

Research Article

Open Access

Emiliya Nosova*, Tatyana Stupina, Artem Chupakhin, Galina Lipunova,
Marina Valova, Pavel Slepukhin, Valery Charushin

Synthesis, crystal structures, and fluorescent properties of zinc(II) complexes with benzazino-2-carboxalidin-2-aminophenols

Abstract: Complexes ZnL_2 with novel fluorinated benzazines as tridentate ligands (HL = 6,7-difluoroquinoxalin- and 6,7-difluoroquinolincarboxalidin-2-aminophenol) have been prepared. The photophysical properties of the ligands and the complexes has been studied.

Keywords: Benzazine-2-carbaldehyde, o-Aminophenol, Schiff base, Zinc (II) complex, Fluorescence

DOI: 10.1515/chem-2015-0005

received October 24, 2013; accepted May 4, 2014.

1 Introduction

Benzazines containing the azomethine fragment in position 2 could be considered as aza-analogs of 2-styrylbenzazines, which garner attention because of their application in materials for electronic devices [1-4]. On the other hand, the presence of an azomethine group allows for the production of metalochelates, which have photoluminescent properties and applications for electroluminescent materials [5-8]. Recently special attention has been paid to N,N,O-ligands, as they are capable to form individual lanthanide complexes with intense luminescence [9].

The presence of a fluorine atom in a ligand leads to an increase of thermal and chemical stability, and

solubility in organic solvents, and as a result, expands possibilities for application in equipment; in particular, it improves the quality of films based on such materials possessing unique physical and chemical properties [10]. Recently we have managed to obtain new fluorine-containing N,N,O-ligands such as (2-phenylquinazolin-4-yl)hydrazones of 2-hydroxybenzaldehydes and have studied their photophysical properties [11]. Quinoxalino-2-carboxalidin-2-aminophenols—which represent attractive tridentate ligands for Mn(II), Fe(III), Ni(II), Cu(II) and Co(II) complexes—have been investigated [12], but data on Zn(II) complexes are extremely limited though. For instance, work [13] reports about the octahedral structure of quinoxalino-2-carboxalidin-2-amino-5-methylphenol zinc complex, and the geometry of the Zn(II) complex is supposedly similar to the structure of the Ni(II) complex, but X-ray data in this publication are absent. 6,7-Difluoro-analogs of such Schiff bases are not described. Even 6,7-difluoroquinoxalin-2-carbaldehyde, the major intermediate for their synthesis, is not mentioned in the literature. In the present paper, new Zn(II) complexes **5a-d** (Scheme 1) have been synthesized and their fluorescent properties investigated.

2 Experimental procedure

2.1 Materials and measurements

2-Methylquinoxaline, quinaldine, selenium(IV) oxide and $Zn(OAc)_2 \cdot 2H_2O$ were purchased from Aldrich Chemical Company Inc. and used as received. All other reagents were of analytical grade.

2.2 Physical techniques

All melting points were determined using a Stuart SMP3 Melting Point Apparatus in open capillary tubes. 1H NMR

*Corresponding author: **Emiliya Nosova:** Department of Organic Chemistry, Chemical Technology Institute, Urals Federal University named after the First President of Russia Boris N. Yestsin, Ekaterinburg 620002, Russia, E-mail: emily74@rambler.ru

Tatyana Stupina, Artem Chupakhin, Galina Lipunova: Department of Organic Chemistry, Chemical Technology Institute, Urals Federal University named after the First President of Russia Boris N. Yestsin, Ekaterinburg 620002, Russia

