom.

For compound **12a**, the structure shown below seems the most probable. Earlier, such a structure has been suggested for the analogous coordination compound with the pyridylmethylidene-substituted thiohydantoine (compound A).¹⁴ Their structural resemblance also is confirmed by their very close redox characteristics (see below).



3-Benzyl-5-pyridylmethylidene-2-(methylseleno)imidazol-4-ones $7\mathbf{a}-\mathbf{c}$ react with cobalt(11), nickel(11), and copper(11) chlorides (Scheme 7) to form coordination compounds $13\mathbf{a}-\mathbf{f}$ of the composition L_2MCl_2 , in a number of

cases containing additional water molecules. Based on the data of electron and IR spectroscopy, as well as on the results of electrochemical studies, it can be suggested that the structure of these complexes is similar to the structure of the sulfur-containing analogs described in the works.^{11,15} The coordination of the metal ions is effected by the pyridine nitrogen atom and the nitrogen atom of the C=N bond, compounds 13a,b with the 2-pyridyl-containing ligand 7a have a six-membered metallacycle in the composition, whereas complexes 13c—f with 3-and 4-pyridyl-containing ligands 7b,c have a polymeric structure.

Scheme 7

	7a—0		MeCl ₂ tOH, ∆ L ₂ N	ICI ₂	
			13a	ı—f	
Com- pound	R	М	Com- pound	R	Μ
13a 13b 13c	2-Py 2-Py 3-Py	Co Cu Co	13d 13e 13f	3-Py 3-Py 4-Py	Cu Ni Cu

Electrochemical studies of ligands and complexes. Electrochemical investigation of selenium-containing ligands and their coordination compounds was carried out in DMF solutions in the presence of $0.1 M Bu_4NClO_4$ as an indifferent electrolyte on a glass-carbon (GC) disk electrode by cyclic voltammetry (CVA) and rotating disk electrode (RDE). The results obtained are summarized in Table 3.

Figure 2 shows the CVA curves of 2-pyridylmethylideneselenohydantoine ligand **5b** and its complex compound with Co^{II} **12a**. The CVA curve of the ligand **5b** has three



Fig. 2. Cyclic voltammograms (DMF, the concentration of 10^{-3} mol L⁻¹, 0.1 *M* Bu₄NClO₄) of ligand **5b** (the dashed line) and its coordination compound with Co^{II} **12a** (the solid line).

Table 3. Electrochemical reduction (E^{Red}) and oxidation (E^{Ox}) potentials of ligands and complexes measured relation	tive
to Ag[AgCl]KCl(sat.) using CVA (E_p is the peak potential) and RDE ($E_{1/2}$ is the half-wave potential) methods	on
a GC electrode (DMF, 0.1 M Bu ₄ NClO ₄ , CVA 200 mV s ⁻¹ , RDE 20 mV s ⁻¹ , 2800 min ⁻¹), the number of electr	ons
(in parentheses) transferred in a given step and determined on the RDE by comparison with the wave of the o	ne-
electron oxidation of ferrocene, as well as peak potentials on the inverse scans of the CVA curves (after the slash)	

Compound	$E_{\rm p}^{\rm Red}$	$E_{1/2}^{\text{Red}}$	$E_{\rm p}^{\rm Ox}$	<i>E</i> _{1/2} ^{Ox}
		V		
Ligand 5 b	$\begin{array}{c} 1) -0.94 \\ 3) -1.70 \\ 4) -2.07 \end{array}$	$\begin{array}{c} 1) -0.87 \\ 2) -1.42 \\ 3) -1.63 \\ 4) -2.03 \end{array}$	1) 1.12 2) 1.46	1) 1.01 (2) 2) 1.22 (2)
Ligand 5c (potassium salt)	1) -1.81 2) -1.90 3) -2.23	_	1) 0.36 2) 1.02 3) 1.49	_
Ligand 7 a	1) -1.17/-1.08 2) -1.57 3) -2.03	1) -1.14 (1) 2) -1.51 (1) 3) -2.26	1) 1.52	1) 1.52
Ligand 7b	1) -1.30/-1.24 2) -1.88/-1.79 3) -2.26	1) -1.20 (1) 2) -1.83 (1)	1) 1.43	1) 1.42 (2)
Complex 9 (3 -H) ₂ Cu ¹ ₂	1) -0.39 2) -0.64 3) $-1.87/-1.81$ 4) -2.24	$\begin{array}{c} 1) -0.55\\ 2) -0.84\\ 2) -1.23\\ 3) -1.84\\ 4) -2.30\end{array}$	1) 0.33/0.31 2) 1.02/0.02 3) 1.46	1) 0.39 (1) 1) 0.97 2) 1.43
Complex 11 $[(5c-H)Cu^{I}]_{n}$	$\begin{array}{c} 1) -0.60 \\ 2) -1.13 \\ 3) -1.59 \\ 4) -1.93 \end{array}$	1) 0.49 2) -1.51 3) -1.70 4) -1.89	1) 0.37/0.47 2) 1.32	1) 1.16
Complex $12a$ (5a-H) ₂ Co ^{II}	1) -0.96/-0.91 2) -1.16/-1.11 3) -1.71/1.60	1) -0.92 (1) 2) -1.13 (1) 3) -1.65 (2)	1) 0.84 2) 1.00	1) 0.90 (2)
Complex 12e $[(5c-H)_2Cu^{II}]_n$	1) $0.38/0.49$ 2) $-0.16/0.23$ 3) -1.16 4) -1.52 5) -1.85	1) 0.50 2) -1.23 3) -1.46 4) -1.73	1) 1.23	1) 1.20
Complex $13b$ (6) ₂ Cu ^{II} Cl ₂	1) 0.37/0.56 2) 0.09/0.14 3) -0.29/0.21 4) -1.38/-1.34 5) -2.26	1) 0.52 (1) 2) 0.10 (1) 3) 0.17 (1) 4) -1.32 (2)	1) 1.02 2) 1.38	1) 1.12 (2) 2) 1.40 (2)
Complex 13c $(7a)_2$ Co ^{II} Cl ₂	1) $-1.30/-1.25$ 2) -1.83 3) -1.92 4) -2.28	1) -0.78	1) 1.18	1) 1.01
Complex 13d $(7a)_2Cu^{11}Cl_2$	1) 0.40/0.46 2) -1.31/-1.25 3) -1.85/-1.76 4) -1.88/-1.74 5) -2.22	1) 0.45 (1) 2) -1.24 (2)	1) 1.30	1) 1.14 (2)
Complex 13e $(7a)_2 Ni^{II} Cl_2$	1) -1.26/-1.18 2) -1.85 3) -2.19 4) -2.23	1) -1.24 2) -1.61 3) -2.05	1) 1.14	1) 1.01

