The complex of zinc with *N*-(5,6-dihydro-4*H*-1,3-thiazine-2-yl)benzamide

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A complex of zinc with *N*-(5,6-dihydro-4*H*-1,3-thiazin-2-yl)benzamide (L) ligand, $LZnCl_2$, was synthesized for subsequent medical trials. The molar extinction coefficients were determined for LHBr solutions in water and physiological saline, and for $LZnCl_2$ ethanol solution. The ligand stability in various solvents was evaluated and the value of its protonation constant was found for the physiological saline solution, $\log K = 5.3 \pm 0.2$. The impossibility of determination of the complex stability constant by the potentiometric titration method was demonstrated. The complex exhibited an insufficient stability in aqueous and physiological saline solutions, but was stable as the solution in alcohol. There was no sorption observed upon the treatment of ligand with hydroxyapatite nanoparticles, which could be a potential carrier for the therapeutic form of $LZnCl_2$, providing additional degrees of freedom for the interaction of ligand with cell membranes and a prolonged action of zinc ions.

Key words: dihydrotiazine derivatives, zinc complex, stability, protonation constant, sorption on hydroxyapatite.

Simple and complex zinc salts have been practically used in medicine for a long time and with different purposes. The zinc administration is known[1] for the immune activity activation by regulating T-lymphocytes, NK-cells, and Interleukin-2 (IL-2), and increases antiviral activity. The protective properties of zinc in tumor processes have also been extensively studied, including children with leukemia in order to improve the quality of life during a chemotherapy. Even a trivial $ZnCl_2$ salt at high concentrations[2] can inhibit the cell migration and proliferation, for example, of HLE B-3 (human lens epithelial cell line) cells. Recently, salts and complexes of zinc and other metal ions with salicylic acid (HSal) and aspirin became especially popular due to their possession of various, including antitumor, properties.[3—8]

Zinc complexes with various organic ligands have been already synthesized and their biological activity has been evaluated. For example, the $[Zn(3,5\text{-}Pr^{i}Sal)_2(H_2O)_2]$ complex demonstrated[9] anticonvulsant properties, while $[Zn(Sal)_2(phen)]$, $[Zn(3,5\text{-}Bu^{t}Sal)_2(H_2O)_2]$,[10] and $[ZnSalNic]Sal \cdot 3H_2O$ (Nic is nicotinamide)[11] also exhibited the biological activity. The prepared[12] mixed heteroligand $Zn(HSal)_2(2\text{-MeHim})_2$ and $Zn(Han)_2(2\text{-MeHim})_2$ complexes (wherein 2-MeHim is 2-methylimidazole and Han is $NH_2C_6H_4COO^-$) are of potential interest for medicine; and also complex cyclic salicylate-containing compounds such as $[Zn_4(C_7H_4O_3)_4(C_{10}H_8N_2)_4] \cdot 10H_2O$,[13] which contain zinc in a distorted trigonal-bipyramidal coordination and bridges between zinc and four carboxylate groups of salicylate ligands, were obtained. Zinc is capable of various coordinations in complexes, which is clearly demonstrated by tetranuclear complexes[14] of zinc citrates with N-donor chelates, $[Zn_4(HCit)_2(phen)_4(H_2O)_4]^{2+} \cdot 2NO_3^- \cdot 10H_2O$ (**1**) and $[Zn_4(HCit)_2(bipy)_4(H_2O)_6]^{2+} \cdot 2NO_3^- \cdot 12H_2O$ (**2**) (HCit is citric acid). Both chelates contain the two crystallographically independent zinc ions with a different coordination geometry. In complex **1**, the Zn(1) atom is five-coordinated due to three O atoms (from two Cit) and two N atoms (from phen), and Zn(2) is six-coordinated due to two O (Cit) atoms, two N atoms (phen) and two water molecules, while Zn(1) and Zn(2) are connected *via* a citrate bridge. In complex **2**, the two citrate bridges and the two pairs of symmetrically bound zinc ions are in a tetranuclear coordination. The difference between these complexes is caused by the different steric hindrance of chelating agents, which having a critical importance in the selection of ligands for zinc chelation. Among the zinc compounds important for biology and medicine, a complex of tris(2-hydroxyethyl)-amine with zinc bis(2-methylphenoxyacetate) (cin-