Galina Lipunova, Marina Valova, Pavel Slepukhin, Valery Charushin: I. Postovsky Institute of Organic Synthesis, Ural Division of the Russian Academy of Sciences, Ekaterinburg 620219, Russia

spectra were recorded on a Bruker DRX 400 instrument (400.13 MHz). Chemical shifts are given in ppm (δ) from the internal TMS standard. Mass spectra were obtained from a MicroTOF-Q II mass spectral instrument (Bruker Daltonics, positive or negative APCI ion source, electrospray ionization). Acetonitrile (99% purity) and 2-methyltetrahydrofuran (99%, stab. with ca 150-400 ppm BHT) (Alfa Aesar, UK) were used at UV-spectroscopy grade. Absorption spectra were scanned on a UV-2401 PC absorption spectrophotometer (Shimadzu, Japan) using a 1 cm quartz cell, concentration: 0.0001 mmol mL⁻¹ (acetonitrile). Emission spectra were recorded on a Cary Eclipse spectrofluorimeter (Varian, USA). The fluorescence of the acetonitrile solution at T = 293 K was measured in a 1-cm cuvette. Low-temperature measurements were carried out in a liquid nitrogen cryostat OptistatDN (Oxford Instrument) in 2-methyltetrahydrofuran solution at T = 293 K and T = 77 K.

All reactions were monitored by thin layer chromatography (TLC) on 0.2 mm silica gel F-254 (Merck) plates using light (254 and 365 nm) for detection. Elemental analyses were performed at the Microanalytical Laboratory of the Postovsky Institute of Organic Synthesis.

2.3 Preparation of 6,7-difluoroquinoxalin-2-carbaldehyde (3d)

2-Methyl-6,7-difluoroquinoxalin **1d** was synthesized using method [14].

[2-(6,7-Difluoroquinoxalin-2-yl)vinyl]dimethylamine (2). To a solution of quinoxaline **1d** (0.87 g, 4.83 mmol) in DMF (4 mL), *N,N*-dimethylformamide dimethyl acetal (1.3 mL, 9.66 mmol) was added. The mixture was refluxed for 12 h, with solid forming after the mixture was washed with ethanol. Yield 0.91 g (80%), mp 120-122°C. ¹H NMR (DMSO-*d*₆): δ 3.05 (6H, s, NMe₂), 5.28 (1H, m, CH=), 7.47 (1H, m, CH=), 7.66 (1H, m, H-8), 7.83 (1H, m, H-5), 8.55 (1H, m, H-3). Anal. calc. for C₁₂H₁₁F₂N₃: C, 61.27; H, 4.71; N, 17.86. Found: C, 61.40; H, 4.62; N, 17.55%.

6,7-Difluoroquinoxalin-2-carbaldehyde (3d). Two grams of NaIO₄ was dissolved in a phosphate buffer (pH=7, 15 mL) and a solution of compound **2** (0.8 g, 3.4 mmol) in THF (15 mL) was added while stirring. The mixture was stirred for 5 h at room temperature. After removing the solvent, colorless residue was washed by ethyl acetate. Ethyl acetate solution was dried over Na₂SO₄, and after removing the solvent, light-brown solid of **3d** was obtained.

Yield 0.3 g (45%), mp 132-134°C. ¹H NMR (DMSO-*d*₆): δ 8.16 (1H, dd, H-5, ³*J* 10.6, ⁴*J* 8.2 Hz), 8.24 (1H, dd, H-8, ³*J* 10.5, ⁴*J* 8.3 Hz), 9.33 (1H, s, H-3), 10.18 (1H, s, CHO). MS (ES⁺): *m/z* 195 [M+H]⁺ (100 %). Anal. calc. for C₉H₄F₂N₂O: C, 55.68; H, 2.08; N, 14.43. Found: C, 55.72; H, 2.14; N, 14.38%.

