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To appear in: Polyhedron

Received Date:8 October 2015Accepted Date:26 December 2015

Please cite this article as: A.S. Burlov, V.G. Vlasenko, N.I. Makarova, K.A. Lyssenko, V.V. Chesnokov, G.S. Borodkin, I.S. Vasilchenko, A.I. Uraev, D.A. Garnovskii, A.V. Metelitsa, E.L. Mukhanov, T.V. Lifintseva, I.V. Pankov, Chemical and electrochemical synthesis, molecular structures, DFT calculations and optical properties of metal-chelates of 8-(2-tosylaminobenzilideneimino)quinoline, *Polyhedron* (2015), doi: http://dx.doi.org/10.1016/j.poly.2015.12.048

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## CHEMICAL AND ELECTROCHEMICAL SYNTHESIS, MOLECULAR STRUCTURES, DFT CALCULATIONS AND OPTICAL PROPERTIES OF METAL-CHELATES OF 8-(2-TOSYLAMINOBENZILIDENEIMINO)QUINOLINE

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#### ABSTRACT

Bis-chelate complexes with composition  $ML_2$  ( $M^{2+}$  = Co, Ni, Cd and Zn) were synthesized on the basis of potential tridentate N, N, O donor Schiff base ligand - 8-(2tosylaminobenzilideneimino)quinoline (HL) by both chemical (CS) and electrochemical synthesis (ES). CS of zinc complexes leads to obtaining the compounds with composition ZnLCOOCH<sub>3</sub>. Structure and properties of the prepared compounds have been studied by means of elemental analysis, IR, <sup>1</sup>H NMR spectroscopy as well as quantum-chemical computations. Electronic spectra of UV-vis absorption and photoluminescence for cadmium and zinc complexes were studied in acetonitrile solution. Crystal structure of zinc and cadmium complexes was determined by X-Ray analysis. In the zinc complex ZnN<sub>6</sub> coordination site was realized due to involving the nitrogen atom of quinoline fragment in coordination to the metal ion. Meanwhile due to X-Ray analysis data cadmium complex

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possesses  $CdN_6O$  surroundings with additional coordination of oxygen atom of tosylamino group from one of the ligand. Cobalt and zinc complexes were assigned to have the octahedral structures on the basis of the physical chemical measurements.

#### **1. Introduction**

Among metal complexes of acyclic azomethine ligands there is special place for chelates of zinc, cadmium and other metals with coordination sites  $MN_4$ ,  $MN_2O_2$  that were obtained on the basis of Schiff bases (I) derived from 2-hydroxy- or 2-tosylaminobenzaldehydes possessing photo- (PL) and electroluminescent (EL) properties. Zinc and cadmium chelate complexes with azomethine ligands are used as emitting and electron-transport layers for OLED devices [1-7] due to their synthetic availability, high PL and EL characteristics, high thermal stability, accessibility of vacuum sublimation for obtaining the homogeneous films during production of OLED layers.

Complexes containing quinoline moiety attract great interest despite more than 20 years of history for proposed by Tang and Van Slyke [8] usage of tris-(8-hydroxyquinolinato) aluminum. This compound was firstly used for development of the OLED device working with low voltage [9-14].

There are well known Schiff base ligands emitting in the blue spectral region such as derivatives of salicylic aldehydes and 2,4-dimethyl-7-aminoquinolines and their zinc complexes [15]. Emission maxima of PL ligands are located in the area  $\lambda_{PL}$ =476-524 nm. For zinc complexes these maxima undergoes bathochromic shift and exhibits in the area  $\lambda_{PL}$ =503-532 nm. Quantum yields of luminescence for ligands are minor ( $\varphi$ =0.001-0.005), while they are increasing for complexes up to  $\varphi$ =0.15.

Complexes of bis{3-methyl-1phenyl-4-[(quinoline-3(or 6)-imino)-methyl]1-Hpyrazol-5-onato}zinc(II) were synthesized [16, 17]. Bis{3-methyl-1-phenyl-4-[(quinoline-3-imino)-methyl]1-H-pyrazol-5-onato}zinc (II) was used to obtain OLED with configuration ITO/Cupc/2-TNTA/Spiro-TPD/Zn complex/BCP/BPhen/LiF/A1 emitting in the yellow spectral region ( $\lambda_{EL} = 600$  nm) with a luminance of 800 Cd/m<sup>2</sup> at a voltage of 10 V that corresponds to luminous efficiency of 0.5 Lm/W. For the device

with electroluminescent layer of bis{3-methyl-1phenyl-4-[(quinoline-6-imino)methyl]1-H-pyrazol-5-onato}zinc (II) brightness characteristics are 200 Cd/m<sup>2</sup> at a voltage of 13 V.

The similar complexes of zinc and cadmium with 3- (or 6)-[2-(N-tosylaminobenzilidene)]aminoquinoline were synthesized [17]. OLED device was produced by using bis{[6-(2-tosylaminobenzilidene)]amino]quinolinato}zinc(II) for an emitting layer. Device emitted yellow light with CIE (x=0.463, y=0.484), brightness was150 Cd/m<sup>2</sup> at a voltage of 10 V.

Here we report the chemical [20] and electrochemical [21] synthesis of novel cobalt, nickel, zinc and cadmium complexes on the base of 8-(2-tosylaminobenzilideneimino)quinoline aimed for searching new metal-chelates with PL properties as potential materials for OLED[18, 19].

