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Cation-dependent structural diversity of zinc(II), calcium(II) mono- and binuclear complexes of aryl-imidazo-1,10-phenanthroline derivatives



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ABSTRACT

The syntheses of azacrown-containing aryl-imidazophenanthroline by reaction of 1,10-phenanthroline-5,6-dion with 4-(1.4.7.10-tetraoxa-13-azacyclopentadecan-13-yl)benzaldehyde producing the ligand **2** in high yield is described. Examination of their Zn(II), Ca(II) and mixed complexes by UV/Vis and NMR spectroscopy suggests electronic communication between the two metal centers of ligand **2**. Stability constants, determined by spectrophotometric titration, indicate that the Zn(II) possesses higher affinity toward phenanthroline residue than Ca(II) and does not bind with azacrown-ether residue. This selectivity allows to prepare a mixed Zn(II)/Ca(II) complex.

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1. Introduction

The design and synthesis of the organometallic systems that exhibit pre-designed functionality on the supramolecular organization are important in physics, chemistry and materials science. Precise control on the nanoscale will allow the development of the devices as well as the development of materials with new, potentially controllable properties, e.g. catalytic, magnetic and sensing [1-8].

1H-imidazo[4,5-f][1,10]phenanthroline (abbreviated as IPh) as N-donor ligand possesses several interesting structural characteristics appropriate for coordination with different types of metal ions (Zn^{2+} , Mn^{2+} [9], Cd^{2+} [10], Co^{2+} [11], Pt^{2+} [12], lanthanides (III) (Ln = Eu, Dy, Er, Tb, Sm, Yb) [13], Ru^{2+} [14])). Imidazophenanthroline complexes are suitable for the various applications, such as fluorescent probes [15,16], DNA binding [17–25], sensing elements for cations and anions [9,26]. Imidazo[4,5-f][1,10]phenanthroline derivatives and their metal complexes are candidates for the third-order NLO materials in virtue of their high harmonic generation and rapid response [27–30]. However, reports on self-assembly with dinuclear imidazophenanthroline complexes

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still remain rare. Thus, a Zn²⁺ complex of the hybrid of terpyridine with 2-phenylimidazo[4,5-f][1,10]phenanthroline acts as a multifunctional optical sensor for multiple analytes (cations and anions) [9]. It was previously reported that bimetallic complex Re–IPh–Ir that demonstrates the ability to react with CO with appreciable changes in spectroscopic measurement reveal an electronic communication between the two metal centers [31]. Two polypyridyl ligands containing macrocyclic unit benzo-12-crown-4 or benzo-15-crown-5, and their mononuclear IPh–Ru(II) complexes have been prepared. These complexes exhibit a modest binding ability to Li⁺ or Na⁺ [32].

Our research in this area is directed towards studies of binuclear complexes containing two types of metal ions, namely, transition Zn^{2+} cation and alkaline earth Ca^{2+} cation. Metal cations such as Ca^{2+} and Zn^{2+} play vital roles in many biologic processes and tracking their homeostasis in living systems via a suitable technique is of great significance to clarify their biological effects [33]. The phenyl-aza-15-crown-5 ether IPh (**2** in Scheme 1) was used as a ditopic ligand. Imidazo[4,5-f][1,10]phenanthroline is well suited as bridging ligand having bidentate coordination center suitable for binding with Zn^{2+} [9]. Phenylazacrown ether forms complex effectively with Ca^{2+} cation [34]. At the same time, the ability of Ca^{2+} to interact with IPh has not been discussed earlier. For study that is more detailed the model compound **1** has been also prepared (see Scheme 1). Our study was to investigate the crown-containing IPh fragment, in order to study the interplay of

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Scheme 1. Synthetic scheme of 1, 2 dye preparing.

 Ca^{2+} and Zn^{2+} complexation and also to assess whether this moiety would be a suitable building block towards the synthesis of mixed cation systems.