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katran)[15] should be mentioned since it is an inhibitor of the synthesis of acidic cholesterol esterase of platelets and mononuclear cells. Moreover, the cinkatran is considered as a possible stimulator for the production of endogenous heparin. 4-Nitrocinnamic acid (L′) (which having different pharmacological properties[16] like all cinnamic acids) with zinc, ethylenediamine, and DMSO forms complexes $[ZnL'_2(H_2O)_2]$ (**3**), $[ZnL'_2(DMSO)_2]$ (**4**), and $[Zn(en)_2(H_2O)_2]L'_2(H_2O)_2$ (**5**), wherein complexes **3** and **5** have a distorted octahedral geometries while **4** is tetrahedral.[17] These complexes (especially **3**) have an inhibitory activity towards the alkaline phosphatase and a significant affinity for DNA. Zinc-containing complexes dichloro[2-(3,4-dichlorophenyl)imino-κ*N*-(2-thiazoline-κ*N*-2-yl)thiazolidine]zinc (**6**) and dichloro[2-(3,4-dichlorophenyl)imino-κ*N*-(4*H*-5,6-dihydro-1,3-thiazine-κ*N*-2-yl)tetrahydrothiazine]zinc (**7**) have a distorted tetrahedral geometry where the zinc atom is coordinated with two Cl atoms, one imine N atom, and one N atom from thiazoline (complex **6**) or thiazine (complex **7**). However, the percentage of phagocytosis efficiency was increased for human neutrophils[18] only in the case of thiazine complex **7**. The phagocytic function of human neutrophils is affected by the following ligands that are thiazine derivatives: 2-(1-pyrazolyl)-1,3-thiazine (PzTz), 2-(3,5-dimethyl-1-pyrazolyl)-1,3-thiazine (DMPzTz), and 2-(3,5-diphenyl-1-pyrazolyl)-1,3-thiazine (DPhPzTz); and also their zinc complexes: $[ZnCl_2(H_2O)(PzTz)]$ (**8**), $[ZnCl_2(DMPzTz)]$ (**9**), and $[ZnCl_2(DPhPzTz)]$ (**10**). However, the activity of cells under the administration of zinc complexes **8**—**10** was much higher than in the case of using only ligands.[19] Complexes of thiosemicarbazones with metals and, in particular, with zinc have the increased lipophilicity and ability to diffuse through the cell membranes.[20] Some Zn-selenosemicarbazones[21—23] have also demonstrated the biological activity. The complex of 2-quinolinecarboxaldehyde selenosemicarbazone (Hqasesc) ligand with zinc $[Zn(Hqasesc)_2](ClO_4)_2 \cdot EtOH$ (**11**) exhibited an antitumor activity against acute monocytic leukemia (THP-1) cells and some other cancers.[24]

A described[25] complex of flavonoid rutin with zinc contains the zinc ion coordinated with rutin *via* the benzofuran and aromatic rings with addition of water molecules. This complex increases the antitumor activity (towards the KG1, K-562, and Jurkat lines) and also prevents side effects of chemotherapy, *i.e.* is having a multiple action.

It should be noted that any zinc chelator with a high binding constant can have a cytotoxic effect on cells due to a successful competition for zinc with important cell constituents, which leading to the apoptosis and/or necrosis. In certain cases of this situation, a specificity was observed towards cancer cells,[26] which should be especially evident in the case of disorders of their zinc homeostasis.

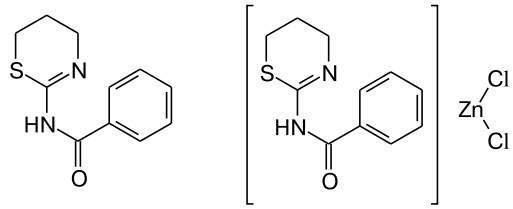
Therefore, the synthesis and study of biologically significant zinc complexes are remaining the actual problem due to their great potential for the chemotherapy.