#### 2. Experimental

#### 2.1. Materials required and general methods

All starting materials and solvents were used as commercial products. 2tosylaminobenzaldehyde was prepared as described earlier [22]. C, H, N elemental analysis was performed in the analytical laboratory of Institute of Physical and Organic Chemistry (SFU, Rostov-on-Don, Russia). The metal content was determined gravimetrically.

Infrared spectra were recorded on a «Varian Excalibur-3100» FT-IR spectrophotometer by attenuated total internal reflection technique.

NMR <sup>1</sup>H spectra were measured on a «Advance-600» (Bruker) spectrometer at ambient temperature in DMSO- $d_6$  with the signal of residual <sup>2</sup>H of the solvent as the internal reference.

The magnetic susceptibility of the solid state samples has been measured by the Faraday's method at room temperature.

UV/vis spectra were registered on «Varian Cary 100» spectrophotometer. Spectra of fluorescence were measured on a «Varian Cary Eclipse» grating spectrofluorometer.

Acetonitrile (Aldrich) of spectral grade were used for preparing the solutions. The fluorescence quantum yield were determined by Parker-Reese technique [23] using 3-methoxybenzathrone in toluene ( $\varphi = 0.1$ ,  $\lambda_{irr.} = 365$  nm) as a standard luminophore [24].

#### 2.2. Ligand synthesis

Synthesis of 8-(2-Tosylaminobenzilideneimino)quinoline I: A hot solution of 1.44 g (0.01 mol) 8-aminoquinoline in 10 ml of ethanol was added to the hot solution of 2.75 g (0.01 mol) 2-tosylaminobenzaldehyde [22] in 50 ml of ethanol. Mixture was refluxed for 2 hours. The formed yellow precipitate was filtered off and recrystallized from ethanol-dioxane (3:1). Yellow crystals with  $T_m$  190 – 192 °C; yield 84%. Found, %: C 68.15, H 4.35, N 10.11. C<sub>23</sub>H<sub>19</sub>N<sub>3</sub>O<sub>2</sub>S calculated, %: C 68.81, H 4.77, N 10.47.

#### 2.3. Synthesis of complexes

#### 2.3.1. Chemical synthesis

Solutions of cobalt(II) or nickel(II) acetate tetrahydrate (0.001 mol) or solution of zinc(II), cadmium(II) acetate dihydrate (0.001 mol) in 10 ml of ethanol were added to the warm solution of 0.8 g (0.002 mol) azomethine I in 40 ml of ethanol. Mixture was refluxed for 2 hours. After cooling precipitate of complexes was filtered off and recrystallized from chloroform-ethanol mixture (1:2).

#### 2.3.2. Electrochemical synthesis

Electrochemical synthesis of complexes **II** was performed by standard method [25] using the reaction of azomethine **I** with anode complex-former (Co, Ni, Zn, Cd) dissolving in methanol.

Electrochemical cell could be described as below:

Cathode (Pt): 2HL + 2e  $\rightarrow$  2L<sup>-</sup>+H<sub>2</sub>

Anode (M= Co, Ni, Zn, Cd):  $M^0 - 2e \rightarrow M^{2+}$ 

Solution:  $2L^{-} + M^{2+} \rightarrow ML_2$ 

Methanol solution (25 ml) containing 0.4 g (0.001 mol) of ligand I and 0.01 g of  $Et_4NClO_4$  as a conductive additive. Electrolysis was carried out during 2 hours under constant electric current of 40 mA and voltage 15V.

Obtained precipitates of metal complexes were filtered off, washed three times with 5 ml of methanol and dried in vacuum.

2.3.3. Bis[8-(2-tosylaminobenzylideneimino)quinolinato]nickel(II) (**Ha**). Brown crystals with  $T_m > 250$  °C, yield 62% (CS), 75% (ES). CS: found, %: C 64.18, H 4.28, N 9.82, Ni 6.79. ES: found, %: C 64.25, H 4.23, N 9.76, Ni 6.82. For C<sub>46</sub>H<sub>38</sub>N<sub>6</sub>O<sub>4</sub>S<sub>2</sub>Ni calculated, %: C 64.27, H 4.22, N 9.78, Ni 6.83.

2.3.4. Bis[8-(2-tosylaminobenzilideneimino)quinolinato]cobalt(II) (**IIb**). Brown powder with  $T_m > 250$  °C, yield 60% (CS), 65% (ES). CS: found, %: C 64.37, H 4.29, N 9.80, Co 6.97. ES: found,%: C 64.39, H 4.25, N 9.87, Co 6.94. For C<sub>46</sub>H<sub>38</sub>N<sub>6</sub>O<sub>4</sub>S<sub>2</sub>Co calculated, %: C 64.25, H 4.22, N 9.77, Co 6.85.

2.3.5. Bis[8-(2-tosylaminobenzilideneimino)quinolinato]zinc(II) (**IIc**). Yellow powder with  $T_m > 250$  °C. Yield 55% (CS). CS: found, %: C 63.71, H 4.25, N 9.82, Zn 7.59. ES: found, %: C 63.68, H 4.22, N 9.77, Zn 7.62. For C<sub>46</sub>H<sub>36</sub>N<sub>6</sub>O<sub>4</sub>S<sub>2</sub>Zn calculated, %: C 63.77, H 4.19, N 9.70 S 7.40 Zn 7.55.