irreversible cathode peaks at -0.94, -1.70, and -2.07 V and two irreversible anode peaks at 1.12 and 1.46 V. Earlier, we have shown that the first steps of both reduction and oxidation of the structurally close 3-phenyl-5-pyridylme-thylidene-2-thiohydantoines¹⁵ proceed irreversibly with respect to the C=S bond at the potentials ~ -1.1 V (one-electron process) and 1.1-1.5 V (two-electron process), respectively. Comparing these data with the results obtained in the studies of selenohydantoine **5b**, it can be suggested that the oxidation and reduction of the latter proceeds similarly at the C=Se bond (Scheme 8).

Scheme 8



Note that both the oxidation and the reduction of selenohydantoine proceed easier than the oxidation and the reduction of its sulfur-containing analog. A comparable easiness of oxidation of compound **5b** can be explained by the greater electron-donating power of the benzyl substituent on the N(3) nitrogen atom in this ligand as compared to the phenyl substituent of the sulfur analog studied earlier,¹⁵ as well as by the lower electronegativity of the Se atom as compared to the S atom. In addition, according to theory of hard-soft acids and bases, a selenium atom is "softer" as compared to a sulfur atom, which from the point of view of molecular orbitals theory means a smaller gap between the HOMO and the LUMO of selenohydantoine than in the case of the sulfur analog.

For the cobalt complex of ligand **5b**, *i.e.*, compound **12a**, the cathode branch of the CVA curve has three reversible peaks (see Fig. 2 and Table 3), of which the first $(E_{1/2} - 0.96 \text{ V})$ and the second $(E_{1/2} - 1.16 \text{ V})$ are the oneelectron ones. The third wave $(E_{1/2} - 1.71 \text{ V})$ is the twoelectron. The anode region has two irreversible peaks with E_p 0.84 and 1.00 V. Very similar pattern has been observed by us earlier during electrochemical studies of the structurally close cobalt thiohydantoine complex (compound **A**).¹⁴ Such similarities of the redox characteristics of compounds **12a** and **A** confirm the structure suggested for compound **12a**. In addition, the electrochemical reversibility of the first reduction wave of complex **12a** shows that the reduced form of the complex (containing either Co^I, if the reduction takes place at the Co atom, or an organic radical anion, if the reduction occurs "at the ligand") is stable in solution.

The complex compounds of copper(1) **11** and copper(11) **12e** with the anionic 4-pyridylmethylideneselenohydantoine ligand **5c** are reversibly reduced in the first step "at the metal" (see Table 3 and Fig. 3). Note that for complex **11** after scanning the potential into the anode region, the re-registrated CVA acquired the form very similar to the CVA curve for complex **12e** (see Fig. 3). Apparently, the oxidation of Cu^I in complex **11** to Cu^{II} leads to the formation of a coordination compound structurally similar to **12e**.

Note that compounds 9 and 11, having the similar simple molecular formula (LH)Cu^I, very strongly differ electrochemically: the CVA curve for the first of these complexes has two reduction peaks $Cu^{I} \rightarrow Cu^{0}$, which proves the presence in its composition of two copper atoms bonded to each other, whereas for the second complex, the curve contains only one such a peak; therefore, the copper atoms in the composition of the complex do not interact.

Ligands **7a**,**b** are reduced in three sequential steps, the first and the second of which are one-electron; the oxidation of the ligands proceeds in one step by a two-electron process (see Table 3, Fig. 2). Their coordination compounds **13b**—**e** have additional peaks on the cathode branch of the CVA curve (see Fig. 2), with the potentials of the first reduction peak of the cobalt- and nickel-containing complexes **13c** and **13e** being very close to the reduction potential of the free ligand. The oxidation potentials of complexes **13b**—**e** correspond to the oxidation of coordinated chloride anions.¹⁵



Fig. 3. Cyclic voltammograms (DMF, the concentration of 10^{-3} mol L⁻¹, 0.1 *M* Bu₄NClO₄) of complex **12e** (the solid line) and complex **11** immediately after the dissolution (the dashed line), as well as after the scanning the potential into the oxidation region (the dashed-and-dotted line).