In the present work, the previously obtained[27,28] *N*-(5,6-dihydro-4*H*-1,3-thiazine-2-yl)benzamide ligand was used for the synthesis of its complex with zinc and further investigations of the stability of both compounds in various solvents, and the ability to sorb on hydroxyapatite, which is necessary for its possible transportation inside the body and subsequent applications as an antitumor medication, and also for the development of radiopharmaceuticals containing radioactive isotopes of zinc.[28]

Experimental

^{1}H NMR spectra were recorded on a Bruker CXP-200 spectrometer (200 MHz).

N-(5,6-Dihydro-4*H*-1,3-thiazine-2-yl)benzamide (L) was prepared in the form of its hydrobromide (LHBr) according to the known procedure.[27] To obtain its complex with zinc, an aqueous solution of the LHBr ligand was treated with NaOH for its conversion into the form of base with m.p. 107—108 °C (the reported[29] m.p. value is 104—105 °C). Then a solution of zinc chloride (0.10 g, 0.7 mmol) in diethyl ether (50 mL) was slowly added to a solution of *N*-(5,6-dihydro-4*H*-1,3-thiazine-2-yl)benzamide (0.16 g, 0.7 mmol) in diethyl ether (35 mL). A formation of white precipitate was started immediately. The reaction mixture was stirred for 0.5 h. The precipitate was filtered off and washed with ether. $LZnCl_2$ was obtained as white crystals in the yield of 0.21 g (64%), m.p. 218—220 °C. Found (%): C, 37.23; H, 3.50; N, 7.88. $[C_{11}H_{12}N_2OS]ZnCl_2$. Calculated (%): C, 37.05; H, 3.39; N, 7.86. ^{1}H NMR (DMSO-d_6), δ: 2.13 (m, CH_2, CCH_2C); 3.10 (t, 2 H, SCH_2, J = 6.8 Hz); 3.54 (t, 2 H, NCH_2, J = 6.8 Hz); 7.36 (m, 3 H, H_{arom}); 8.04 (m, 2 H, H_{arom}); 11.30 (br.s, 1 H, NH).



L $LZnCl_2$

Spectrophotometry. Spectrophotometric measurements of the stability of the LHBr ligand and complex were carried out on a UV-1280 spectrophotometer (Shimadzu, Japan) in the wave range of 190—400 nm with 0.2 nm spectral resolution, using a 1 cm quartz cell at the temperature of 22±2 °C. The calibration for the ligand hydrobromide and the complex was performed in aqueous, physiological saline (0.15 *M* NaCl), and alcohol (95% EtOH) solutions. The molar extinction coefficients of the complex in alcohol solution and the ligand in aqueous, physiological saline, and alcohol solutions were also determined. The molar extinction coefficients were measured for two major absorption bands in the spectra for both the ligand and complex.

Sorption of the ligand on hydroxyapatite (HAP). The procedure of HAP preparation was reported[30] by us earlier; HAP_T is