2.3.6. [8-(2-tosylaminobenzylideneimino)quinolinato]zinc(II) acetate (IIIb). Yellow powder with  $T_m > 250$  °C. Yield 65% (ES). ES: found, %: C 57.42, H 4.09, N 8.10, Zn 12.57. For C<sub>25</sub>H<sub>21</sub>N<sub>3</sub>O<sub>4</sub>SZn calculated, %: C 57.21, H 4.03, N 8.00, Zn 12.46.

2.3.7. Bis[8-(2-tosylaminobenzilideneimino)quinolinato]cadmium(II) (IId). Yellow crystals with  $T_m > 250$  °C, yield 56% (CS), 68% (ES). CS: found, %: C 60.51, H 3.68, N 9.25, Cd 12.42. ES: found, %: C 60.56, H 3.73, N 9.21, Cd 12.49. For C<sub>46</sub>H<sub>38</sub>N<sub>6</sub>O<sub>4</sub>S<sub>2</sub>Cd calculated, %: C 60.49, H 3.47, N 9.20, Cd 12.31. Chemical shifts in NMR <sup>1</sup>H and <sup>13</sup>C spectra of solutions I, IIc, IId and IIIb in  $DMSO-D^6$  are presented in table 1. 190R

Table 1.

2.4. X-ray diffraction

X-ray diffraction of compounds IIc and IId was carried out on the diffractometer «Bruker SMART APEX2» (MoK $\alpha$ -irradiation, graphite monochromator,  $\theta$ -scanning). Structure was solved by method of least squares with anisotropic full-matrix approximation with F<sup>2</sup><sub>hkl</sub>. Analysis of differential Fourier synthesis shown that in crystal of IIc and IId there is disorder of solvent molecules: molecules of water in six positions for Zn and dichloromethane in three positions for Cd. Impact of solvent molecules on the dissipation was excluded by using Squeeze procedure [26] taking into consideration complex type of their disordering. In both cases presence of solvent molecules was accounted for calculation of all structural characteristics such as density, F (000) etc. Positions of hydrogen atoms were calculated geometrically and refined in the isotropic approximation by the riding model.

Main crystallographic data and parameters of refining are presented in table 2. All calculations were carried out with SHELXTL PLUS software [27]. Crystals of **IIc** and **IId** suitable for XRD were obtained by slow evaporation of chloroform-methanol (1:1) solutions.

Table 2

#### 2.5. Quantum-chemical calculations

All geometries **I-III** in the ground state were fully optimized at the DFT level using GAUSSIAN-03 computer program [28]. For calculations the hybrid three-parameter functional B3LYP [29] and the standard split-valence polarization basis set 6-31G(d) [30] were chosen. Simulations of UV-vis absorption spectra for these molecules were accomplished in the framework of Dependent Density Functional Theory (TD-DFT) using optimized atomic structure parameters with account of solvent effects by the standard polarizable continuum model (PCM) with integral equation formalism method [31].

#### 3. Results and discussion

As it was shown previously [10, 18] for complexes  $CuL_2$  the reaction between the potentially tridentate azomethine I (LH, X=NTs) and copper(II) acetate dehydrate leads to mononuclear CuLCOOCH<sub>3</sub> complex (IIIa) preserving acetate group instead of expected bis-chelate II (Scheme 1). Bis-chelate CuL<sub>2</sub> complexes (II) are obtained in the case of ES.



Scheme 1

All complexes II synthesized by CS and ES methods possess  $ML_2$  composition due to elemental analysis. The only exception is zinc complex IIIb obtained by CS

method. According to data of elemental analysis **IIIb** possess ZnLCOOCH<sub>3</sub> composition.

#### 3.1. Spectroscopic properties and magnetochemical measurements

NH-group proton signals have been registered in the spectra of azomethine I at  $\delta$ =13.22 ppm and they were shown to disappear in NMR 1H spectra of **IIc,d** and IIId (M = Zn, Cd) that indicates deprotonation of ligand and obtaining the chelate complexes.

Comparative analysis of <sup>1</sup>H, <sup>13</sup>C, <sup>15</sup>N NMR spectra for compound I and its metallochelates **IIc,d** and **IIIb** has been presented in table 1. Chemical shift for <sup>113</sup>Cd nuclei is -525.51 ppm. Signals were assigned by using the correlation of COSY, HSQC, HMBS techniques.

Positions of <sup>13</sup>C signals change insignificantly (for <sup>13</sup>C signals scale) both for atoms located on the periphery of ligands system as well as for atoms close to the coordination site (specifically C(5-8), C(10-18), C(20-25), atoms numeration is on the scheme 1). On the other side shift of the protons signals for H(10), H(18), H(22) and H(23) in the high field region in comparison with azomethine **I** spectra (table 1) could be related to the closeness with electron-donor atoms forming coordination sphere. Involving the N(3) atom into coordination is confirmed by the disappearance of proton's signal of H(3) in tosylamino-group near the 13.22 ppm region.

Involving the N(1) and N(19) atoms into coordination is directly proved by 30-50 ppm shift of their signals in the high-field region. Also it is proved by the spin – spin coupling through coordinated nitrogen atoms with constants  ${}^{3}J_{H(10)-Cd} = 20.65$  Hz and  ${}^{3}J_{H(18)-Cd} = 13.85$  Hz. Unfortunately we were not able to find signals of N(3) nitrogen atom in the  ${}^{15}$ N NMR spectra but its involving in the coordination is of no doubt.