2. Experimental

2.1. Materials

Anhydrous MeCN, $Zn(ClO_4)_2 \cdot 6H_2O$, $Ca(ClO_4)_2 \cdot 4H_2O$ (Aldrich), 70% HClO₄ (Sigma–Aldrich) were used as received. For study of ligands **1** and **2** protonation 0.01 M HClO₄ was prepared by diluting of 70% HClO₄ with MeCN (total 0.04% water in MeCN–water mixture). 2-Phenyl-1H-imidazo[4,5-f][1,10]phenantroline (**1**) was prepared as described [35,36].

2.2. Syntheses of 2-[4-(1,4,7,10-tetraoxa-13-azacyclopentadecan-13yl)phenyl]-1H-imidazo[4,5-f][1,10]phenanthroline (**2**)

To a solution of 4-(1.4.7.10-tetraoxa-13-azacyclopentadecan-13-yl)benzaldehyde (70 mg, 0.216 mmol) in ice-cold acetic acid (5 ml) 1,10-phenanthroline-5,6-dion (45.5 mg, 0.216 mmol) and ammonium acetate (350 mg, 4.55 mmol) were added. The mixture was refluxed for 8 h. After cooling to room temperature, water solution of ammonium acetate (5 M) was added until pH = 8. Precipitated solid was filtered, washed with water and diethyl ether. Drying in vacuo at 75 °C for 1 h yielded 51.5 mg (0.1 mmol, 46%) of a brown powder, m.p. 130–133 °C. ¹H NMR (DMSO-d₆, δ ; ppm, J/Hz): 3.52 (s, 4H), 3.57 (m, 8H), 3.70 (m, 8H) (CH₂O), 6.85 (d, 2H, ${}^{3}J$ = 8.36), 8.08 (d, 2H, ${}^{3}J$ = 8.37) H(Ph), 7.81 (m, 2H, H(3',6')), 8.90 (d, 2H, ${}^{3}J$ = 7.00), 9.00 (m, 2H) H(2',4',5',7'). ${}^{13}C$ NMR (APT) (DMSO-d₆, δ , ppm): 52.41, 68.30, 69.51, 69.99, 70.77 [CH₂O],111.70, 123.55, 128.07, 129.91, 147.79 [CH], 117.45, 143.67, 148.98, 152.21, 172.84 [C_{quat}]. Anal. Calc. for C₂₉H₃₁N₅O₄: C, 67.82; H, 6.08, N, 13.64. Found: C, 67.90; H, 6.11; N, 13.68%. ESI-mass m/z (I, (%)): 514 [M]⁺ (100).

2.3. Analytical and physical measurements

Mass spectra were recorded using Agilent 1100 Series LC/MSD trap interface operated in positive-ion mode. Direct infusion of the analyzed solution was used. Optimum flow rate of the gas dryer was 11 l/m. The dry gas temperature was 150–250 °C. Gas pressure was 60 psi. Overload on the nebulizer tip was 2–3 kV.

¹H NMR spectra were recorded on a Bruker Avance 600 spectrometer (working frequency 600.13 MHz). Chemical shifts were measured with an accuracy of 0.01 ppm, and a measurement error of spin–spin coupling constants was 0.1 Hz. The measurements were done using the CD₃CN signal as an internal reference (1.94 ppm at 295 K). Data acquisition and processing were performed with Topspin 2.1 software (Bruker).

DOSY experiments were performed on a Bruker Avance spectrometer at 25 °C using the DOSY-ONESHOT pulse sequence [37]. The following experimental parameters of the pulse sequence were used: diffusion time 0.2 s, gradient pulse duration 1 ms,

unbalancing factor alpha 2.0, relaxation delay 5.0 s. Signal attenuation was achieved by increasing the gradient strength from 5% to 80% as defined by the pulse sequence in 32 steps with 32 scans, each with the maximum gradient strength of 0.27 T/m.