Fig. 4. Cyclic voltammograms (DMF, the concentration of 10^{-3} mol L⁻¹, 0.1 *M* Bu₄NClO₄) of ligand 7b (the dashed line) and its coordination compound with Cu^{II} 13d (the solid line).

The copper-containing complexes **13b**,**d** undergo a reversible redox transition at the potential of 0.30-0.40 V. From this it follows that the reduction of these complexes, unlike of Ni- and Co-containing analogs, proceeds "at the metal" (Cu^{II} \rightarrow Cu^I). It should be especially noted that even when the potential reaches the level of -2.3 V during an inverse potential scanning, no decomposition of the complex with the isolation of metallic copper is observed. This means that a zero-valence copper is held exclusively strong by the complexes of such a structural type. After the copper in the coordination compound does not cause any noticeable shift of the ligand reduction wave potentials (see Table 3, Fig. 4).

It should be noted that the electrochemical behavior of the complexes depends on the electrode material. Thus, when complex **13e** was studied on an Au electrode, an additional peak appeared on the CVA curve in the reduction region at -0.76 V. Apparently, the complexes under study can be adsorbed on the surface of the metallic electrode. Moreover, the first reduction peak of complex **13d** loses its reversibility on metallic (Au and Pt) electrodes, probably, as a result of disproportionation of the copper(1) complex to Cu^{II} and Cu⁰.

In conclusion, we have developed approaches to the preparation of 3-phenyl- and 3-benzyl-substituted 2-selenoimidazolidin-4-ones and 2-selenoimidazol-4-ones containing phenyl- or pyridylmethylidene group at position 5. Their coordination compounds with Co^{II}, Ni^{II}, Cu^{II}, and Cu^I were obtained. Electrochemical data showed that the reduced forms of the copper-containing complexes of these ligands are stable, that makes them promising subjects for further studies as catalysts of redox reactions including electrochemically induced.

Experimental

¹H NMR spectra were recorded on a Brucker-Avance spectrometer (400 MHz). IR spectra were recorded on a TermoNicolet IR200 infra-red Fourier transform spectrometer (USA), UV spectra were recorded on a Hitachi U-2900 spectrometer. Elemental analysis was performed on a Perkin-Elmer CHNanalyzer (model 2400). In order to trap selenium oxide, the tail part of the oxidation and reduction reactor additionally was equipped with a \sim 3 cm long silver net rolled as a stopper. Mass spectra MALD were recorded on a Bruker Autoflex II instrument (the FWHM resolution of 18000) equipped with a nitrogen laser with an operational wavelength of 337 nm and time-offlight mass analyzer, accelerating voltage of 20 kV; the samples were deposited on a support made of polished steel; the spectra were recorded in the positive ions mode; the resulting spectrum was a sum of 300 spectra obtained in the different sites of the sample. 2,5-Dihydroxybenzoic acid (DHB) (Acros, 99%) and α -cyano-4-hydroxycinnamic acid (HCCA) (Acros, 99%) were used as matrices. For all the indicated mass-spectral peaks, the isotopic distribution corresponded to the calculated data.

X-ray diffraction studies were performed on a Bruker Smart APEX2 CCD Area Detector single-crystal automatic diffractometer (graphite monochromator, λ (Mo-K α) = 0.71073 Å, φ - and ω -scan technique). The structure was solved using the SHELXTL ver. 5.1 program package.¹⁶ Positions of hydrogen atoms were calculated in isotropic approximation using the riding model.

For electrochemical studies we used a PI-50-1.1 potentiometer connected to a PR-8 program block. A glass carbon disk (d = 2 mm) served as a reference electrode, 0.1 M solution of Bu₄NClO₄ in DMF was used as a supporting electrolyte, Ag/AgCl/KCl(sat.) was used as a comparison electrode, a platinum plate was used as an auxilary electrode. In the CVA studies, the potential sweep speed was 200 mV s⁻¹, in the RDE studies, 20 mV s⁻¹. The potentials are given with allowance for the iR-compensation. The number of transferred electrons in the redox processes was determined by comparison of the wave limit current in the experiments on RDE with the current of the oneelectron oxidation of ferrocene taken in the equal concentration. All the measurements were carried out under dry argon; The samples were dissolved in a pre-degassed solvent. DMF (pure grade) was purified by stirring for 4 days over freshly calcined K₂CO₃ with subsequent distillation *in vacuo* over CaH₂.

3-Phenyl-5-phenylmethylidene-2-thioimidazolidin-4-one (1) and 3-phenyl-5-phenylmethylidene-2-(methylthio)imidazol-4-one (2) were obtained according to the procedures described earlier.^{17,18} Benzyl isoselenocyanate was synthesized according to the known procedure¹⁹ from benzyl isocyanate; the conversion of the starting compound in the latter reaction was monitored by ¹³C NMR spectroscopy: the spectrum of isocyanate has a signal for the isonitrile carbon atom at δ 165, while in the spectrum of isoselenocyanate has a signal for the carbon atom of the isoselenocyanate group (-N=C=Se) at δ 132.