IR spectral and magnetic properties for compounds **I**, **II** and **IIIb** are presented in table 3. All IR-spectra of **IIa-d** complexes are identical (table 3). Disappearance of the vNH absorption band (near 3040 cm<sup>-1</sup>) is observed as well as reducing of the frequency of valent vibrations for CH=N (at 3-15 cm<sup>-1</sup>),  $v_{as}SO_2$  (at 45-50 cm<sup>-1</sup>) and  $v_sSO_2$  (at 24-28 cm<sup>-1</sup>) that indicates the formation of chelate structures. In IR spectrum of **IIIb** absorption band at 1644 cm<sup>-1</sup> corresponding to vCO of acetate group is registered.

Proton signals for  $CH_3$  moiety of acetate group are presented in NMR <sup>1</sup>H spectra of **IIIb** complex in the high field region at 1.73 ppm that indicates the formation of complex with preserving the acetate anion.

Values of the effective magnetic moment for chelates **IIa** (3.07 MB) and **IIb** (4.85 MB) (table 3) are typical for Ni(II) and Co(II) ions with octahedral surroundings.

#### Table 3.

IR and <sup>1</sup>H, <sup>13</sup>C spectra of compounds obtained by ES method coincide with data for complexes obtained by CS.

#### 3.2. Molecular structures of **IIc** and **IId**

Molecular structure of complexes **IIc,d** was determined by X-Ray analysis and shown on Fig. 1. Both organic ligands in the complex are tridentate-coordinated to zinc ion by quinoline (N(1), N(1')), azomethine (N(2), N(2')) and amine (N(3), N(3')) nitrogen atoms. Coordination polyhedron of Zn(1) is distorted octahedral. Ligands in complex possess almost the similar structure. Both ligands are non-planar: dihedral angles between average planes of atoms from benzene and quinoline cycles are 45.97 and 44.68° correspondingly.

Six-membered metal-chelate rings of Zn(1)N(2)C(10)C(11)C(12)N(3) and Zn(1)N(2')C(10')C(11')C(12')N(3') have chair conformations and Zn(1) ion is significantly displaced from average plane of other atoms (on 1.030 and 0.911 Å correspondingly).

Five-membered rings of Zn(1)N(1)C(5)C(6)N(2)  $\mu$  Zn(1)N(1')C(5')C(6')N(2') have envelope conformations with Zn(1) as a flap atom that displaced from average plane of other atoms on 0.575 and 0.601 Å correspondingly.

Fig. 1.

There is weak stacking interaction in single crystal of complex **IIc** between quinoline cycles of two nearby molecules; cycles are strictly coplanar, distance between average planes is 3.326 Å, distance between centers - 3.616 Å (Fig. 2).

#### Fig. 2.

Structure of cadmium complex **IId** (Fig. 3) exhibits the number of significant distinctions. One ligand is tridentate-coordinated to cadmium ion by N(1), N(2) and N(3) atoms; second ligand has additional coordination of oxygen atom of tosyl group O(1') (d Cd(1)-O(1') 2.665(2) Å). Coordination polyhedron of cadmium ion could be described as distorted pentagonal bipyramidal with N(2), N(1'), N(2'), N(3') and O(1') atoms lying in the basis while N(1) and N(3) atoms occupied axial positions.

#### Fig. 3.

Coordination of oxygen atoms of tosyl group to cadmium ion leads to noticeable flattening of the tetradentate-coordinated structure of the ligand.

Dihedral angle between average planes of atoms from benzene and quinoline cycles is 28.87°, whereas it is equal to 41.41° for tridentate-coordinated structure. It leads to significant inequality as concerns to structure of metallochelate rings. Both sixmembered rings have chair conformation, but Cd(1) ion is displaced from average plane of other atoms on 0.470 Å for tridenate-coordinated ligand and on 0.998 Å for the second ligand

Five-membered metallochelate rings Cd(1)N(1')C(5')C(6')N(2') and Cd(1)N(1)C(5)C(6)N(2) possess envelope conformations with Cd(1) as a flap atom that displaced from average plane of other atoms on 0.621 and 0.477 Å, correspondingly.

Structure of complex **IId** also contains 0.5 molecule of water forming hydrogen bond O(1W)-H(1WB)...O(1') in crystal with following characteristics: d(D-H) 0.90, d(H...A) 2.05, d(D...A) 2.947(9) Å,  $\angle$ (DHA) 174°.

Select interatomic distances and bond angles for **IIc,d** coordination compounds are presented in tables 4 and 5.

#### table 4

#### table 5

#### 3.3. Photoluminescent properties

The study of optical and photoluminescent behavior of 8-(2-tosylaminobenzilideneimino)quinoline **I** as well as cadmium (IId) and zinc (**IIIb**) complexes obtained on its base has been carried out in acetonytrile solution.

Obtained data are presented in table 6. Electronic absorption spectrum and photoluminescent of solutions **I**, **IId**, **IIIb** are presented in figure 4 as an illustration.

#### Table 6

#### **Fig. 4.**

The structural analogues of azomethine I were previously investigated by methods of absorption and luminescent spectroscopy [31] and it was shown that azomethine molecules could exist in at least two tautomeric forms - benzoid Ia and quinoid Ib (scheme 2). The equilibrium between the forms depends on temperature and solvent properties.

The structural and electronic properties of the tautomeric forms **Ia** and **Ib** have been calculated in the frame of density functional theory both in gas phase and DMSO solution. The most stable isomer is **Ia** due to results of quantum-chemical modeling and its energy is on 6.22 kcal/mol lower than that for **Ib** both in gas phase and acetonytrile solutions.

