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Original research paper

NICKEL(II) COMPLEXES WITH 'NON INNOCENT' LIGANDS – CYCLOAMINOMETHYL DERIVATIVES OF 1,2-DIHYDROXYBENZENE: SOD-LIKE AND ANTIMICROBIAL ACTIVITY*

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Abstract. *The process of Ni(II) ion complexation with cycloaminomethyl derivatives of 1,2-dihydroxybenzene in a water-ethanol medium was investigated. It was found potentiometrically that the complexes with the ratio M : L = 1 : 2 were formed in the solution, their overall stability constants were equal to $7{,}9 \cdot 10^{14}$–$1{,}6 \cdot 10^{15}$. The Ni(II) complexes synthesized were shown to be amorphous, neutral, and thermally stable up to 150 °C. Their coordination polyhedra have the composition $[NiO_2N_2]$ and planar square geometry. It was shown that the Ni(II) complexes demonstrate a moderate or high level of antimicrobial activity against bacteria and fungi strains tested, as well as the ability to neutralize superoxide.*

Key words: *Ni(II) complexes, catechol derivatives, SOD-like activity, antimicrobial activity*

1. INTRODUCTION

In an earlier investigation [1], we have found that antimicrobial activity of 1,2-dihydroxybenzene derivatives can be adjusted by introducing substituents into benzene ring and by complexation with metal ions. These improvements are aimed at changing hydrophilic-lipophilic balance, acid-base and redox properties of the molecules, as well as reducing toxicity of phenolic derivatives [1]. Besides, it is known that some sterically hindered 1,2-dihydroxybenzene derivatives and their metal complexes possess reducing properties that correlate with their antimicrobial activity and ability to reduce cytochrome *c* (Cyt *c*), one of the key proteins in the microbial respiratory chain and a possible target for action of antimicrobial agents [1].

It is known, that complexation reactions of 1,2-dihydroxybenzene derivatives with metal ions underlie many analytical identification methods for these compounds within plants, biological media and drugs [2]. Moreover, metal complexes are often more biologically active (antioxidant, antiradical, antimicrobial and antiviral activities) than primary ligands [1, 2]. One of the ways to broaden the biological activity spectrum of 1,2-dihydroxybenzene derivatives is the synthesis of their Ni(II) complexes. Ni(II) deserves attention as a complexing agent for synthesizing biologically active complexes, as it is considered biometal and cofactor for important enzymes, such as hydrolases (urease), hydrogenases, CO-dehydrogenase, methyl-coenzyme M reductase, superoxide dismutase, etc. [3]. Besides, Ni(II) compositions can inhibit microbial growth. The explanation for their antimicrobial activity is that Ni(II) ions can change the morphology of the cytoplasmic membrane, increase its permeability and upset the matter transport. It was shown that Ni(II) ions can interact with biomolecules containing sulfhydryl and phosphate groups, for example DNA, disturbing its replication, or with different enzymes, inducing their deactivation [4]. There is data on heavy metal ions participation in electron transport chain inactivation and reactive oxygen species generation resulting in microbial death [5]. Active oxygen forms (superoxide, hydrogen peroxide, singlet oxygen and hydroxyl radical) which are generated in phagolisosome and are involved in bactericide mechanisms can produce an antimicrobial effect. But some microorganisms, being the active producers of extracellular superoxide themselves, are able to prevent their action [6]. Superoxide dismutases (SOD) are oxidoreductases catalyzing the transformation of superoxides (one of the main factors of oxidative stress) into hydrogen peroxide and oxygen [7]. SOD are demanded as pharmaceuticals [8], but the use of the native SOD in medicine is limited by their thermolability, low ability to penetrate cells and others [2]. Many of the limiting factors could be overcome by

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developing synthetic, low-molecular-weight mimics of the SOD enzyme and by using a direct method to measure the SOD-like activity of these complexes [9]. It was found that Ni-containing low-molecular analogues of Ni-SOD can interfere in the inactivation mechanism of active oxygen forms of fungi and some bacteria and exhibit antimicrobial activity through competition with the native SOD [10]. Thus there are facts suggesting that redox-active metal complexes with antioxidants as ligands possess antimicrobial activity together with the SOD-like one.