2.4 Preparation of ligands 4

[2-(6,7-Difluoroquinoxalin-2-ylmethylene)amino]phenol (4d). To a solution of *o*-aminophenol (0.3 g, 2.75 mmol) in ethanol (15 mL) warmed to 60-70°C, a solution of aldehyde **3d** (0.5 g, 2.58 mmol) in ethanol (3 mL) was added dropwise. The mixture was heated to 80°C for 30 min, and then cooled to room temperature; the resulting orange-brown solid was filtered off. Yield 0.32 g (43%), mp 225-227°C. ¹H NMR (DMSO-*d*₆): δ 6.86 (1H, m, H-4'), 6.92 (1H, m, H-6'), 7.16 (1H, m, H-5'), 7.38 (1H, m, H-3'), 8.03 (2H, m, H-5, H-8), 8.95 (1H, s, CH=N), 9.26 (1H, c, H-3), 9.97 (1H, c, OH). MS (ES⁺): *m/z* 286 [M+H]⁺ (100%). Anal. calc. for C₁₅H₉F₂N₃O: C, 63.16; H, 3.18; N, 14.73. Found: C, 63.20; H, 3.15; N, 17.75%.

Ligands **4a-c** were prepared by the same method; preparation of compound **4a** was reported [15].

[2-(Quinolin-2-ylmethylene)amino]phenol (4a): yield 78%, mp 113-115°C. ¹H NMR (DMSO-*d*₆): δ 6.84 (1H, m, H-4'), 6.91 (1H, m, H-6'), 7.11 (1H, m, H-5'), 7.32 (1H, m, H-3'), 7.61 (1H, m, H-7), 7.76 (1H, m, H-6), 7.95 (1H, m, H-5), 8.07 (1H, m, H-8), 8.36 (1H, d, H-3, *J* 8.6 Hz), 8.57 (1H, d, H-4, *J* 8.6 Hz), 8.88 (1H, s, CH=N), 8.99 (1H, s, OH). MS (ES⁺): *m/z* 249 [M+H]⁺ (100%). Anal. calc. for C₁₆H₁₂N₂O: C, 77.40; H, 4.87; N, 11.28. Found: C, 77.45; H, 4.93; N, 11.24%.

[2-(6,7-Difluoroquinolin-2-ylmethylene)amino]phenol (4b): yield 74%, mp 173-175°C. ¹H NMR (DMSO-*d*₆): δ 6.84 (1H, m, H-4'), 6.91 (1H, m, H-6'), 7.12 (1H, m, H-5'), 7.31 (1H, m, H-3'), 7.94 (1H, m, H-5), 7.96 (1H, m, H-8), 8.41 (1H, d, H-3, *J* 8.6 Hz), 8.60 (1H, d, H-4, *J* 8.6 Hz), 8.86 (1H, s, CH=N), 9.06 (1H, s, OH). MS (ES⁺): *m/z* 285 [M+H]⁺ (100%). Anal. calc. for C₁₆H₁₀F₂N₂O: C, 67.60; H, 3.55; N, 9.85. Found: C, 67.63; H, 3.60; N, 9.79%.

[2-(Quinoxalin-2-ylmethylene)amino]phenol (4c): yield 69%, mp 236-238°C. ¹H NMR (DMSO-*d*₆): δ 6.87 (1H, m, H-4'), 6.93 (1H, m, H-6'), 7.16 (1H, m, H-5'), 7.39 (1H, m, H-3'), 7.86 (2H, m, H-6, H-7), 8.12 (2H, m, H-5, H-8), 8.96 (1H, s, CH=N), 9.24 (1H, s, H-3), 9.95 (1H, s, OH). MS (ES⁺): *m/z* 250 [M+H]⁺ (100%). Anal. calc. for C₁₅H₁₁F₂N₃O: C, 72.28; H, 4.45; N, 16.86. Found: C, 72.34; H, 4.50; N, 16.82%.