Molecules of aniles of ortho-tosylaminoaldehydes as well as aniles of orthohydroxyaldehydes undergo intermolecular proton transfer in excited state under UV irradiation. This process is responsible for appearing the fluorescence with anomalous Stokes shifts at 77 K and obtaining the fluorescent keto-structures.



Wide absorption band at the 300 - 400 nm region with maximum at 337 nm that is typical for the benzoid **Ia** form is observed in the electronic absorption spectra of azomethine **I** in acetonitrile solution at 293 K (Table 6, Fig 4).

PL properties were not observed in the solution as it was the case for previously studied aniles of ortho-tosylaminobenzaldehydes which were non fluorescent in benzoid form at room temperature [33].

Electronic absorption spectra of solutions of Cd complex (**IId**) and Zn complex (**IIIb**) (Table 6, Fig 4) in acetonytrile solution are characterized by the longwave absorption bands with maxima at 398 nm (**IId**) and 399 nm (**IIIb**) as well as molar extinction coefficient equal to 28400 and 14900 mol<sup>-1</sup>cm<sup>-1</sup> correspondingly.

As it is shown on the Fig. 4 intensity of the absorption of bis-chelate complex with composition  $CdL_2$  (IId) is approximately twice as large as the absorption of complex with ZnLCOOCH<sub>3</sub> composition (IIIb).

According to experimental data (Table 6) emission bands for zinc and cadmium **IIIb** and **IId** complexes undergo bathochromic shift on 127 nm ( $\lambda_{PC}$  =524-527 nm) in comparison with the absorption bands.

Emission bands in fluorescent spectra of **IIIb** and **IId** are bathochromically shifted on approximately 30 nm in comparison with previously obtained complexes have being synthesized on the base of 3- or 6-(2-tosylaminobenzilideneimino) quinoline ligands [17].

Complexes exhibit fluorescent properties in solution (green light was observed): metal complexes (Fig. 4) are characterized by wide band of fluorescence at the 420 – 750 nm region with maxima at 527 (**IId**) and 524 nm (**IIIb**).

PL band's maxima undergo bathochromic shift of about 27 nm compared to PL peaks of previously studied zinc (II) and cadmium (II) bis[3- or 6- (tosylaminobenzilideneimino)quinoline] [32] that have  $\lambda_{PL} = 495-497$  nm.

cadmium Comparing of PL properties of zinc bis[8-(2and complexes with zinc bis[8-(2tosylaminobenzilideneimino)quinoline] hydroxybenzilideneimino)quinoline] complex ( $\lambda_{PL} = 540 \text{ nm}, \phi = 0.39$ ) [33] reveals that replacing hydroxy group at the 2-tosylamino group leads to insignificant (about 11-12 nm) hypsochromic offset of PL bands maxima and about two order of magnitude reduction of the quantum yield of PL.

The excitation spectra were also registered as dependence between wave length of the exiting radiation and intensity of luminescence at a fixed wave length. Fluorescent excitation spectrum combined with absorption spectrum of Cd complex (**IId**) is shown at Figure 5 as an illustration.

#### Figure 5

Fluorescent excitation spectrum is in a good agreement with absorption spectrum that indicates the validity of assignment of fluorescence to complex compound of the identified structure. Quantum yields of fluorescence of Cd and Zn complexes (**IId**) and (**IIIb**) are low and equal to 0.007 and 0.003 correspondingly, which is more than two orders of magnitude less than the quantum yield of similar complexes containing 3- or 6-aminoquinoline fragment [32]. Therefore the EL properties of cadmium (**IId**) and zinc (**IIIb**) complexes have not been studied in this work.

3.4. DFT study of UV-vis spectra and molecular structures of IId and IIIb

Calculations of absorption spectra of the **IIIb** and **IId** complexes have been accomplished in the present work using the time-dependent density functional theory (TD-DFT) method. The assignment of the excitation energies to the experimental bands

was performed on the basis of the energy values and oscillator strengths. The B3LYP functional and 6-31(d) basis set were chosen because it was proved to provide accurate structures and reasonable UV-vis spectra for a variety of organometallic complexes.

Experimental and theoretical absorption spectra for **IIIb** and **IId** are compared on Fig. 4. Quantitative characteristics of absorption bands of the theoretical electronic absorption spectra and their interpretations are presented in Tables 6, 7.

#### Table 7

In electronic absorption spectra of **IIIb** absorption band at 329 nm reveals the high value of oscillator strength and is determined by single electronic transition from  $\pi$ -bonding orbital (HOMO) up to  $\pi^*$  - antibonding orbital (LUMO) of ligands. HOMO and LUMO of **IIIb** is presented on Fig. 6. As it is shown HOMO has maximal contribution of  $\pi$  MO of benzilideneimine part of the ligand while  $\pi^*$  LUMO is mostly localized on quinoline moiety.