The rows of quasi-2D diffusion dataset were phased and baseline corrected. Pseudo-2D DOSY spectra were obtained using a standard fitting procedure of Bruker Topspin 2.1 software. The actual diffusion coefficients were determined using T1/T2 analysis module of the Bruker Topspin 2.1 software. As the signals corresponding to the protons of crown fragments were characterized by the highest signal-to-noise ratio, their intensities were used for the computation of the signal decay curves. Viscosities of solutions were obtained by comparing the measured diffusion coefficient of the residual solvent signal with the known value ($4.14 \times 10^{-9} \text{ m}^2 \text{s}^{-1}$ for CD₃CN [38]). The hydrodynamic radii and volumes were calculated from viscosity-corrected diffusion coefficients *via* Stokes–Einstein relation.

UV–Vis spectra recorded with a Varian Cary 50 spectrophotometer, FLUORAT-02-Panorama fluorescence spectrophotometer, and Avantes spectrophotometer.

2.4. Equilibrium constant determination

Complex formation of ligands with $Zn(ClO_4)_2$, $Ca(ClO_4)_2$ in acetonitrile at 20 ± 1 °C was studied by spectrophotometric titration. The ratio of $Me(ClO_4)_2$ to ligand was varied by adding aliquots of a solution of known concentrations $Me(ClO_4)_2$ to a solution of ligand alone of the known concentration. The UV–Vis absorption spectrum of each solution was recorded and the stability constants of the complexes were determined using the SPECFIT/32^M program [39], a program designed to extract equilibrium constants from spectrophotometric titration data. SpecFit starts with an assumed complex formation scheme and uses a least-squares approach to derive the spectra of the complexes and the stability constants. Typically, 12–15 spectra were taken for calculations.

Those equilibriums were used to model the data:

$$L + Zn \xrightarrow{+Zn} L_3 Zn \xrightarrow{+Zn} L_2 Zn \xrightarrow{+Zn} LZn$$

$$K_{31} = \frac{[L_3Zn]}{[L]^3 * [Zn]}$$
 $K_{21} = \frac{[L_2Zn]}{[L]^2 * [Zn]}$ $K_{11} = \frac{[LZn]}{[L] * [Zn]}$

$$\mathbf{I} + \mathbf{Ca} \underbrace{\overset{+\mathbf{Ca}}{\longleftarrow}}_{K_{21}} \mathbf{1}_{2}\mathbf{Ca} \underbrace{\overset{+\mathbf{Ca}}{\longleftarrow}}_{K_{11}} \mathbf{1}\mathbf{Ca} \quad K_{21} = \frac{[\mathbf{1}_{2}\mathbf{Ca}]}{[\mathbf{1}]^{2} * [\mathbf{Ca}]} \quad K_{11} = \frac{[\mathbf{1}\mathbf{Ca}]}{[\mathbf{1}] * [\mathbf{Ca}]}$$

$$\mathbf{2} + \mathbf{Ca} \xrightarrow[K_{21}]{} \mathbf{2}_{2}\mathbf{Ca} \xrightarrow[K_{11}]{} \mathbf{2}\mathbf{Ca} \xrightarrow[K_{12}]{} \mathbf{2}\mathbf{Ca}_{2}$$

$$K_{21} = \frac{[\mathbf{2}_{2}Ca]}{[\mathbf{2}]^{2} * [Ca]} \quad K_{11} = \frac{[\mathbf{2}Ca]}{[\mathbf{2}] * [Ca]} \quad K_{12} = \frac{[\mathbf{2}Ca_{2}]}{[\mathbf{2}] * [Ca]^{2}}$$

$$L=\text{ligands } \mathbf{1.2.}$$

UV–Vis spectra recorded with a Varian Cary 50 spectrophotometer.

Steady-state fluorescence spectra were recorded with a Fluorolog-3 (Model FL3-22) fluorescence spectrophotometer at 20 ± 1 °C. Fluorescence quantum yields of the ligands and their complexes were determined in air-saturated acetonitrile at 20 ± 1 °C relative to quinine sulfate in 0.5 M H₂SO₄ as standard (φ_F = 0.546) with excitation at 315 nm for ligand **1**, 360 nm for ligand **2** and its complex with Zn²⁺ and 320 nm for mixed Zn–Ca complex of ligand **2**.