2.5 Preparation of Zn(II) complexes 5

Zn(II) Complex of [2-(6,7-difluoroquinoxalin-2-ylmethyl)amino]phenol (5d). A methanol solution (7 mL) of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (0.035 g, 0.19 mmol) was added to a methanol solution (18 mL) of ligand **4d** (0.1 g, 0.35 mmol) while stirring. The mixture was stirred for 48 h at room temperature, the solvent was evaporated, and the violet residue was washed by acetonitrile (5 mL) and diethyl ether (10 mL). Yield 0.05 g (45 %), mp > 300°C. ^1H NMR ($\text{DMSO}-d_6$): δ 6.44 (1H, m, H-4'), 6.69 (1H, m, H-6'), 7.12 (1H, m, H-5'), 7.60 (1H, m, H-3'), 8.08 (1H, m, H-5), 8.37 (1H, m, H-8), 9.17 (1H, s, H-3), 9.36 (1H, s, CH=N). Anal. calc. for $\text{C}_{30}\text{H}_{16}\text{F}_4\text{N}_6\text{O}_2\text{Zn}$: C, 56.88; H, 3.16; N, 13.26. Found: C, 56.90; H, 3.21; N, 13.25%.

Complexes **5a-c** were prepared by the same method.

Zn(II) Complex of [2-(quinolin-2-ylmethyl)amino]phenol (5a): yield 81%, mp > 300°C. ^1H NMR ($\text{DMSO}-d_6$): δ 6.31 (1H, m, H-6'), 6.36 (1H, m, H-4'), 6.98 (1H, m, H-5'), 7.42 (2H, m, H-6, H-7), 7.58 (1H, m, H-5), 7.78 (1H, m, H-3'), 7.89 (1H, m, H-8), 8.09 (1H, d, H-3, J 8.5 Hz), 8.56 (1H, d, H-4, J 8.5 Hz), 9.31 (1H, s, CH=N). Anal. calc. for $\text{C}_{32}\text{H}_{22}\text{N}_4\text{O}_2\text{Zn}$: C, 68.64; H, 3.96; N, 10.01. Found: C, 68.58; H, 3.92; N, 10.08%.

Red crystals suitable for X-ray diffraction were obtained by slow cooling of hot saturated solution of **5a** in dry dimethylformamide.

Zn(II) Complex of [2-(6,7-difluoroquinolin-2-ylmethyl)amino]phenol (5b): yield 73%, mp > 300 °C. ^1H NMR ($\text{DMSO}-d_6$): δ 6.36-6.43 (3H, m, 2H-6', H-4'), 6.02 (1H, m, H-4'), 7.02-7.11 (2H, m, 2H-5'), 7.26-7.31 (1H, m, H-3'), 7.56 (1H, d, H-3, J 9.6 Hz), 7.79 (1H, d, H-3, J 8.6 Hz), 7.97 (2H, m, 2H-5), 8.05-8.18 (2H, m, 2H-8), 8.39-8.44 (1H, m, H-3'), 8.61 (1H, d, H-4, J 9.6 Hz), 8.64 (1H, d, H-4, J 8.6 Hz), 9.02 (1H, s, CH=N), 9.39 (1H, s, CH=N). Anal. calc. for $\text{C}_{32}\text{H}_{18}\text{F}_4\text{N}_4\text{O}_2\text{Zn}$: C, 60.83; H, 2.87; N, 8.87. Found: C 60.79; H 2.83; N 8.93%.