#### Figure 6

Electronic absorption spectra of Cd complex reveals longwave absorption band at 401 nm which is determined by the series of electronic transitions HOMO  $\rightarrow$  LUMO, HOMO  $\rightarrow$  LUMO+1, HOMO-1 $\rightarrow$  LUMO. Oscillation strength for the most longwave transition HOMO  $\rightarrow$  LUMO is insignificant and electronic transition HOMO-1 $\rightarrow$  LUMO makes main contribution into appearing of the absorption band. HOMO for **IId** makes the maximal contribution of  $\pi$  MO of quinoline fragment while  $\pi^*$  LUMO is mostly localized on benzilidenimime moiety in contrast to Zn complex **IIIb**. The bands at 329 nm (**IIIb**) and 341 nm (**IId**) in the electronic absorption spectra correspond to electronic transitions HOMO-2  $\rightarrow$  LUMO and HOMO-3  $\rightarrow$  LUMO, HOMO-3  $\rightarrow$  LUMO, HOMO-2  $\rightarrow$  LUMO+1, correspondingly (Table 7).

#### 4. Conclusion

Thus, the present results and the data [17] show that the implementation of different composition and structure of the metal complexes depend on the position of the amino

group (3, 6 or 8) in the quinoline moiety of azomethine I, the nature of the metal and the method of synthesis. Five-coordinated chelate complexes of copper (II)  $CuL_2$  and  $CuLCOOCH_3$  [18] were synthesized from potentially tri-dentate ligand - 8-(2-tosylaminobenzilideneimino)quinoline. Chemical synthesis from metal acetates leads to obtaining of the complexes  $ML_2$  (M=Ni, Co, Cd) and ZnLCOOCH<sub>3</sub> for zinc. Chelates  $ML_2$  were obtained with nitrogen atom of quinoline fragment participating in the coordination under the conditions of electrochemical synthesis. Additional coordination of the nitrogen atom of quinoline fragment is realized only in the case of 8-aminoquinoline based ligands.

PL and EL properties of zinc and cadmium complexes depend on the position of the amino group in 3, 6 or 8-quinoline moiety. PL band's maxima of zinc and cadmium bis[8-(2-tosylaminobenzilideneimino)quinolines] undergo bathochromic shift by about 27 nm compared to PL peaks of previously studied zinc(II) and cadmium(II) bis[ 3- or 6-(2-tosylaminobenziledeneimino)quinoline] complexes, and fluorescence quantum yields are two orders of magnitude smaller.

Spectral properties of zinc and cadmium complexes are determined by the position (3, 6 or 8) of quinoline moiety in azomethine ligand. Additional coordination to nitrogen atom of metal by quinoline moiety of 8-(2atom tosylaminobenzilideneimino)quinoline ligand leads to the obtaining of more rigid structures of Zn and Cd complexes that appears in more significant bathochromic shift of the fluorescent bands. Quantum yields of the fluorescence are insignificantly affected by the position of amino group in the quinoline moiety.

### Acknowledgements

IR and NMR spectra were obtained using facilities of the "Molecular Spectroscopy" Multi-user Center of the Southern Federal University. This work was performed in the framework of the Project Part of the State Assignment in Academic Areas (Project No. 4.742.2014/K).

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**Fig. 1.** Molecular structure of **IIc** complex (thermal ellipsoids are presented with 30 % possibility, hydrogen's atoms are not shown).



**Fig. 2.** Packing of molecules of complex **IIc** in single crystal (view along crystallographic axis c, hydrogen's atoms are not shown )



30 % possibility , hydrogen's atoms are not shown).



**Fig. 4.** UV-vis (l - 3) and fluorescence emission ( $\lambda_{ex}$ =400 nm) (4, 5) spectra of compounds **I** (1), **IId** (3, 4) and **III** (2, 5) in acetonitrile ( $c = 2 \cdot 10^{-5}$  M, l = 1 cm) at 293 K. For comparison UV–Vis spectra of **IId** and **III** calculated by TD-DFT (dash line). The spectra have been broadened using a Lorentzian function.



**Fig. 5.** UV-vis (1), fluorescence emission ( $\lambda_{ex}$ =400 nm) (2) and fluorescence excitation ( $\lambda_{obs}$ =530 nm) (3) spectra of **IId** in acetonitrile ( $c = 2 \cdot 10^{-5}$  M, l = 1 cm) at 293K.

6



**Fig.6**. Visualization of HOMO and LUMO distributions and the calculated frontal orbital energies for **III** and **IId**.

**Table 1**. Chemical shifts in NMR <sup>1</sup>H, <sup>13</sup>C, <sup>15</sup>N spectra of compounds I, IIc, IId and III (DMSO-d<sup>6</sup>)

Compound	Nucl.	1( <sup>15</sup> N)	2( <sup>113</sup> Cd)	$3(^{1}\mathrm{H},^{15}\mathrm{N})$	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19( <sup>15</sup> N)	20	21	22	23	24	25	26
T	<sup>1</sup> H			13.22		7.68	7.46	7.19	7.72		8.86		7.56	7.67	7.91		8.43	7.63	9.00				7.95	7.31		2.29	
1	<sup>13</sup> C/ <sup>15</sup> N	309.69		122.13	138.79	117.86	132.14	122.92	134.02	121.94	163.64	146.17	117.83	126.60	126.12	128.46	135.91	121.91	150.10	307.10	141.60	136.54	126.82	129.47	143.36	20.66	
IIc	<sup>1</sup> H					7.23	7.31	7.01	7.68		9.23		8.27	7.84	8.12		8.77	7.89	9.04				7.71	7.18		2.18	
	<sup>1</sup> H					7.50	7.21	6.82	7.68		8.92		7.84	7.60	7.70		8.20	7.34	8.72				7.57	7.00		2.21	
11a	<sup>13</sup> C/ <sup>15</sup> N	274.61	-525.51		150.42	119.76	132.51	117.95	139.22	122.72	169.28	144.24	118.64	127.55	126.09	127.69	137.75	121.82	148.56	273.04	138.84	140.83	126.86	128.73	130.22	20.69	
III	<sup>1</sup> H					7.23	7.31	7.00	7.68		9.23		8.27	7.85	8.11		8.75	7.89	9.01				7.71	7.18		2.26	1.73
111	<sup>13</sup> C/ <sup>15</sup> N	255.83			147.63	122.12	133.23	120.57	136.70	124.00	164.89	139.49	116.98	127.96	127.50	128.62	139.87	123.23	150.48	254.60	139.67	140.97	126.69	129.05	141.20	20.77	
													5														