2. Materials and methods

For the synthesis of Ni(II) complexes, 1,2-dihydroxybenzene derivatives were chosen, namely 5-*tert*-butyl-3-(pyrrolidine-1-ilmethyl)-1,2-dihydroxybenzene (HL^{I}), 5-*tert*-butyl-3-(piperidine-1-ilmethyl)-1,2-dihydroxybenzene (HL^{II}), 5-*tert*-butyl-3-(azenone-1-ilmethyl)-1,2-dihydroxybenzene (HL^{III}), 5-*tert*-butyl-3-(morpholine-1-ilmethyl)-1,2-dihydroxybenzene (HL^{IV}), and 5-*tert*-butyl-3-(methylpiperazine-1-ilmethyl)-1,2-dihydroxybenzene (HL^{V}). The complexation of Ni(II) ions with these ligands was investigated by the method of potentiometric titration in water-ethanol medium, using Microprocessor laboratory ion meter I-160MP, under inert atmosphere (argon), the ionic strength being constant. The stability constants of the complexes in solution were calculated by the means of a general program MathCad.

The Ni(II) complexes were synthesized according to the following method: a saturated solution of nickel(II) acetate (0.1-0.2 M) in methanol was gradually added to a saturated ligand (compounds HL^{I}–HL^{V}) solution (0.05–0.1 M) in methanol. The mixture was dried under vacuum for 0.5h.

The X-ray diffraction analysis of the compounds was carried out using DRON-2 (CuK_{α}-emission). Infrared spectra of solids were recorded at room temperature by FT-IR «Nicolet 380» spectrophotometer of the firm «Thermo Electron Corporation», using «Smart Performer», in the wavelength range 4000–400 cm^{-1}. Thermal analysis was performed with a device NETZSCH STA 449 C. TG/DTA measurements were run in nitrogen between 30 and 600°C (10 °C·min^{-1}). Elemental analyses were carried out with a Vario EL (CHNS mode) instrument. Nickel was determined using an atomic emission spectrometer with an inductively coupled plasma excitation source (Spectroflame Modula). UV-Vis spectra of solutions of the ligands and their Ni(II) complexes in acetonitrile ($1 \cdot 10^{-4}$ mol·l^{-1}) were registered with SOLAR PB2201 spectrophotometer in the wavelength range 200–1000 nm using a standard (1 cm) cell. ESR spectra of polycrystalline samples were measured with ERS-220 X-band spectrometer (9.45 GHz) at room temperature and at 77 K, using 100-kHz field modulation; *g*-factors were quoted with reference to the standard marker DPPH (g=2.0036). The molar conductance of 10^{-3} M solutions of the Ni(II) complexes in acetonitrile was measured at 20°C using a TESLA BMS91 conductometer (cell constant 1.0). The lipophilicity test was made by determining the *n*-octanol/water partition coefficient (P_{ow}) [11].

The antimicrobial activity of the compounds was determined by the broth dilution method [12]. To investigate the SOD-like activity of the compounds being discussed, the procedure of generating superoxide with the use of alkaline DMSO was selected, as it is well reproducible, economical and simple to perform. It was confirmed by ESR spectroscopy that alkaline DMSO contains superoxide: the corresponding signal ($g_{\parallel}$=2.087 and $g_{\perp}$=2.006) is present in ESR spectra at 77 K, as described elsewhere [13]. 0.1 ml of the test compounds solutions in acetonitrile were added to 0,9 ml of 0,02 mol·l^{-1} phosphate buffer (pH 8.60), containing 10^{-4} mol·l^{-1} EDTA and $5 \cdot 10^{-4}$ mol·l^{-1} nitroblue tetrazolium (NBT). 1 ml of the alkaline DMSO (DMSO, containing 1 % water and $5 \cdot 10^{-3}$ mol·l^{-1} sodium hydroxide) was added to the mixture under stirring. After five-minute exposure, the optical density of the blue formazan formed from the NBT was measured at 550 nm. The experiment was carried out at room temperature (18–20 °C). As a reference solution, a similarly prepared mixture containing no sodium hydroxide was used. The control experiment was carried out using 0.1 ml of acetonitrile instead of the test compounds solutions.