Fluorescence quantum yields were calculated using

$$\varphi_x = \varphi_s(A_x/A_s) \Big[(1 - 10^{-D_s}) / (1 - 10^{-D_x}) \Big] (n_x^2/n_s^2)$$

where φ_s is the fluorescence quantum yield of the standard, *A* is the integrated area under the emission spectrum, *D* is the absorbance at the wavelength of excitation, and *n* is the refractive index of the solvent. Subscripts *x* and *s* refer to unknown and standard, respectively.

3. Results and discussion

Imidazo[4,5-f][1,10]phenanthroline based ligands **1** and **2** are easily prepared by condensation of 1,10-phenanthroline-5,6-dione and corresponding aldehydes in the presence of ammonium acetate in ice-cold acetic acid. The structure of prepared compounds **1**, **2** was confirmed by ¹H, ¹³C, COSY, NMR spectroscopy, elemental analysis and mass-spectrometry methods (see Experimental part and Figs. S1–S5 in Supporting Information (SI)).

Electronic absorption spectra of phenanthroline derivatives **1** and **2** in acetonitrile (MeCN) showed an intense lowest energy charge-transfer absorption band in the UV-visible region (Fig. 1). The position of this band depends on the electronic nature of the substituent at position 4 of the aryl moiety. The reason for the substantial red shift in the investigated compound **2**, functionalized with donor group, λ_{max} 342 nm, relative to that of unsubstituted phenanthroline **1** (λ_{max} = 274 and 333 nm) is the strong conjugative electron donor effect of the azacrown substituent at the *para* position of the phenyl ring.

Firstly, we analyzed the protonation of the compounds **1** and **2** that could help in the understanding of the binding process with metal ions. To define the protonation order of nitrogen atoms in ligands **1** and **2** we studied the protonation with HClO₄ by spectrophotometric titration method. The addition of the increasing amount of HClO₄ causes the appearance of **1**·H⁺ (λ_{max} = 308 nm) followed by **1**·(H⁺)₂ (λ_{max} = 290 nm) (see Figs. 2 and S6a, b in SI).



Fig. 1. The absorption spectra of ligands 1 and 2 (1.67×10^{-5} M) in MeCN solution.



Fig. 2. The absorption spectra of ligand 1 (1), $1\cdot H^*$ (2) and $1\cdot (H^*)_2$ (3) $(1.67\times 10^{-5}\,M)$ in MeCN.

Upon the addition of 0 to 1 equivalent of perchloric acid absorption spectra demonstrates up to 7 isosbestic points that indicates the formation of a single-type strong complex (see Fig. S6a in SI). The first protonation induces an enhancement of the low-energy band, which would correspond to an increase of intramolecular charge transfer in the protonation species. Such effect can been rationalized by considering that the first protonation of phenan-throline residue and the strength of formed complex is due to coordination of the proton with both N-atoms of phenanthroline, which increases the electron acceptor character of the phenanthroline unit. Upon the addition of 1 to 40 equivalents of acid absorption spectra demonstrates another set of isosbestic points that indicates transition of monoprotonated complex to diprotonated through the protonation of imidazolium part (see Fig. S6b in SI).

Ligand **2** can coordinate three protons (see Scheme 2 and Figs. S7, S8 in SI). Based on the position of long wavelength bands of **2**·H⁺ ($\lambda_{max} = 347 \text{ nm}$) and **2**·(H⁺)₂ ($\lambda_{max} = 310 \text{ nm}$) the coordination of protons with phenanthroline and imidazole units can be suggested. At the large amount of HClO₄, the formation of **2**·(H⁺)₃ ($\lambda_{max} = 280 \text{ nm}$) was observed. The position of its long wavelength band is shifted to the short region. This fact points on the coordination of the third proton with N-atom of azacrown ether what switches off the lone pair of the azacrown ether nitrogen atom from conjugation with the chromophore.

The analysis of ¹H NMR spectra of the ligand **2** in the presence of increasing amount of $HClO_4$ showed the significant changes of the position of imidazophenanthroline proton signals even at small amount of $HClO_4$ (see Fig. S9a, b in SI). This confirms that firstly the protonation of imidazophenanthroline residues occurs.