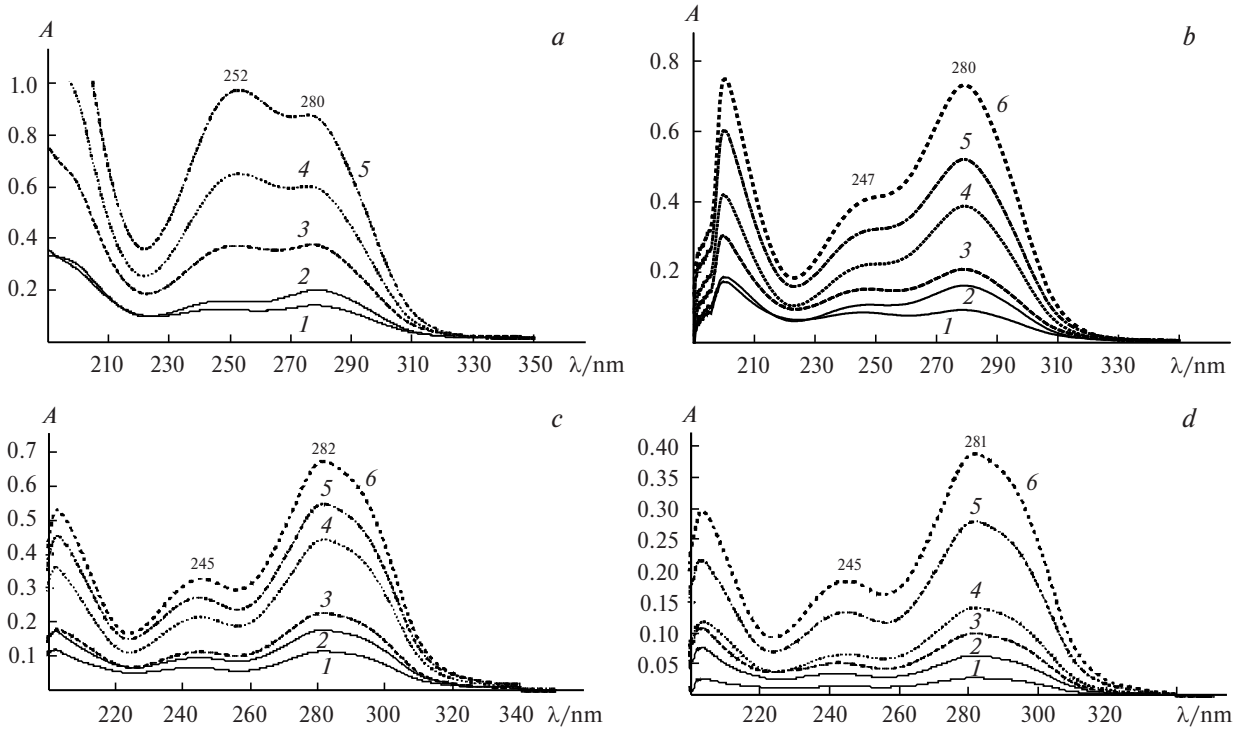


Fig. 1. Determination of the molar extinction coefficient of L ligand in aqueous (*a*), physiological saline (*b*), and alcohol (*c*) solutions, and $LZnCl_2$ complex in alcohol solution (*d*); the numbers at the curves indicate the wavelengths of the maxima (nm); *a*: $C = 1.80$ (*1*), 2.70 (*2*), 5.40 (*3*), 9.00 (*4*), and 13.50 μg L^{-1} (*5*); *b*: $C = 1.07$ (*1*), 2.14 (*2*), 3.57 (*3*), 5.35 (*4*), 7.13 (*5*), and 10.7 μg L^{-1} (*6*); *c*: $C = 1.51$ (*1*), 2.26 (*2*), 3.01 (*3*), 6.02 (*4*), 7.53 (*5*), and 9.04 μg L^{-1} (*6*); *d*: $C = 1.29$ (*1*), 2.58 (*2*), 5.17 (*3*), 25.8 (*4*), 38.8 (*5*), and 51.7 μg L^{-1} (*6*).

an aqueous suspension of HAP that was subjected to a thermal treatment at 95 °C for 4—5 h. To estimate the sorption kinetics of the ligand on the HAP and HAP_T nanoparticles, a solution of ligand (0.7 mL, 0.2 mg mL^{-1}) was mixed in plastic vials (volume of 30 mL) with physiological saline solution (13.3 mL, 0.9% NaCl) to make the final concentration of 10^{-2} mg mL^{-1}. A suspension (1 mL) of HAP (5 wt.%) or HAP_T (6 wt.%) was added to the vials, the vials were placed on a S3-0.8L orbital shaker (Elmy, Latvia) and mixed for 5, 10, 15, 30, and 60 min. The phases were separated by centrifugation at 4000 rpm for 2 min on a T-51.1 centrifuge (MLW, GDR). An aliquot of the liquid phase was transferred into the quartz cuvette for spectrophotometric analysis. The measurements were repeated in the same way for the control solution (0.7 mL of ligand solution with $C = 0.2$ mg mL^{-1} dissolved in 13.3 mL of physiological saline solution).