3-Phenyl-5-phenylmethylidene-2-selenoimidazolidin-4-one (3). Selenium (0.16 g, 2 mmol) was added to anhydrous EtOH (15 mL) with stirring under argon. The mixture was cooled to 0 °C, followed by addition of NaBH₄ (0.182 g, 4 mmol). After the reaction mixture became colorless, 3-phenyl-5-phenylmethylidene-2-(methylthio)imidazol-4-one (2) (0.28 g, 1 mmol) was added and this was refluxed for 40 min. Then, the reaction mixture was cooled to ~20 °C and acidified to pH 5, which was accompanied by formation of a brick-red precipitate. The reaction mixture was stirred for another 20 min to remove residual hydrogen selenide, which was absorbed in a washer filled with an alkaline solution and attached to the reaction flask. A precipitate formed was filtered off, the mother liquor was diluted with water (20 mL), the thus formed precipitate was filtered off on a glass filter and dried in air. Compound **3** (0.079 g, 25%) was obtained as an orange powder. M.p. 120 °C. ¹H NMR (DMSO-d₆), δ : 6.82 (s, 1 H, =CH); 7.50 (m, 8 H, Ph); 7.92 (s, 2 H, Ph); 13.14 (s, 1 H, NH). IR, v/cm⁻¹: 3164 (NH), 1714 (C=O), 1643 (C=N), 1590 (C=C).

3-Benzyl-2-selenoimidazolidin-4-one (4). An ethanolic solution of benzyl isoselenocyanate (3 g, 15.3 mmol) was added dropwise under argon to an equal volume of a solution of glycine (1.147 g, 15.3 mmol) and KOH (0.857 g, 15.3 mmol) in minimum water placed in a two-necked flask. The reaction mixture was acidified to pH 4, a light orange precipitate formed was filtered off, washed with water, and refluxed for 4 h in a mixture of HCl—EtOH (1 : 1). A precipitate formed on cooling was filtered off and dried in air. The yield was 1.7 g (45%). M.p. 202–204 °C. ¹H NMR (DMSO-d₆), δ : 4.12 (s, 2 H, CH₂); 4.93 (s, 2 H, CH₂); 7.35 (m, 5 H, Ph); 10.95 (br.s, 1 H, NH).

5-Phenyl(pyridyl)methylidene-2-selenoimidazolidin-4-ones 5a-d. Method A. Glacial acetic acid (8 mL) AcONa (2 equiv.), and 3-benzyl-2-selenoimidazolidin-4-one (4) (1 equiv.) were placed into a round-bottom flask, followed by a dropwise addition of an aldehyde (1 equiv.) with stirring. The reaction mixture was refluxed for 4 h, cooled to ~20 °C, and poured onto ice. A precipitate obtained was filtered off, sequentially washed with EtOH and diethyl ether, and dried in air.

Method B. 3-Benzyl-2-selenoimidazolidin-4-one (4) (1 equiv.) was dissolved in 2% ethanolic KOH (14 mL) with vigorous stirring, an aldehyde (1 equiv.) was added dropwise. The reaction mixture was stirred for 12 h. A precipitate was filtered off and dissolved in water. The solution, with vigorous stirring, was neutralized with dilute hydrochloric acid to pH = 7. A precipitate formed was filtered off and recrystallized from a mixture of EtOH-DMF (3 : 1).

The yields of compounds 5a-d and amounts of the starting reactants are given in the description of method *A*.

3-Benzyl-5-(phenylmethylidene)-2-selenoimidazolidin-4-one (5a). Compound 5a (0.2 g, 74%) was obtained from compound 4 (0.2 g, 0.8 mmol), AcONa (0.13 g, 0.16 mmol), and benzalde-hyde (0.081 mL, 0.8 mmol) as a brown powder. M.p. 231 °C. ¹H NMR (DMSO-d₆), δ : 5.13 (s, 2 H, CH₂); 6.79 (s, 1 H, =CH); 7.35 (m, 5 H, HPh); 7.45 (m, 3 H, HPh); 7.85 (m, 2 H, HPh); 13.03 (s, 1 H, NH). IR, v/cm⁻¹: 3250 (NH), 1740 (C=O), 1650 (C=N), 1600 (C=C). MS (MALDI), *m/z* (I_{rel} (%)): 342 [M]⁺ (100).

3-Benzyl-5-(2-pyridylmethylidene)-2-selenoimidazolidin-4-one (**5b**). Compound **5b** (0.616 g, 91%) was obtained from compound **4** (0.5 g, 2 mmol), AcONa (0.324 g, 4 mmol), and 2-pyr-idinecarbaldehyde (0.19 mL, 2 mmol) as a dark brown powder. M.p. 228–230 °C. ¹H NMR (DMSO-d₆), δ : 5.24 (s, 2 H, CH₂); 6.65 (s, 1 H, =CH); 7.45 (m, 7 H, HPy, HPh); 7.75 (m, 1 H, HPy); 8.69 (d, 1 H, HPy, J = 4.9 Hz); 11.9 (s, 1 H, NH). IR, v/cm⁻¹: 3330 (NH), 1717 (C=O), 1620 (C=N), 1584 (C=C). MS (MALDI), m/z (I_{rel} (%)): 343 [M]⁺ (100).