Detailed investigations were carried out to understand the coordinating behaviors of $\mathbf{1}$ and $\mathbf{2}$ with Zn^{2+} . In literature, there are a few examples of Zn²⁺complexes with IPh. The synthetic procedure of obtaining of $[Zn_2(Hcpip)_2(ox)]_n \cdot 2nH_2O$ and $[Zn_4(Hcpip)_2(cpip)_2(ox)]_n \cdot 5nH_2O$, where $H_2cpip = 2-(2-carboxy$ phenyl)imidazo[4,5-f][1,10]phenanthroline, $H_2ox = oxalic$ acid, was described in [40]. The complex was formed only after boiling of metal-ligand water solution for 8 h. An imidazophenanthroline scaffold with a boronic acid unit. viz. 3-(1H-imidazo[4,5-f][1,10] phenanthrolin-2-yl)phenylboronic acid, is found that IPh induces fluorogenic responses when Zn(II) ion coordinates with phenanthroline residue [41]. The observed complex has the composition 1:1. In mixture THF-MeOH ZnCl₂ forms exclusively the 2 ligands to 1 metal ion complex with IPh [42]. Nevertheless, ligand does not exhibit any zinc-corresponding emission. Furthermore, the complex is not stable in the presence of DMSO or water. In [9] the composition of IPh-Zn²⁺ complex in DMF-MeCN mixture has not been determined.

In our experiments, we would like to understand how the complex formation between **1**, **2** and $Zn(ClO_4)_2$ in MeCN solution at room temperature occurs. The UV–Vis absorption spectra of **1**, **2** in the presence of $Zn(ClO_4)_2$ in MeCN are displayed in Fig. 3, Table 1 and Figs. S10–S17 in SI.

Upon addition of Zn^{2^+} , the band at 276 nm of **1** showed a substantial increase of intensity with absorption tail extending to about 410 nm, indicating that Zn^{2^+} has a strong interaction with **1** (Figs. 3 and S10–S12 in SI). The analysis of the spectral data with SpecFit32 program showed that depending on Zn^{2^+} amount the formation of three types of complexes $\mathbf{1}_3 \cdot Zn^{2^+}$, $\mathbf{1}_2 \cdot Zn^{2^+}$, $\mathbf{1} \cdot Zn^{2^+}$ occurs (Scheme 3). The calculated stability constants are presented in Table 1. We proposed the formation of all types of complexes through the coordination of metal ions with phenanthroline residue. According the known literature data cited in the introduction of the paper, phenanthroline is the preferable place for metal ion coordinated with IPh.

As optical investigation showed (Figs. S13–S16 in SI), the process of interaction of Zn^{2+} with ligand **2** is similar to what we



Scheme 2. Protonation of dye 2 in reaction with HClO₄.



Fig. 3. Electronic absorption spectra of: (1) **1**; (2) $1 \cdot \text{Zn}^{2*}$. Initial concentration of **1** was C₁ = 1.67×10^{-5} M, concentration of zinc perchlorate was varied in the interval 0–0.005 M. Solvent–acetonitrile, *T* = 294 K.

observed for **1**. It is known that azacrown ether does not bind heavy and transition metal ions [43]. This is why in our experiment we did not see the complex formation of Zn^{2+} with azacrown ether unit. Moreover, the calculated electronic absorption spectra of both (**1**)₃Zn and (**2**)₃Zn in MeCN show an increase of the charge transfer band at low energy, which indicates that complexations does involve the nitrogen atoms of the phenathroline unit, as observed in the case of the first protonation.

The formation of zinc complexes of the ligand 2 was followed by NMR titration of the ligand in CD₃CN solution by the corresponding metal ions. To supplement the data of routine 1D ¹H NMR measurements, the diffusion-ordered spectroscopy (DOSY) [44] was employed to obtain diffusion coefficients of the complexes in solution. As the direct interpretation of the diffusion coefficients is notoriously troublesome, especially for charged species, we used the approach [45] based on the comparison of effective hydrodynamic volumes of the complexes with that of the free ligand. Note that in most cases, we observed the dynamic equilibrium in solution, and the corresponding line broadening dramatically decreased the accuracy of our measurements. Although the resulting data provide valuable complementary information on the composition of the complexes, no quantitative characteristics (such as equilibrium constant values, etc.) can be reliably obtained.