The protonation and stability constants were determined potentiometrically using a Metrohm 848 Titrino Plus autotitrator (Switzerland). During evaluation of the protonation constant of the ligand, solutions of potassium nitrate (1 mol L^{-1} in the case of an aqueous solution) and physiological saline were used as the background electrolyte. The stability constant of the complex was determined while the titration was carried out on the autotitrator with a glass indicator electrode. Hyperquad 2013 software was used for the calculations.

Results and Discussion

The molar extinction coefficients of the ligand and complex (Fig. 1) were determined in various solvents (Table 1). The ligand stability in the aqueous solution was dependent on its concentration, which may be related to

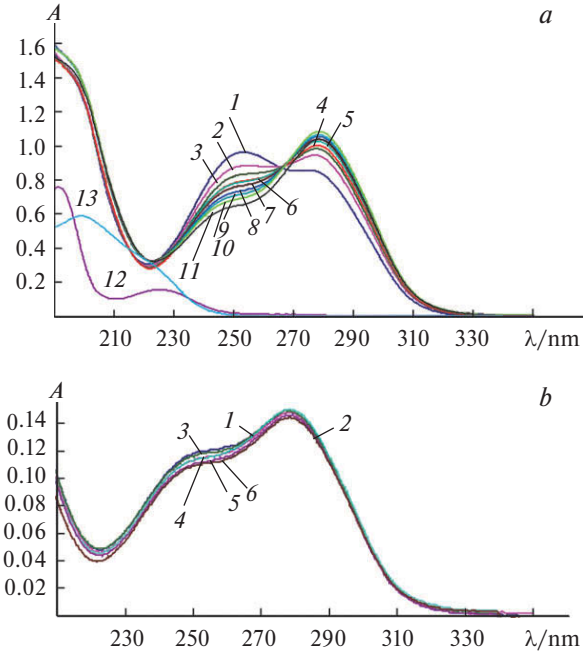


Fig. 2. The ligand stability in aqueous solution at large (>6 μg mL^{-1}, *a*) and low (2—6 μg mL^{-1}, *b*) concentrations; (*a*): initial solution (*1*), the solution was stored for 1 (*2*), 2 (*3*), 3 (*4*), 4 (*5*), 5 (*6*), 7 (*7*), 8 (*8*), 9 (*9*), 10 (*10*), and 11 days (*11*), benzoic acid (*12*), and thiazine (*13*); (*b*): initial solution (*1*), the solution was stored for 1 (*2*), 2 (*3*), 3 (*4*), 5 (*5*), and 6 days (*6*).*

* Figures 2, 8, and 9 are available in full color on the web page of the journal (http://www.link.springer.com/journal/11172).

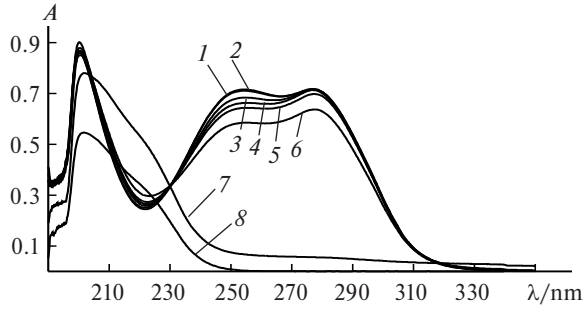


Fig. 3. The ligand stability in physiological saline solution: initial solution (*1*), the solution was stored for 1 (*2*), 2 (*3*), 3 (*4*), 4 (*5*), 5 (*6*), and 7 days (*7*), and thiazine (*8*).

Table 1. The molar extinction coefficients of the ligand and complex in different solvents

Compound (solvent)	λ/nm	$\varepsilon \cdot 10^{-4}$ /L mol^{-1} cm^{-1}
LHBr	252	2.15±0.03
(aqueous)	280	2.13±0.07
LHBr	247	1.26±0.04
(physiological saline)	280	2.53±0.06
LHBr	245	1.09±0.01
(alcohol)	282	2.26±0.02
$LZnCl_2$	245	1.12±0.04
(alcohol)	281	2.37±0.07

tautomeric transitions and/or a possibility of the hydrogen bonding. LHBr was stable for at least 7 days (Fig. 2, *b*) at the concentration of $8 \cdot 10^{-6}$ mol L^{-1}, while it remained stable for at least 11 days (Fig. 2, *a*) at the concentration of $5.6 \cdot 10^{-5}$ mol L^{-1}. In the physiological saline solution, there was no observed concentration dependence, the ligand was stable for 6 days and then decomposed with the formation of thiazine (Figs 3 and 4), which is in agreement with the reported data.[29]