3-Benzyl-5-(3-pyridylmethylidene)-2-selenoimidazolidin-4-one (5c). Compound 5c (0.56 g, 83%) was obtained from compound 4 (0.5 g, 2 mmol), AcONa (0.324 g, 4 mmol), and 3-pyridinecarbaldehyde (0.1852 mL, 2 mmol) as a black powder. M.p. 190–194 °C. ¹H NMR (DMSO-d₆), 8: 5.12 (s, 2 H, CH₂); 6.80 (s, 1 H, =CH); 7.35 (m, 5 H, HPh); 7.48 (dd, 1 H, HPy, $J_1 = 4.7$ Hz, $J_2 = 8.1$ Hz); 8.28 (d, 1 H, HPy, J = 8.0 Hz); 8.61 (d, 1 H, HPy, J = 4.7 Hz); 8.94 (d, 1 H, HPy, J = 1.76 Hz); 13.15 (s, 1 H, NH). MS (MALDI), m/z (I_{rel} (%)): 343 [M]⁺ (100).

3-Benzyl-5-(4-pyridylmethylidene)-2-selenoimidazolidin-4-one (5d). Compound 5d (0.515 g, 77%) was obtained from compound 4 (0.5 g, 2 mmol), AcONa (0.324 g, 4 mmol), and 4-pyridinecarbaldehyde (0.186 mL, 0.002 mol) as a red powder. M.p. 242—244 °C. ¹H NMR (DMSO-d₆), δ : 5.15 (s, 2 H, CH₂); 6.74 (s, 1 H, =CH); 7.30 (m, 5 H, HPh); 7.78 (d, 2 H, HPy, J = 6.1 Hz); 8.64 (d, 2 H, HPy, J = 6.3 Hz); 13.20 (s, 1 H, NH). IR, v/cm⁻¹: 320 (NH), 1748 (C=O), 1625 (C=N), 1599 (C=C). MS (MALDI), m/z (I_{rel} (%)): 343 [M]⁺ (100).

5-Arylmethylidene-3-benzyl(phenyl)-2-(methylseleno)imidazol-4-ones 6 and 7a–c (general procedure). 5-Arylmethylidene-2selenoimidazolidin-4-one (1 equiv.) and KOH (1 equiv.) were added to a mixture of H_2O –EtOH (1 : 1, 10 mL). Methyl iodide (1 equiv.) was added dropwise after the complete dissolution of the reactants. A precipitate formed was filtered off and dried in air.

3-Phenyl-5-phenylmethylidene-2-(methylseleno)imidazol-4one (6). Compound **6** (0.207 g, 81%) was obtained from compound **3** (0.27 g, 0.75 mmol), KOH (0.042 g, 0.75 mmol), and methyl iodide (0.125 mL, 0.75 mmol) as a light yellow powder. M.p. 158–160 °C. ¹H NMR (CDCl₃), δ : 2.60 (s, 3 H, Me); 7.10 (s, 1 H, =CH); 7.50 (m, 8 H, Ph); 8.22 (d, 2 H, Ph, *J* = 7.0 Hz). MS (MALDI), *m/z* (I_{rel} (%)): 342 [M]⁺ (100).

3-Benzyl-5-(2-pyridylmethylidene)-2-(methylseleno)imidazol-4-one (7a). Compound **7a** (0.567 g, 88%) was obtained from compound **5b** (0.616 g, 2 mmol), KOH (0.1 g, 2 mmol), and methyl iodide (0.27 mL, 2 mmol) as a light brown powder. M.p. 160 °C. ¹H NMR (CDCl₃), δ : 2.05 (s, 3 H, Me); 4.45 (s, 2 H, CH₂); 6.65 (s, 1 H, =CH); 7.25 (m, 6 H, HPy, HPh); 7.86 (m, 1 H, HPy); 8.61 (m, 1 H, HPy); 9.05 (d, 1 H, HPy, *J* = 4.9 Hz). IR, v/cm⁻¹: 1717 (C=O), 1635 (C=N), 1562 (C=C). Found (%): C, 58.09; H, 3.94; N, 12.59. C₁₇H₁₅N₃OSe. Calculated (%): C, 57.30; H, 4.21; N, 11.80.

3-Benzyl-5-(3-pyridylmethylidene)-2-(methylseleno)imidazol-4-one (7b). Compound **7b** (0.459 g, 88%) was obtained from compound **5c** (0.5 g, 14.6 mmol), KOH (0.082 g, 14.6 mmol), and methyl iodide (0.22 mL, 14.6 mmol) as a light green powder. M.p. 152–154 °C. ¹H NMR (CDCl₃), &: 2.59 (s, 3 H, Me); 4.80 (s, 2 H, CH₂); 6.95 (s, 1 H, =CH); 7.35 (m, 5 H, HPh); 7.50 (dd, 1 H, HPy, $J_1 = 5.2$ Hz, $J_2 = 8.1$ Hz); 8.59 (d, 1 H, HPy, J = 8.1 Hz); 8.71 (d, 1 H, HPy, J = 5.2 Hz); 9.25 (d, 1 H, HPy, J = 1.8 Hz). IR, v/cm⁻¹: 1708 (C=O), 1634 (C=N), 1582 (C=C). MS (MALDI), m/z (I_{rel} (%)): 357 [M]⁺ (100).