3. Results and discussion

According to the potentiometric titration data, Ni(II) ions form complexes with HL^{I}–HL^{V} with molar ratio M(II):L=1:2 and stability constants $7.9 \cdot 10^{14}$–$1.6 \cdot 10^{15}$. The X-ray diffraction data suggest the amorphous structure of the solid residues. Based on the elemental analysis data (Table 1), the general composition of the complexes is NiL_2. Thermal analysis in a nitrogen flow, with the identification of the final products by X-ray powder diffraction, shows all the Ni(II) complexes to be unsolvated, their DTA curves lacking any endothermic peaks in the area 60–120°C. Peaks in the range 210–700°C may be assigned to the ligand destruction and following decomposition of the complexes. The final product of decomposition of the complexes is NiO [14].

The Ni(II) complexes are practically insoluble in water, moderately soluble in acetonitrile, soluble in ethanol and acetone, highly soluble in dimethyl sulfoxide and tetrahydrofuran. The values of the molar conductivity in acetonitrile (7.7–19.8 Ω^{-1} cm^2 mol^{-1}) for all these complexes indicate their being non-electrolytes [15]. Partition coefficients of Ni(II) complexes with the ligands HL^{I}–HL^{V} were determined in the octanol-1–water system. It is revealed that logarithms of the partition coefficients ($\log P_{ow}$) of the complexes (2.1–2.8) are bigger than those of the ligands (0.9–1.2), pointing to the lower lipophilicity and transmembrane capacity of the latter.

The coordination cores of the Ni(II) complexes were characterized on the basis of the results of their spectroscopic investigation. The coordination behavior of the ligands HL^{I}–HL^{V} in complexes was determined using IR spectroscopy.

In the IR spectra of the ligands, there are some bands in the range 3250–3410 cm^{-1}, which belong to hydroxyl groups' stretching vibrations. In the spectra of corresponding complexes these bands are shifted. This

fact supports the assumption that one of the phenolic hydroxyl groups is involved in complexation. A change in the vibration frequency $\nu(C=C)_{arom}$ of the aromatic ring (1490-1550 cm^{-1}) in Ni(II) complexes spectra confirms the coordination bond formation between the metal ions and ligands [16]. Tertiary amino groups of the ligands also participate in complexation, as their IR spectral bands (1000–1150 cm^{-1}) are red-shifted. The coordination behaviour of oxygen and nitrogen atoms in ligands with metal ions is also proved by the appearance of new bands at 600–500 cm^{-1}, which may be assigned to the stretching vibrations of the Ni–O and Ni–N bonds [17] (Table 2).

In the UV-Vis spectra of the $Ni(L^{I})_2$ – $Ni(L^{V})_2$ complexes, there is a small bathochromic shift (5–10 nm) of the internal ligand absorption (ILA) bands (225–300 nm) because of the conformation changing on complexation [18]. This shift does not occur in the ligand absorption spectra (Table 3).

Table 1. Elemental analysis data of Ni(II) complexes with HLI–HLV

Complex	Brutto formula	Elemental content (calculated / found, %)			
		C	H	N	Ni
$Ni(L^{I})_2$	$C_{30}H_{44}N_2O_4Ni$	65.53/64.88	8.07/7.99	4.99/5.04	10.67/10.57
$Ni(L^{II})_2$	$C_{32}H_{48}N_2O_4Ni$	66.54/65.88	8.21/8.29	4.75/4.8	10.16/10.06
$Ni(L^{III})_2$	$C_{34}H_{52}N_2O_4Ni$	67.45/66.78	8.49/8.57	4.54/4.58	9.50/9.60
$Ni(L^{IV})_2$	$C_{30}H_{44}N_2O_6Ni$	60.73/61.35	7.47/7.55	4.72/4.77	9.89/9.99
$Ni(L^{V})_2$	$C_{32}H_{50}N_4O_4Ni$	62.03/62.65	8.30/8.21	9.22/9.13	9.47/9.57