The protonation constants o f the ligand obtained by the potentiometric titration method (Figs 5 and 6) were equal for the aqueous (log$K$ = 5.1±0.1) and physiological (log$K$ = 5.3±0.2) saline solutions. An attempt was made to determine the stability constant of the complex, thus the potentiometric titration was performed (Fig. 7) for this purpose. During Hyperquad 2013 calculations, formation constants of the following substances were taken into account: $Zn(OH)_2$, $Zn(OH)_3^-$, $Zn(OH)_4^{2-}$, $Zn_2(OH)_6^{2-}$, Zn_2OH^{3+}, $Zn_4(OH)_4^{4+}$, and $ZnOH^+$. However, the calculations of the complex stability constant were unsuccessful. This might be explained by the

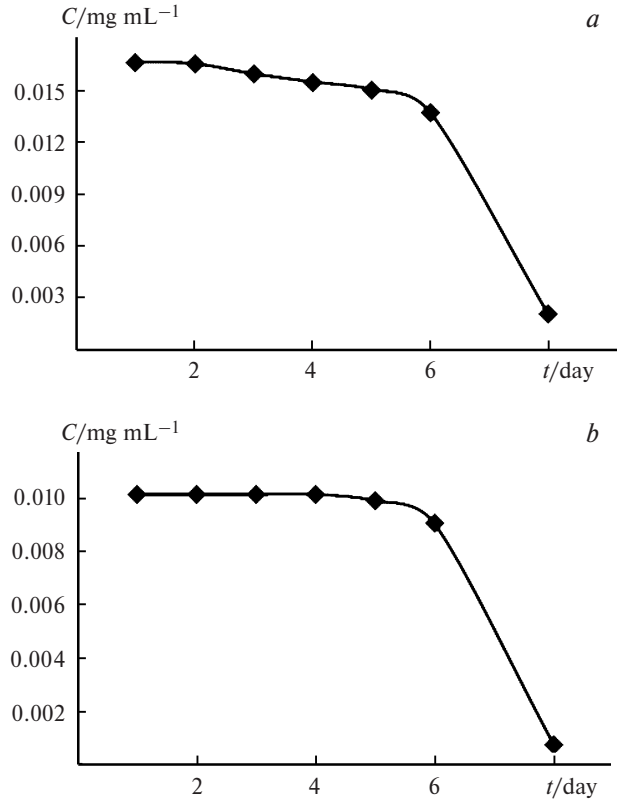


Fig. 4. Dependences of the ligand concentration change on time, calculated from changes in the maxima of the ligand absorption bands at 247 (*a*) and 280 nm (*b*).