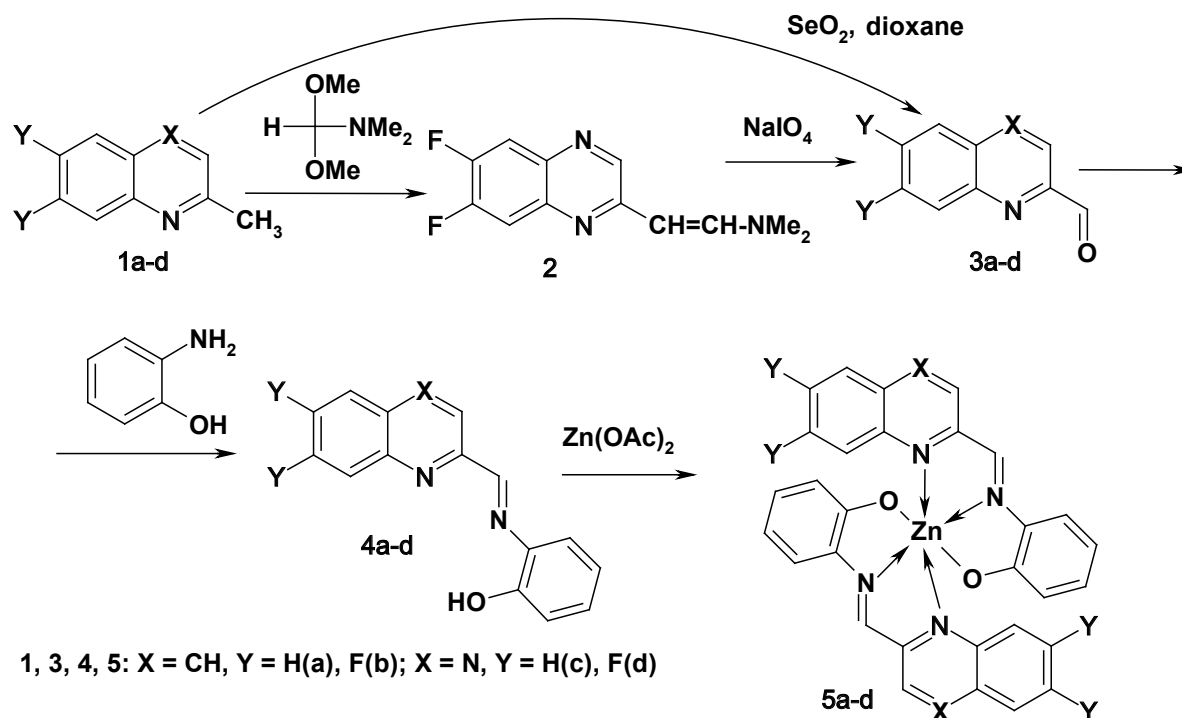
Zn(II) Complex of [2-(quinoxalin-2-ylmethyl)amino]phenol (5c): yield 77%, mp > 300°C. ^1H NMR ($\text{DMSO}-d_6$): δ 6.40 (1H, m, H-6'), 6.45 (1H, m, H-4'), 7.05 (1H, m, H-5'), 7.50 (1H, m, H-3'), 7.56 (1H, m, H-8), 7.69 (1H, m, H-7), 7.82 (1H, m, H-5), 8.01 (1H, m, H-6), 9.44 (1H, s, H-3), 9.48 (1H, s, CH=N). Anal. calc. for $\text{C}_{30}\text{H}_{20}\text{N}_6\text{O}_2\text{Zn}$: C, 64.13; H, 3.59; N, 14.96. Found: C 64.09; H 3.55; N 15.01%.

Table 1: Crystallographic data of **5a**.

Empirical formula	$\text{C}_{38}\text{H}_{36}\text{N}_6\text{O}_4\text{Zn}$ ($\text{C}_{32}\text{H}_{22}\text{N}_4\text{O}_2\text{Zn} \cdot 2\text{C}_3\text{H}_7\text{NO}$)
Temperature/K	295(2)
Crystal size	0.25×0.20×0.15
Crystal system	Monoclinic
Space group	$C2/c$
$a/\text{\AA}$	21.429(3)
$b/\text{\AA}$	10.2256(3)
$c/\text{\AA}$	17.0330(2)
$\beta/^\circ$	117.49
$V/\text{\AA}^3$	3310.7(4)
Z	4
μ/mm^{-1}	0.793
$D_c/\text{g cm}^{-3}$	1.417
Reflections collected	14041
Unique reflections	3386
Observed reflections [$I \geq 2\sigma(I)$]	1810
R_{int}	0.0609
$R_1 [I \geq 2\sigma(I)]$	0.0469
$R_w [I \geq 2\sigma(I)]$	0.1108
$GOOF$	1.004
$\Delta\rho_{\text{min}}/\Delta\rho_{\text{max}} \text{ e}/\text{cm}^{-3}$	0.522/-0.185
θ range for data collection	2.70° to 26.39°