Table 2. Prominent IR absorption bands (ν, cm^{-1}) of the compounds HL^{I}–HL^{V} and their Ni(II) complexes

Compound	ν(O–H)	$\nu(C=C)_{aro}$	ν(C–O)	ν(C–N)	ν(Ni–O, Ni–N)
HL^{I}	3409s	1596w, 1490s	1393m, 1366m, 1320m, 1301m, 1190s	1120m, 1102m, 1033w	–
$Ni(L^{I})_2$	3500m	1557s, 1479m	1361w, 1274m, 1240m	1046m, 1016m	597w, 536w, 529w, 511m, 500w
HL^{II}	3403s	1588w, 1490s	1362m, 1334m, 1326m, 1307s, 1287m, 1198s, 1188s, 1152m	1098s, 1029w	–
$Ni(L^{II})_2$	3500m	1556s, 1484m	1361m, 1282m, 1245m, 1153m	1102w, 1082w, 1036s	577w, 566w, 553w, 534w, 525w
HL^{III}	3402m	1606w, 1489s	1362m, 1307m, 1224m, 1188s	1103m, 1063m	–
$Ni(L^{III})_2$	3500m	1557s, 1482m	1361m, 1318m, 1277m, 1242m, 1209m	1083m, 1013m	568m, 537w, 516m, 503w
HL^{IV}	3375s	1595w, 1493s	1394m, 1327m, 1299s, 1273s, 1249m, 1228m, 1192m	1127m, 1107s, 1071s, 1031m, 1003m	–
$Ni(L^{IV})_2$	3500m	1564s, 1557s	1361m, 1271m, 1225m, 1202m, 1146s	1070m, 1034m, 1003m	599w, 570w, 549w, 523m, 504m
HL^{V}	3250m	1594m, 1497m	1365m, 1348m, 1335m, 1326m, 1299m, 1257s, 1233s, 1216m, 1168m	1146m, 1136m, 1111m, 1036w, 1003s	–
$Ni(L^{V})_2$	3500m	1557s, 1484m	1361s, 1281s, 1200m, 1161m, 1146m	1119w, 1005m	536w, 528w, 515w, 508m, 501m

Table 3. Prominent UV-Vis absorption bands of the compounds HL^{I}–HL^{V} and their Ni(II) complexes

Compound	Chromophore	Absorption bands, λ_{max}, nm	lg ε_{max}	Polyhedron shape
HL^{I}–HL^{V}	–	220–230 (ILA)	4.1–4.2	–
		270–300 (ILA)	3.8–3.9	
$Ni(L^{I})_2$–$Ni(L^{V})_2$	$[NiO_2N_2]$	225–230 (ILA)	4.2–4.5	Planar square
		280–300 (ILA)	3.7–3.9	
		300–310sh ($N(\sigma)\rightarrow Ni(II)$ LMCT)	3.6–3.7	
		320–330sh ($O_{phen}\rightarrow Ni(II)$ LMCT)	3.1–3.4	
		430–470 (*d–d*)	2.3–2.5	

Shoulders in the ranges 300–310 nm and 320–310 nm relate to the charge transfer transition involving orbitals of the ligand and the metal (LMCT): respectively $N(\sigma)\rightarrow Ni(II)$ and $O_{phen}\rightarrow Ni(II)$. In the range of 430–470 nm, the spectra include the crystal field transition (*d-d*) bands with low intensity (ε = 2.3–2.5). These bands present in the spectra of the Ni(II) complexes may be indicative of the planar square shape of their chromophore $[NiO_2N_2]$ [18].

According to the value of effective magnetic moment μ_{eff}=0, Ni(II) complexes with the strong-field ligands are diamagnetic. Based on the spectroscopic features of the complexes and some previous results [19], the planar square polyhedra of low-spin

complexes $Ni(L^{I})_2$–$Ni(L^{V})_2$ are found to be formed by Ni(II) ions and the ligands in the monoanionic form. The ESR spectra of these compounds displayed no singlet signals (g=2.004–2.006, ΔH<7) specific for phenoxyl radicals [20], which indicates that the ligands HL^{I}–HL^{V} do not undergo oxidation in the coordinated state upon crystallization. The plausible coordination mode of the Ni(II) complexes with HL^{I}–HL^{V} is presented in Fig.1.