Parameter	IIc	IId
Formula	C <sub>46</sub> H <sub>36</sub> N <sub>6</sub> O <sub>4</sub> S <sub>2</sub> Zn, 0.5	C <sub>46</sub> H <sub>36</sub> CdN <sub>6</sub> O <sub>4</sub> S <sub>2</sub> , 0.5 (H <sub>2</sub> O),
Tornula	$(H_2O)$	$CH_2Cl_2$
Molecular weight	875.31	1009.28
Т, К	120	120
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
Z	2	2
a, Å	12.0859(13)	13.5684(8)
$b, \mathrm{\AA}$	13.3355(15)	13.7208(8)
<i>c</i> , Å	15.5460(17)	14.1257(8)
$\alpha$ , degree	70.291(2)	68.8299(10)
$\beta$ , degree	67.365(2)	79.2373(11)
γ, degree	68.573(2)	66.1039(10)
$V, Å^3$	2095.6(4)	2239.6(2)
$ ho_{ m выч},\ \Gamma \cdot cm^{-3}$	1.387	1.497
$\mu$ , cm <sup>-1</sup>	7.39	7.53
<i>F</i> (000)	906	1030
$2\theta_{\rm max}$ , °	60	58
Number of measured reflections	25118	20627
Number of independent reflections	12132	11811
Number of reflections with $I > 2\sigma(I)$	6157	9879
Number of parameters refined	534	543
$R_1$	0.0550	0.0391
$wR_2$	0.1129	0.0894
GOF	0.953	0.864
<b>Residual electron density</b> , $(\Delta \rho_{min}/\Delta \rho_{max})$ , e·Å <sup>-3</sup>	0.698/-0.552	1.857/-0.616
Data CCDC	CCDC 1415982	CCDC 1415987

### Table 2. Crystal data and structure refinement parameters for IIc and IId

No	Μ	vNH,cm <sup>1</sup>	vCO,cm <sup>-1</sup>	vCH=N,cm <sup>-1</sup>	$v_{as}SO_2, cm^{-1}$	$v_s SO_2, cm^{-1}$	$\mu_{\varphi\varphi\phi}, MB$
Ι		3040 br.	-	1620	1334	1157	-
IIa	Ni	-	-	1615	1289	1129	3.07
IIb	Co	-	-	1617	1268	1133	4.85
IIc	Zn	-	-	1620	1280	1129	-
IId	Cd	-	-	1605	1283	1133	-
III	Zn		1644	1619	1280	1130	-
	C						

Table 3. Physical-chemical characteristics of azomethine I and complexes II, III

Bond	$d, \mathrm{\AA}$	Bond	d, Å
Zn(1)–N(2')	2.062(2)	Zn(1)–N(3)	2.138(2)
Zn(1)–N(2)	2.088(2)	Zn(1)-N(1)	2.275(2)
Zn(1)–N(3')	2.112(2)	Zn(1)–N(1')	2.313(2)
Angle	α, degree.	Angle	α, degree.
N(2')Zn(1)N(2)	161.74(9)	N(3')Zn(1)N(1)	99.79(8)
N(2')Zn(1)N(3')	86.51(8)	N(3)Zn(1)N(1)	159.33(8)
N(2)Zn(1)N(3')	107.55(8)	N(2')Zn(1)N(1')	75.61(8)
N(2')Zn(1)N(3)	105.80(8)	N(2)Zn(1)N(1')	89.05(8)
N(2)Zn(1)N(3)	85.24(9)	N(3')Zn(1)N(1')	161.40(8)
N(3')Zn(1)N(3)	94.03(9)	N(3)Zn(1)N(1')	95.69(8)
N(2')Zn(1)N(1)	90.41(8)	N(1)Zn(1)N(1')	75.66(8)
N(2)Zn(1)N(1)	76.00(9)		

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**Table 4.** Selected bond lengths *d* and angles  $\alpha$  in coordination polyhedron of zinc atom in molecule **IIc** 

Table 5	5.	Selected	bond	lengths	d	and	angles	α	in	coordination	polyhedron	of
cadmiu	m	atom in n	nolecu	le IId								

Bond	d, Å	Bond	<i>d</i> , Å
Cd(1)–N(3)	2.3072(19)	Cd(1)–N(2)	2.4017(18)
Cd(1)–N(3')	2.3575(19)	Cd(1)–N(1)	2.4059(19)
Cd(1)–N(2')	2.3678(19)	Cd(1)–N(1')	2.433(2)
Angle	α, degree	Angle	α, degree
N(3)Cd(1)N(3')	110.79(7)	N(2')Cd(1)N(1)	91.51(7)
N(3)Cd(1)N(2')	118.78(7)	N(2)Cd(1)N(1)	69.09(6)
N(3')Cd(1)N(2')	78.00(7)	N(3)Cd(1)N(1')	91.21(7)
N(3)Cd(1)N(2)	77.44(7)	N(3')Cd(1)N(1')	146.74(7)
N(3')Cd(1)N(2)	123.58(7)	N(2')Cd(1)N(1')	69.44(7)
N(2')Cd(1)N(2)	148.66(7)	N(2)Cd(1)N(1')	84.47(6)
N(3)Cd(1)N(1)	146.52(7)	N(1)Cd(1)N(1')	86.35(7)
N(3')Cd(1)N(1)	87.94(7)		