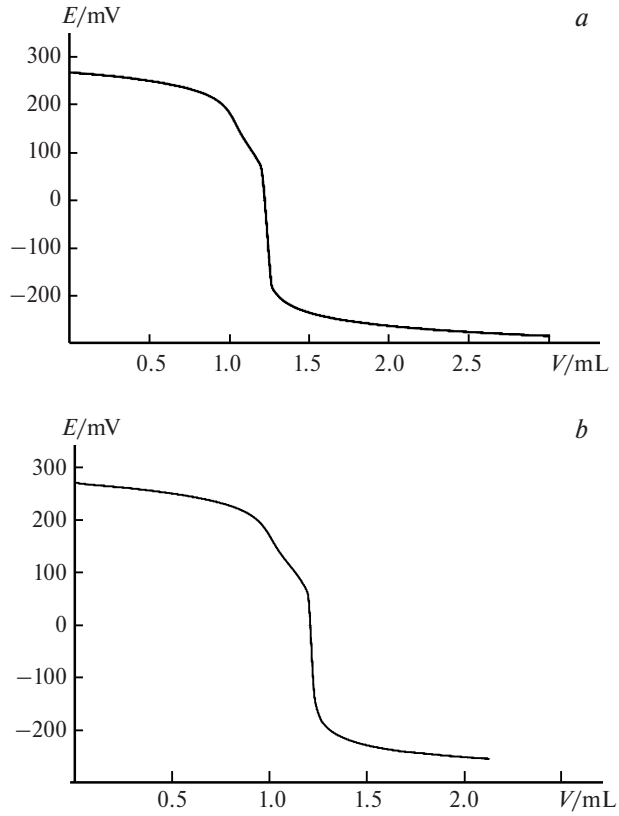


Fig. 5. Titration curves of LHBr ligand for aqueous (*a*) and physiological saline (*b*) solutions; V is the titrant volume.

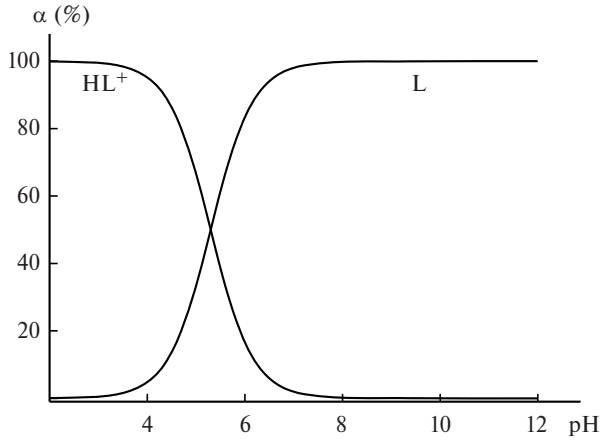


Fig. 6. Distribution of ligand forms as a function of pH calculated using the Hyperquad 2013 software; $C(L) = 1 \cdot 10^{-3}$ mol L^{-1}, $I = 0.15$ mol L^{-1} of NaCl (0.1 mol L^{-1} of KNO_3); α is the percentage of the form.

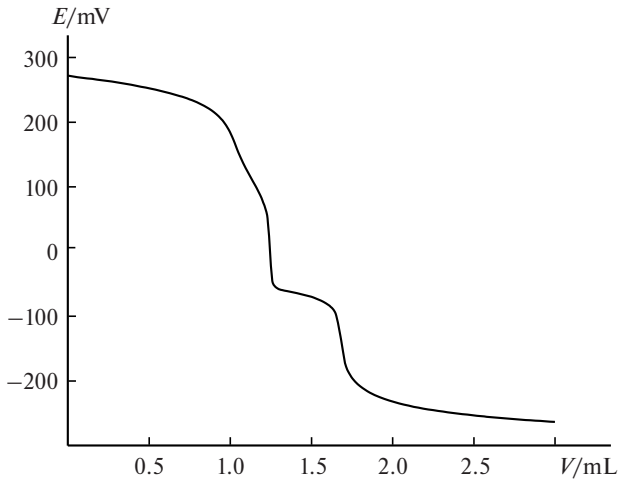


Fig. 7. Titration curve of the $LZnCl_2$ complex.

formation of zinc hydroxide, which hindered the titration experiments.

The spectrophotometric study (Fig. 8) revealed insufficient stability of the complex in aqueous solutions, while it remained stable in the alcohol solution for 3—4 days.

At the first moment during the ligand sorption on HAP and HAP_T (Fig. 9), the major absorption bands of the ligand were shifted with changing of the peak heights. After that, no changes were observed. One might assume that the ligand initially interacts with calcium, which presented in the solution due to the increased solubility of HAP_{nano} (HAP with particle size <100 nm). The absence of further changes might indicate that the ligand was almost not sorbed on either HAP or HAP_T. This could be a positive factor since the binding of HAP nanoparticles specifically to zinc could be expected upon $LZnCl_2$ complex deposition on HAP, while the ligand would retain a certain degree of freedom for interactions. Zinc poorly passes through