The changes in the ¹H NMR spectra of the ligand **2** following the addition of $ZnClO_4$ solution are consistent with the successive formation of several complexes of different compositions (Fig. 4). Only signals of aromatic protons were shifted upon the complex formation, while the signals of a crown fragment remained constant, which confirms very low affinity of Zn^{2+} ions to the crown ether moiety. Although the exchange-induced broadening of the signals in the aromatic part of the spectra prevents the full assignment of all the signals observed, the data obtained suggest the formation of two distinctly different complexes. The addition of the first portion of Zn^{2+} solution leads to the shift of signals corresponding to the protons of phenanthroline moiety, signaling the

Table 1

Stability constants (LogK) of complexes 1 and 2 with metal cations in MeCN (293 K).

Ligand	Log K of Zn ²⁺ -complexes (L: Zn ²⁺)			LogK of Ca ²⁺ -complexes (L:Ca ²⁺)			$Log K$ of $Zn^{2+}-Ca^{2+}$ -complex (L: $Zn^{2+}:Ca^{2+}$)	
	LogK ₁₁	$Log K_{21}$	Log K ₃₁	Log K ₂₁	$Log K_{11}$	$Log K_{12}$	Log <i>K</i> ₂₁₂	
1	6.0 ± 0.17 6.0 ± 0.32	12.7 ± 0.21 139 ± 0.24	18.7 ± 0.27 20.5 ± 0.31	11.1 ± 0.19 128 ± 0.45	5.4 ± 0.14 55 ± 0.29	- 84+029	- >20	
2	0.0 ± 0.02	13.3 ± 0.24	20.3 ± 0.31	12.0 ± 0.45	5.5 ± 0.25	0.4 ± 0.23	- 20	



Scheme 3. The suggested structures of Zn²⁺ and Zn²⁺-Ca²⁺ complexes.



Fig. 4. Dependence of ¹H NMR spectra of 1.33×10^{-3} M CD₃CN solution of the ligand **2** and zinc perchlorate on the molar Zn/ligand ratio. The low-field region of the spectra is scaled to ensure the visibility of the signals assigned to amine protons.

formation of ZnL_3 complex that is in equilibrium with the excess of the free ligand. However, when a molar ligand-to-zinc ratio is 3:1, the second set of signals emerges, suggesting the formation of the second, more stable complex ZnL_2 . The latter is further stabilized with increasing concentration of zinc ions. Spectra do not change significantly if the molar ligand-to-zinc ratio increases beyond 2:1, and there was no indication of the presence of a ZnL complex even in the case of the ten-fold excess of Zn^{2+} .

The consecutive formation of two different complexes also follows from the diffusion data. The initial addition of zinc ions significantly increases the complex-to-free ligand volume ratio (Fig. 5) owing to the formation of a bulky ZnL_3 complex. Further addition of zinc ions reduces this volume ratio because of the formation of a more compact ZnL_2 complex.

In opposite to Zn^{2+} , Ca^{2+} can bind with macrocyclic azacrown ether units [34]. The addition of calcium perchlorate to the acetonitrile solution of **1** or **2** causes firstly the bathochromic shift of long wavelength band at 274 nm up to 294 nm for **1** and 2 nm shift of 342 nm band for **2** (Figs. 6 and S17–S23 in SI). The obtained spectrophotometric data fit well with the formation of **2** (or **1**)₂·Ca²⁺, **2** (or **1**)·Ca²⁺ complexes (Scheme 4, Table 1). Obviously, that solution



Fig. 5. Dependence of the ratio of effective hydrodynamic volumes of the complexes to that of the free ligand **2** on the molar Zn/ligand ratio.