3-Benzyl-5-(4-pyridylmethylidene)-2-(methylseleno)imidazol-4-one (7c). Compound **7c** (0.439 g, 84%) was obtained from compound **5d** (0.5 g, 14.6 mmol), KOH (0.082 g, 14.6 mmol), and methyl iodide (0.22 mL, 14.6 mmol) as a black powder. ¹H NMR (CDCl₃), δ : 2.60 (s, 3 H, Me); 4.80 (s, 2 H, CH₂); 6.90 (s, 1 H, =CH); 7.35 (m, 5 H, HPh); 8.12 (d, 2 H, HPy, J = 6.1 Hz); 8.65 (d, 2 H, HPy, J = 6.1 Hz). IR, v/cm⁻¹: 1717 (C=O), 1637 (C=N), 1562 (C=C). MS (MALDI), m/z (I_{rel} (%)): 357 [M]⁺ (100).

2,2[']-(Alkane- α , ω -diyldiselenyldiyl)bis[3-benzyl-5-(2-pyridylmethylidene)-3,5-dihydro-4*H*-imidazol-4-ones] 8a,b (general procedure). Dibromoalkane (0.028 g, 0.15 mmol) was added dropwise into a flat-bottom flask containing DMF (20 mL), compound **7a** (0.1 g, 0.3 mmol), and K_2CO_3 (0.06 g, 0.4 mol). The reaction mixture was stirred for 8 h at ~20 °C, followed by addition of water (50 mL). A precipitate formed was filtered off and dried in air.

2,2'-(Ethane-1,2-diyldiselenyldiyl)bis[3-benzyl-5-(2-pyridylmethylidene)-3,5-dihydro-4*H***-imidazol-4-one] (8a). The yield was 0.093 g (90%), a violet powder. M.p. 190–192 °C. ¹H NMR (CDCl₃), \delta: 3.89 (s, 4 H, CH₂); 4.82 (s, 4 H, CH₂); 7.12 (s, 2 H, =CH); 7.20 (m, 2 H, HPy); 7.35 (m, 12 H, HPy, HPh); 7.52 (m, 2 H, HPy); 8.65 (d, 2 H, HPy,** *J* **= 8.0 Hz). IR, v/cm⁻¹: 1710 (C=O), 1633 (C=N), 1581 (C=C). Found (%): C, 57.83; H, 4.17; N, 12.15. C₃₄H₂₈N₆O₂Se₂. Calculated (%): C, 57.46; H, 3.94; N, 11.83.**

2,2'-(**Propane-1,3-diyldiselenyldiyl)bis**[**3-benzyl-5-(2-pyr-idylmethylidene)-3,5-dihydro-4***H*-imidazol-4-one] (**8b**). The yield was 0.057 g (54%), a light beige powder. M.p. 150 °C. ¹H NMR (CDCl₃), &: 2.78 (quint, 2 H, CH₂, J = 6.9 Hz); 3.74 (t, 4 H, CH₂, J = 6.9 Hz); 5.05 (s, 4 H, CH₂); 7.42 (s, 2 H, =CH); 7.55 (m, 12 H, HPy, HPh); 7.84 (m, 2 H, HPy); 8.92 (d, 2 H, HPy, J = 4.82 Hz); 8.98 (d, 2 H, HPy, J = 8.0 Hz). IR, v/cm⁻¹: 1716 (C=O), 1637 (C=N), 1580 (C=C). Found (%): C, 57.72; H, 4.20; N, 11.35. C₃₅H₃₀N₆O₂Se₂. Calculated (%): C, 58.01; H, 4.14; N, 11.60.

Bis(3-phenyl-5-phenylmethylidene-2-selenoimidazolidin-4-one)dicopper(1) (9). A solution of $CuCl_2 \cdot 2H_2O(0.015 \text{ g}, 0.09 \text{ mmol})$ in EtOH (5 mL) was added to a solution of compound **3** (0.061 g, 0.18 mmol) and KOH (0.01 g, 0.18 mmol) in EtOH (5 mL) and the mixture was stirred for 2 h. A precipitate formed was filtered off, washed with water and EtOH and dried in air to obtain compound **9** (0.052 g, 88%) as an orange powder. M.p. 260 °C. IR, v/cm⁻¹: 1729 (C=O), 1634 (C=N), 1597 (C=C). EAS, λ /nm (ϵ /L mol⁻¹ cm⁻¹): 427 (800). Found (%): C, 50.33; H, 2.89; N, 7.43. C₃₂H₂₂Cu₂N₄O₂Se₂. Calculated (%): C, 49.29; H, 2.82; N, 7.19.

Bis(3-phenyl-5-phenylmethylidene-2-selenoimidazolidin-4-one)copper(II) (10). Potassium hydroxide (0.017 g, 0.3 mmol) was added to a solution of compound **3** (0.1 g, 0.3 mmol) in MeCN (5 mL). After KOH dissolved, a solution of CuCl₂ · 2H₂O (0.026 g, 0.15 mmol) in MeCN (5 mL) was added and the reaction mixture was stirred for 2 h. A precipitate formed was filtered off and dried in air to obtain compound **10** (0.1 g, 79%) as a light brown powder. M.p. 254 °C. IR, v/cm⁻¹: 1728 (C=O), 1636 (C=N), 1597 (C=C). MS (MALDI), m/z (I_{rel} (%)): 717 [M]⁺ (100).