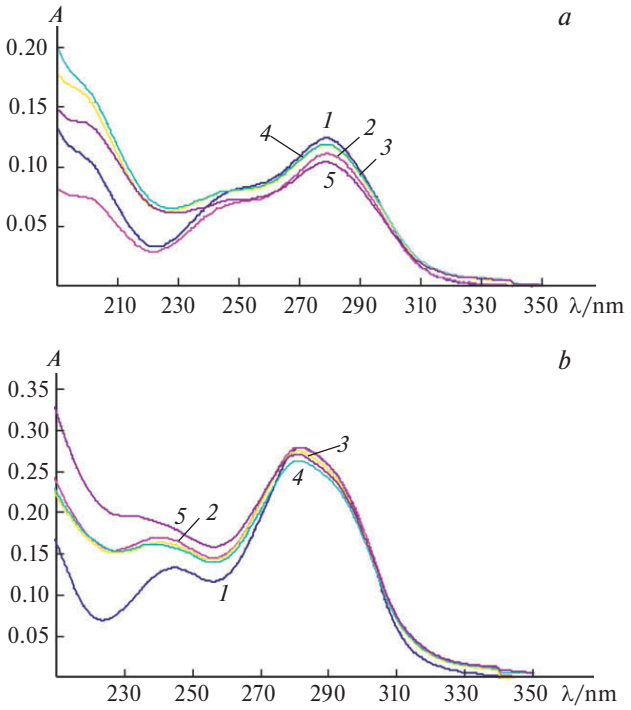


Fig. 8. The complex stability in aqueous (*a*) and alcohol (*b*) solutions: the initial solution (*1*), the solution was stored for 5 (*2*), 6 (*3*), 7 (*4*), and 13 days (*5*).

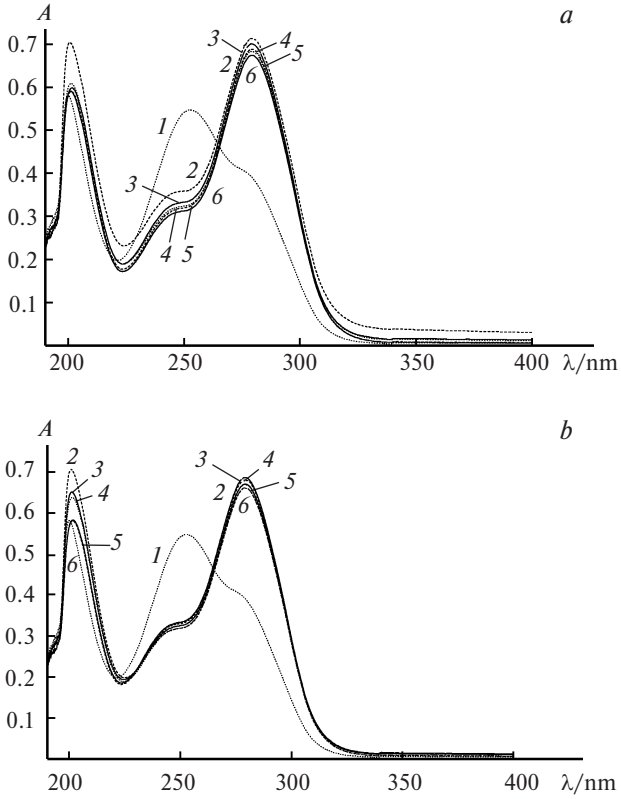


Fig. 9. Spectra of the LHBr solution (10^{-2} mg mL^{-1}), which was in contact with HAP_T (*a*) and HAP (*b*) for 0 (*1*), 5 (*2*), 10 (*3*), 15 (*4*), 30 (*5*), and 60 min (*6*).

the plasma membrane since its concentration in the cell is under the strongest control (buffering and extinguishing[31]). The ligand design of the zinc complex may facilitate the zinc absorption by cells in some cases. It is especially important to choose the ligand, which is mainly recognized by the cancer cells. Therefore, it is crucially important for the choice of ligand design to take into account not only the biochemical effect on the cell constituents, but also the increased absorption of the compounds carrying zinc ions by the cancer cell due to the ligand properties. Such approach may provide the increased selectivity of zinc delivery.

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