2.6 X-ray crystallography

X-Ray analysis, including data collection, cell refinement and data reduction, was carried out with an Oxford Diffraction XcaliburSCCD diffractometer using CrysAlisPro software package on standard procedure (graphite monochromatized radiation with $\lambda(\text{MoK}\alpha) = 0.71073 \text{ \AA}$, ω -scanning with a step 1°); the empirical absorption correction [16] was applied. The structure was solved by direct method and refined against F^2 by full-matrix least-squares using the SHELXTL package [17]. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were placed in idealized positions and were constrained to ride on their parent atoms. The crystallographic data for the complex **5a** are summarized in Table 1. Selected bond lengths and angles are summarized in Table 2.



Scheme 1: Synthesis of the Schiff bases 4a-d and their Zn(II) complexes 5a-d.

Table 2: Selected bond lengths (Å) and angles (°) for 5a.

Bond	Length (Å)	Angle	(°)
Zn(1)-O(1)	2.074(2)	O(1)-Zn(1)-N(2)	79.26(9)
Zn(1)-N(2)	2.087(2)	O(1)-Zn(1)-N(1)	151.25(9)
Zn(1)-N(1)	2.346(2)	N(2)-Zn(1)-N(1)	73.68(9)
O(1)-C(11)	1.290(4)	C(11)-O(1)-Zn(1)	112.72(18)
N(1)-C(2)	1.317(4)	C(2)-N(1)-C(10)	118.3(2)
N(1)-C(10)	1.368(4)	C(2)-N(1)-Zn(1)	110.14(19)
N(2)-C(1)	1.277(4)	C(10)-N(1)-Zn(1)	130.76(19)
N(2)-C(12)	1.396(4)	C(1)-N(2)-C(12)	127.3(3)
C(12)-C(11)	1.424(4)	C(1)-N(2)-Zn(1)	119.9(2)
C(2)-C(1)	1.456(4)	C(12)-N(2)-Zn(1)	112.62(18)
C(1)-H(1A)	0.9300	C(13)-C(12)-N(2)	125.1(3)
C(3)-C(2)	1.413(4)	N(2)-C(1)-C(2)	118.5(3)
C(10)-C(9)	1.397(4)	C(16)-C(11)-C(12)	116.0(3)
C(10)-C(5)	1.430(4)	O(1)-C(11)-C(16)	122.4(3)
C(11)-C(16)	1.411(4)	O(1)-C(11)-C(12)	121.5(3)
		N(1)-C(2)-C(1)	117.1(3)
		N(1)-C(2)-C(3)	123.1(3)
		N(2)-C(12)-C(11)	113.2(3)
		N(1)-C(10)-C(9)	119.9(3)
		N(1)-C(10)-C(5)	121.4(3)

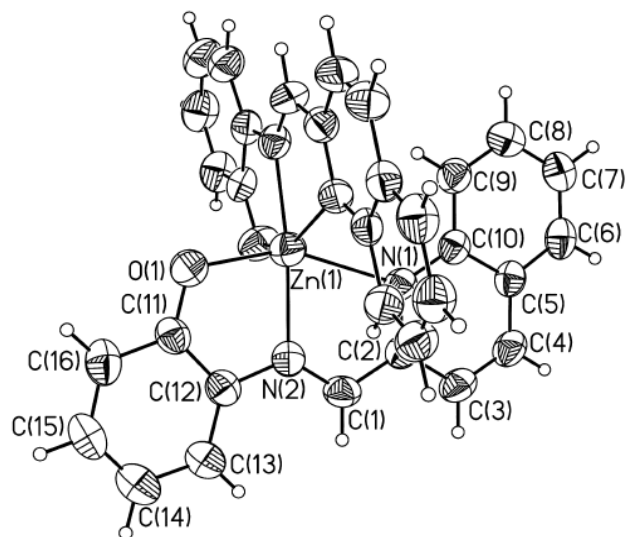


Figure 1: The structure of **5a** showing the atom-numbering scheme (crystallographic independent non-hydrogen atoms are numbered).