[3-Benzyl-5-(4-pyridylmethylidene)-2-selenoimidazolidin-4one]copper(1) (11). A solution of $Cu^{I}(MeCN)_{4}ClO_{4}$ (0.06 g, 0.18 mmol) in MeCN (5 mL) was added to a solution of compound 5d (0.125 g, 0.37 mmol) and KOH (0.02 g, 0.37 mmol) in EtOH (5 mL). The reaction mixture was refluxed until a precipitate was formed. The precipitate was filtered off and dried in air to obtain compound 11 (0.057 g, 41%) as a dark brown powder. M.p. 296–300 °C. IR, v/cm⁻¹: 3050–3650 (OH), 1727 (C=O), 1637 (C=N), 1588 (C=C). EAS, λ /nm (ε /L mol⁻¹ cm⁻¹): 615.5 (670). Found (%): C, 46.83; H, 2.37; N, 9.81. C₃₂H₂₄Cu₂N₆O₂Se₂·H₂O. Calculated (%): C, 46.36; H, 3.14; N, 10.15.

Reaction of 3-benzyl-5-pyridylmethylidene-2-selenoimidazolidin-4-ones 5b-d with $CuCl_2 \cdot 2H_2O$, $CoCl_2 \cdot 6H_2O$, and $NiCl_2 \cdot 6H_2O$ (general procedure). Potassium hydroxide (1 equiv.) was added to a solution of 3-benzyl-5-pyridylmethylene-2-selenoimidazolidin-4-one 5b-d in EtOH. After KOH dissolved, a metal salt (0.5 equiv.) in EtOH was added to the reaction mixture. A precipitate formed was filtered off and dried in air.

Bis[3-benzyl-5-(2-pyridylmethylidene)-2-selenoimidazolidin-4one]cobalt(II) (12a). Compound 12a (0.091 g, 43%) was obtained from compound 5b (0.1 g, 0.3 mmol), KOH (0.017 g, 0.3 mmol), and CoCl₂•6H₂O (0.03 g, 0.5 mmol) as a brown powder. M.p. 305 °C. IR, v/cm⁻¹: 1720 (C=O), 1640 (C=N), 1600 (C=C). EAS, λ /nm (ε/L mol⁻¹ cm⁻¹): 711 (350), 653 (400). MS (MALDI), *m/z* (*I*_{rel} (%)): 743 [M]⁺ (100).

Bis[3-benzyl-5-(2-pyridylmethylidene)-2-selenoimidazolidin-4one]nickel(11) (12b). Compound 12b (0.09 g, 43%) was obtained from compound 5b (0.1 g, 0.3 mmol), KOH (0.017 g, 0.3 mmol), and NiCl₂•6H₂O (0.03 g, 0.5 mmol) as a red powder. M.p. 292 °C. IR, ν/cm^{-1} : 3050–3650 (OH), 1721 (C=O), 1637 (C=N), 1597 (C=C). Found (%): C, 51.25; H, 3.47; N, 11.08. C₃₂H₂₄N₆NiO₂Se₂•H₂O. Calculated (%): C, 50.59; H, 3.42; N, 11.06.

Bis[3-benzyl-5-(2-pyridylmethylidene)-2-selenoimidazolidin-4-one]copper(II) (12c). Compound **12c** (0.078 g, 37%) was obtained from compound **5b** (0.1 g, 0.3 mmol), KOH (0.017 g, 0.3 mmol), and CuCl₂·2H₂O (0.03 g, 0.5 mmol) as a brown powder. M.p. 282 °C. IR, v/cm⁻¹: 3000–3600 (OH), 1714 (C=O), 1637 (C=N), 1587 (C=C). MS (MALDI), m/z (I_{rel} (%)): 747 [M]⁺ (100).

Bis[3-benzyl-5- (4-pyridylmethylidene)-2-selenoimidazolidin-4one]cobalt(π) (12d). Compound 12d (0.074 g, 54%) was obtained from compound 5d (0.125 g, 0.37 mmol), KOH (0.02 g, 0.37 mmol), and CoCl₂•6H₂O (0.043 g, 0.18 mmol) as a dark brown powder. M.p. >350 °C. IR, v/cm⁻¹: 1717 (C=O), 1630 (C=N), 1606 (C=C). EAS, λ /nm (ε/L mol⁻¹ cm⁻¹): 435.5 (4800), 595.5 (470), 621 (430), 660 (370). MS, *m*/*z*: 744 [M + H]⁺. Found (%): C, 52.07; H, 3.63; N, 10.76. C₃₂H₂₄CoN₆O₂Se₂. Calculated (%): C, 51.82; H, 3.24; N, 11.34.

Bis[3-benzyl-5-(4-pyridylmethylidene)-2-selenoimidazolidin-4one]copper(II) (12e). Compound 12e (0.128 g, 93%) was obtained from compound 5d (0.125 g, 0.37 mmol), KOH (0.02 g, 0.37 mmol), and CuCl₂·2H₂O (0.031 g, 0.18 mmol) as a brown powder. M.p. 284–286 °C. IR, ν/cm^{-1} : 1723 (C=O), 1643 (C=N), 1588 (C=C). EAS, λ/nm (ε/L mol⁻¹ cm⁻¹): 437.5 (1400). Found (%): C, 52.36; H, 3.52; N, 11.16. C₃₂H₂₄CuN₆O₂Se₂. Calculated (%): C, 51.47; H, 3.22; N, 11.26.