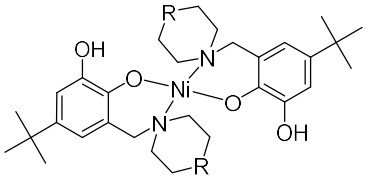

Figure 1. The plausible coordination mode of the Ni(II) complexes with HL^{I}–HL^{V}

According to the results of microbiological investigation, Ni(II) complexes have a moderate antibacterial activity *in vitro* (*MIC* = 0.082–0.171 μmol ml^{-1}) against the Gram-positive bacteria *Staphylococcus aureus*, mould *Aspergillus niger* and yeast *Candida albicans*. The Gram-negative bacteria (*Pseudomonas aeruginosa*) are less sensitive to these compounds (MIC>0.323 μmol ml^{-1}). Much more hydrophilic ligands have lower antibacterial activity (MIC ≥ 0.718 μmol ml^{-1}) compared with the corresponding Ni(II) complexes.

Using the method of superoxide generation from alkaline DMSO solution [13], the superoxide dismutase activity (IC_{50}, Table 4) of the complexes synthesized was determined, which was equal to 1.6-6.2 μmol·l^{-1}. The scheme of the reaction of HL^{I}–HL^{V} with superoxide is shown below (Fig. 2). Since one of the main requirements for synthetic SOD-mimics is their high ability to penetrate cellular walls and membranes, their lipophilicity should be also taken into account when searching for and developing these bioactive compounds. Ni(II) complexes were found to be more lipophilic in comparison to the corresponding ligands.

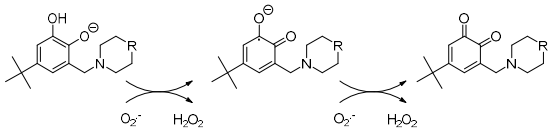

Figure 2. The scheme of the reaction of HL^{I}–HL^{V} with superoxide

Table 4. SOD-like activity of the compounds HL^{I}–HL^{V} and their Ni(II) complexes

Compound	IC_{50}, μmol·l^{-1}	Compound	IC_{50}, μmol·l^{-1}
HL^{I}	1.1	$Ni(L^{I})_2$	6.2
HL^{II}	1.2	$Ni(L^{II})_2$	1.6
HL^{III}	2.4	$Ni(L^{III})_2$	4.1
HL^{IV}	2.2	$Ni(L^{IV})_2$	4.1
HL^{V}	1.8	$Ni(L^{V})_2$	3.7

Thus the high SOD-like activity of the lipophilic Ni(II) complexes with the compounds HL^{I}–HL^{V} allows one to consider them as promising hit-compounds to produce new effective antioxidants – traps for superoxide.

4. Conclusions

The results of the study show that Ni(II) chelation plays an important role in the antibacterial and SOD-like activity of the novel redox-active 1,2-dihydroxybenzene derivatives. Their Ni(II) complexes were found to have a low inhibition activity against the Gram-negative bacteria, while the Gram-positive ones, yeasts and moulds are more sensitive to these compounds *in vitro*. This level of antimicrobial activity was achieved by structural modification of the ligands and complexation with metal ions, which purposefully change the hydrophilic-lipophilic balance, acid-base and redox properties of these substances. All the Ni(II) complexes are more lipophilic and more active against the test microorganisms than the ligands forming them. Both the 1,2-dihydroxybenzene derivatives and their Ni(II) complexes exhibited the SOD-like activity. The correlation between the antimicrobial activity of these compounds and their reducing ability deserves particular attention since they possess both antioxidant and antimicrobial activities. In this connection, the Ni(II) complexes with 1,2-dihydroxybenzene derivatives can be effective against poly-resistant bacterial and fungal strains, as they can act on many biological targets simultaneously.

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