**Table 6.** UV/vis and photoluminescence data of **I**, **IId**, **III** in acetonitrile at 293 K:  $\varepsilon$  -molar extinction coefficient,  $\varphi$  – quantum yield of the fluorescence.

	Absorption	Pho	toluminescence	;
No.	$\frac{1}{2} nm \left( c M^{-1} cm^{-1} \right)$	Excitation	Emission	
	$\lambda_{\rm max}$ , IIII (c, IVI CIII )	$\lambda_{max}$ , nm	$\lambda_{max,} \ nm$	φ
	232 (52900)			
Ι	264sh (13950)	-	-	0
	337 (11900)			
	226 (103600)			
	244sh (77430)		9	
IId	295 (27550)	400	527	0.007
	334 (23800)			
	398 (28400)			
	226 (63000)			
	241sh (49100)			
III	314sh (16940)	397	524	0.003
	335 (17350)			
	399 (14900)			
sh – sho	ulder			
C ,				

**Table 7**. Wavelengths ( $\lambda$ ), energies (*E*), oscillator strengths (*f*) of principle vertical electron transitions and their assignment according to TD-DFT calculations for **III** and **IId**.

		III				IId	
λ, nm	E, eV	Electron transitions and their contributions, $\%^*$	f	λ, nm	E, eV	Electron transitions and their contributions, %	f
438.11	2.830	HOMO $\rightarrow$ LUMO (89 %)	0.29	467.25	2.654	HOMO $\rightarrow$ LUMO (98 %)	0.003
362.01	3.425	HOMO-2 $\rightarrow$ LUMO (17 %) HOMO-1 $\rightarrow$ LUMO (70 %)	0.23	455.78	2.720	HOMO $\rightarrow$ LUMO+1 (94 %)	0.08
347.67	3.566	$HOMO \rightarrow LUMO+1 (92)$ %)	0.05	446.5	2.777	$\begin{array}{c} \text{HOMO-1} \rightarrow \text{LUMO} (88 \\ \%) \end{array}$	0.15
337.93	3.669	HOMO-2 $\rightarrow$ LUMO (73 %) HOMO-1 $\rightarrow$ LUMO (17 %)	0.15	368.85	3.361	HOMO $\rightarrow$ LUMO+2 (95 %)	0.02
300.65	4.124	HOMO-6 $\rightarrow$ LUMO (18 %) HOMO-3 $\rightarrow$ LUMO (14 %) HOMO-1 $\rightarrow$ LUMO+1 (36 %) HOMO $\rightarrow$ LUMO+3 (19 %)	0.03	349.59	3.547	HOMO-3 → LUMO (71 %)	0.20
238.36	5.202	HOMO-6 $\rightarrow$ LUMO+1 (21 %) HOMO-2 $\rightarrow$ LUMO+3 (51 %) HOMO-1 $\rightarrow$ LUMO+3 (13 %)	0.11	348.86	3.554	HOMO-3 $\rightarrow$ LUMO (10 %) HOMO-2 $\rightarrow$ LUMO+1 (64 %)	0.21
233.4	5.312	HOMO-8 → LUMO+1 (20 %) HOMO-7 → LUMO+1 (44 %) HOMO → LUMO+5 (14 %)	0.17	344.29	3.601	HOMO-3 → LUMO+1 (91 %)	0.04
232.85	5.325	HOMO-2 $\rightarrow$ LUMO+3 (38 %) HOMO-1 $\rightarrow$ LUMO+3 (17 %)	0.17	297.95	4.161	HOMO-3 $\rightarrow$ LUMO+2 (55 %) HOMO-2 $\rightarrow$ LUMO+2 (12 %)	0.05
229.77	5.396	HOMO-8 $\rightarrow$ LUMO+1 (59 %) HOMO-2 $\rightarrow$ LUMO+2 (10 %)	0.17	295.23	4.200	HOMO-3 $\rightarrow$ LUMO+2 (12 %) HOMO-2 $\rightarrow$ LUMO+2 (42 %) HOMO-2 $\rightarrow$ LUMO+3	0.07

				(10  M)	
				(10%)	
	HOMO-1 $\rightarrow$ LUMO+4	(14			
220 54 5 401	%)	0.11			
229.34 3.401	HOMO $\rightarrow$ LUMO+6 (	47			
	%) HOMO 3 \LUMO+2	(64			
218.66 5.670	$\begin{array}{c} 110110-3 \rightarrow 120110+2\\ \end{array}$	0.28			
*only electron	n transitions with contribut	ions >10% are sh	own.		



#### Graphical abstract

The metal-chelates with the composition  $ML_2$  (M = Co(II), Ni(II), Cd(II) and Zn(II)) were synthesized and characterized by X-ray, UV–Vis, IR, NMR and luminescent properties. The UV–Vis spectra were detail studied by DFT calculations.

Accepting