Reaction of 3-benzyl-2-(methylseleno)-5-pyridylmethylideneimidazol-4-ones 7a—c with CuCl₂, CoCl₂ and NiCl₂ (general procedure). A solution of a metal salt (0.5 equiv.) in EtOH (5 mL) was added to a solution of 3-benzyl-5-pyridylmethylene-2-(methylseleno)imidazol-4-one 7a—c (1 equiv.) in EtOH (5 mL). The reaction mixture was refluxed until a precipitate was formed. The precipitate was filtered off, washed with water and EtOH, and dried in air.

Bis[3-benzyl-5-(2-pyridylmethylidene)-2-(methylseleno)imidazol-4-one]cobalt(II) dichloride (13a). Compound **13a** (0.052 g, 48%) was obtained from compound **7a** (0.14 g, 0.4 mmol) and CoCl₂ (0.025 g, 0.196 mmol) as a brown powder. M.p. 210 °C. IR, v/cm⁻¹: 1717 (C=O), 1664 (C=N), 1586 (C=C). Found (%): C, 49.01; H, 3.48; N, 10.14. $C_{34}H_{30}Cl_2CoN_6O_2Se_2$. Calculated (%): C, 48.46; H, 3.56; N, 9.98.

Bis[3-benzyl-5-(2-pyridylmethylidene)-2-(methylseleno)imidazol-4-one]copper(1) dichloride (13b). Compound 13b (0.06 g, 56%) was obtained from compound 7a (0.14 g, 0.4 mmol) and CuCl₂ (0.026 g, 0.2 mmol) as a light brown powder. M.p. 182 °C. IR, v/cm⁻¹: 3300–3600 (OH), 1717 (C=O), 1664 (C=N), 1635 (C=C). Found (%): C, 45.97; H, 3.24; N, 9.47. $C_{34}H_{30}Cl_2CuN_6O_2Se_2\cdot 2H_2O$. Calculated (%): C, 46.18; H, 3.88; N, 9.51.

Bis[3-benzyl-5-(3-pyridylmethylidene)-2-(methylseleno)imidazol-4-one]cobalt(II) dichloride (13c). Compound **13c** (0.079 g, 73%) was obtained from compound **7b** (0.11 g, 0.3 mmol) and CoCl₂ (0.019 g, 0.15 mmol) as a brown powder. M.p. 256 °C. IR, v/cm⁻¹: 3300–3600 (OH), 1720 (C=O), 1631 (C=N), 1600 (C=C). Found (%): C, 46.16; H, 3.81; N, 9.36. C₃₄H₃₀Cl₂CoN₆O₂Se₂·2H₂O. Calculated (%): C, 46.49; H, 3.90; N, 9.57.

Bis[3-benzyl-5-(3-pyridylmethylidene)-2-(methylseleno)imidazol-4-one]copper(II) dichloride (13d). Compound **13d** (0.079 g, 73%) was obtained from compound **7b** (0.11 g, 0.3 mmol) and CuCl₂ (0.021 g, 0.15 mmol) as a green powder. M.p. 250 °C. IR, v/cm⁻¹: 3300–3600 (OH), 1720 (C=O), 1643 (C=N), 1594 (C=C). Found (%): C, 46.21; H, 3.17; N, 9.54. $C_{34}H_{30}Cl_2CuN_6O_2Se_2 \cdot 2H_2O.$ Calculated (%): C, 46.18; H, 3.88; N, 9.51.

Bis[3-benzyl-5-(3-pyridylmethylidene)-2-(methylseleno)imidazol-4-one]nickel(n) dichloride (13e). Complex compound 13e (0.057 g, 53%) was obtained from compound 7b (0.11 g, 0.3 mmol) and NiCl₂ (0.019 g, 0.15 mmol) as a light green powder. M.p. 280 °C. IR, v/cm⁻¹: 3100–3600 (OH), 1714 (C=O), 1643 (C=N), 1597 (C=C). EAS, λ /nm (ε/L mol⁻¹ cm⁻¹): 490.5 (1200), 464 (1250). Found (%): C, 46.01; H, 3.28; N, 9.14. C₃₄H₃₀Cl₂N₆NiO₂Se₂·2H₂O. Calculated (%): C, 46.47; H, 3.87; N, 9.57.

Bis[3-benzyl-5-(4-pyridylmethylidene)-2-(methylseleno)imidazol-4-one]copper(II) dichloride (13f). Compound 13f (0.068 g, 69%) was obtained from compound 7c (0.109 g, 0.3 mmol) and CuCl₂ (0.021 g, 0.15 mmol) as a black powder. M.p. 204 °C. IR, v/cm⁻¹: 3200–3650 (OH), 1720 (C=O), 1634 (C=N), 1609 (C=C). Found (%): C, 45.66; H, 4.17; N, 9.73. C₃₄H₃₀Cl₂CuN₆O₂Se₂·2H₂O. Calculated (%): C, 46.18; H, 3.88; N, 9.51.

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