Fig. 6. Electronic absorption spectra of the solution of dye **2** with increasing concentration of calcium perchlorate: (1) **2**; (2) $\mathbf{2}_2 \cdot \mathbf{Ca}^{2+}$; (3) $\mathbf{2} \cdot \mathbf{Ca}^{2+}$; (4) $\mathbf{2} \cdot (\mathbf{Ca}^{2+})_2$. Initial concentration of dye $C_2 = 1.67 \times 10^{-5}$ M, concentration of calcium perchlorate vary in the interval 0–0.005 M. Solvent–acetonitrile, T = 294.

of **2** and Ca²⁺ can contain complexes with both macrocyclic and heterocyclic types of coordination. In the presence of large amount of Ca²⁺ cations the substantial hypsochromic shift was observed indicating that complex in which Ca²⁺ ions is placed in macrocyclic unit is dominant (complex **2**·(Ca²⁺)₂) (Fig. 6, Scheme 4). The titration of the ligand **2** by Ca²⁺ ions resulted in changes in

The titration of the ligand **2** by Ca^{2+} ions resulted in changes in chemical shifts in the aromatic and crown fragment regions of the ¹H NMR spectra, implying the possible binding of calcium ions to both these moieties. Unfortunately, even at 335 K the exchange was slow enough to significantly broaden the signals, which, together with relatively low signal-to-noise ratio, prevented the assignment of the signals and obtaining the meaningful diffusion data. However, it is clear that in contrast to zinc, which shows the affinity to the phenanthroline binding site, calcium ions bind to both the phenanthroline and crown ether fragments, but the affinity is significantly lower than that for the phenanthroline/zinc pair.

We studied the possibility to obtain the complex containing two different metal ions. According to the data in Table 1, Zn^{2+} forms complexes with ligand **2** that are more stable than those of Ca^{2+} . Thus, we can suggest that complexes with Zn^{2+} should not be dissociated upon the addition of Ca^{2+} ions. So as in Zn^{2+} – complex macrocyclic coordination place is free, Ca^{2+} ions can interact with azacrown ether. For this purpose, firstly we prepared **2**₂· Zn^{2+} complex by taking into account the obtained spectrophotometric data. The addition of Ca^{2+} perchlorate to **2**₂· Zn^{2+} complex causes the hypsochromic shift of the absorption band that points out on Ca^{2+} coordination with crown ether part (see Fig. 7). The spectrophotometric analysis showed the formation of mixture complex **2**₂· $Zn^{2+}(Ca^{2+})_2$.

The effect of simultaneous presence of zinc and calcium ions in solution on the composition of the resulting complexes was studied by the titration of a mixture of the ligand **2** with two equimolar amount of zinc ions, where predominance of a $2_2 \cdot Zn^{2+}$ complex was expected. The addition of calcium ions leads to a significant shift of the signals assigned to the crown fragment (Fig. S24 in SI), while in the aromatic region of the spectra only the signals of phenyl protons adjacent to the crown moiety were shifted.

This, together with a larger affinity of zinc ions to phenanthroline binding site in comparison to calcium ions, suggests the gradual occupation of both crown moieties by calcium ions and the formation of the complex ZnL₂Ca₂. This result is in a good agreement with the diffusion data: the addition of calcium ions steadily increases the effective hydrodynamic volume of the complex (Fig. 8).

Both ligands **1** and **2** demonstrate the fluorescence with closed values of quantum yield. The analysis of the fluorescence showed



Scheme 4. The structures of Ca²⁺ complexes.



Fig. 7. Electronic absorption spectra of the solution of: (1) **2**; (2) **2**₂·Zn²⁺; (3) **2**₂·Zn²⁺.(Ca²⁺)₂. Initial concentration of **2** was C₂ = 1.67×10^{-5} M, concentration of calcium perchlorate was varied in the interval 0–0.005 M. Solvent–acetonitrile, *T* = 294.



Fig. 8. Changes in the effective hydrodynamic volumes' ratio for the mixed zinc/calcium complexes upon titration of equimolar 7.13×10^{-3} M acetonitrile-d³ solution of the ligand **2** and ZnClO₄ by calcium perchlorate.

that addition of metal ions to crown free ligand causes the shift of the fluorescence band to longer wavelengths (Table 2, Fig. S27 in SI). The quantum yield of fluorescence of ligand **1** slightly changes upon complex formation. In contrary, practically full fluorescence quenching additionally to bathochromic shift was found upon complex formation of crown-containing phenanthroline ligand **2** with both Zn^{2+} and Ca^+ cations (Table 2). The phenomenon could be connected with ligand–metal charge transfer (LMCT) between electron donor azacrown ether part and metal ions bound with phenanthroline residue. Indeed, the optimized geometry of free



Scheme 5. Optimized structure of ligand 2 calculated by MOPAC 7 program.

ligand showed its plane structure (Scheme 5) providing the easy communication between the end groups of the ligand. In addition, the plane structure of **2** points out that the reason of fluorescence quenching could be LMCT but not the photoinduced electron transfer (PET) process.

4. Conclusion

The analysis of the obtained data allows making the following conclusions. This research showed that in crown-containing phenanthroline derivative **2** the phenanthroline residue is the preferable place for binding as heavy Zn^{2+} as well as alkaline earth Ca^{2+} metal ions. According our observation imidazole nitrogenatom does not participate in complex formation. As demonstrated the NMR analysis at high concentration of ligand **2** the strong complex **2**₂·Ca²⁺ forms through the coordination of Ca²⁺ with phenanthroline residue. At equimolar **2** and Ca²⁺ ratio, complex **2**·Ca²⁺ was observed which is presented the mixture of two complexes possessing different structures. The first complex forms through the coordination of Ca²⁺ with phenanthroline heterocyclic part, in the other one Ca²⁺ is located in crown ether moiety.

The nature of metal ion influences on the structures of the formed complexes. Thus, at the large ligand concentration in case of Zn²⁺the formation of $2_3 \cdot Zn^{2+}$ was found, whereas, for Ca²⁺ we observed the complex $2_2 \cdot Ca^{2+}$. The composition of complexes changes as $2_3 \cdot Zn^{2+} \rightarrow 2_2 \cdot Zn^{2+} \rightarrow 2 \cdot Zn^{2+}$ and $2_2 \cdot Ca^{2+} \rightarrow 2 \cdot Ca^{2+} \rightarrow 2 \cdot (Ca^{2+})_2$ upon increase of metal ion concentration. Interestingly, that coordination of Ca²⁺ by $2_2 \cdot Zn^{2+}$ causes the gradual occupation of both the crown moieties by calcium ions resulting in the $2_2 \cdot Zn^{2+} \cdot (Ca^{2+})_2$ complex.

Plane ligand **2** structure provides long chromophoric molecule reached out from phenanthroline residue up to N-atom of the macrocyclic part. Due to the structure, it is possible to monitor the interaction of the metal with heterocyclic or macrocyclic parts

Table 2

Quantum yields of fluorescence of ligands **1**, **2** and their complexes with Zn²⁺ and Ca²⁺ cations, MeCN.

Compound	1	1 ·Ca ²⁺	$1_3 \cdot \mathbf{Zn}^{2+}$	2	$2 \cdot Ca^{2+}$	$2_{3} \cdot Zn^{2+}$	$2_2 \cdot Zn^{2+} \cdot (Ca^{2+})_2$
Quantum yield, φ	0.11	0.17	0.09	0.1	0.002	0.6×10^{-3}	$\textbf{0.68}\times 10^{-3}$

of ligand. Thus, the coordination of metal ions with phenanthroline residue causes the bathochromic shift in absorption and fluorescence spectra. In opposite, the binding of metal ion by macrocyclic moiety results in the hypsochromic spectral shift.

Molecular binuclear complexes of the metal-ligand-metal type in their mixed nature are useful systems to study the basic aspects of electron, energy, charge transfer reactions. The understanding of the synthetic chemistry associated with the preparation of highlyconjugated, polymetallic metal complexes and the availability of spectroscopic and computational methods which permit detailed assessments of electronic structure provide a growing capacity to identify and rationalize the intricacies of conductance measurements in metal|molecule|metal junctions.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2016.02.029.

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