Table 3: Photophysical data for UV and FL spectra Schiff bases **4** and Zn(II) complexes **5** in 2-methyltetrahydrofuran at 77 K.

Compound	X	Y	λ_a , nm	λ_f , nm (I, a. u)*
4a	CH	H	248, 368	–
5a	CH	H	360, 556	651 (334)
4b	CH	F	368	–
5b	CH	F	362, 550	616 (478)
4c	N	H	378	–
5c	N	H	375, 589	715(160)
4d	N	F	375	570 (40)
5d	N	F	366, 553	657 (650)

*Excitement was carried out to areas of a long-wave band of absorption

3 Results and discussion

3.1 Synthesis and NMR spectra

2-Formylbenzazines **3a-c** are successfully formed at oxidation of 2-methyl derivatives **1a-c** with selenium dioxide in boiling dioxane [18-20]. This way did not allow individual aldehyde **3d** to be obtained, owing to a condensation process between formed aldehyde with residue of 2-methyl derivative **1d**. For this reason we chose the method described for 2-methyl-3-phenyl-3H-quinazolin-4-ones [21], for the synthesis of aldehyde **3d**. This method

is based on the interaction of 2-methylbenzazine with *N,N*-dimethylformamide dimethyl acetal and oxidation of the intermediate obtained with sodium periodate. The structures of aldehyde **3d** and intermediate **2** were confirmed by the ^1H NMR data. *o*-Hydroxyazomethynes **4a-d** have been synthesized by interaction of aldehydes **3a-d** with *o*-aminophenol in boiling ethanol during 30 min. The subsequent reaction of **4a-d** with zinc acetate in methanol led to formation of the Zn(II) complexes **5a-d** (Scheme 1).

There are no signals of OH-groups in ^1H NMR spectra of **5a-d**. The downfield shift of H-8 proton signals for difluoroderivatives **5b,d** and the upfield shift of such protons for non-fluorinated derivatives **5a,c** are observed in comparison with signals of the corresponding ligands **4**. Shift of CH=N proton signal of complexes **5a-d** in the weak field was noted, as was shift of H-6' protons signals for **5a-d** and H-3' protons signals for **5a,b,d** in the strong field, in comparison with signals of **4**.

3.2 Crystal structure

X-ray crystal structure determination was performed to confirm the structure of the complex **5a** (Fig. 1, the numbering of atoms accepted in structural experiment is shown). In x-ray data, the compound grown up from DMF is crystallized as solvate **5a**:DMF 1:2.

The complex is crystallized in the centrosymmetric space group. The molecule of the complex is placed in a private position on a rotation axis, while the Zn atom coordinates around itself two tridentate ligands. The ligand molecule closes two five-membered helate cycles. Coordination around the central atom is a distorted octahedron, thus bond lengths Zn(1)-O(1) and Zn(1)-N(2) are comparable (2.074(2) and 2.087(2) Å respectively), bond length Zn(1)-N(1) is much greater (2.346(2) Å), which indicates a mutual pushing away of a proton at C(9) from the atoms of the second ligand, and a general removal of the quinoline fragment from its plane. Fragments of the ligands are planar; the maximal deviations of non-hydrogen atoms from least-squared plane is 0.077 Å. The planes of the ligands are situated almost perpendicularly (with a deviation less 1°). This stereometry of the complex is typical and, in particular, is comparable with a stereometry of Ni-complex of quinoxaline derivative from paper [13]. However, in the Ni-complex [13], the deviations of the atoms of ligands from least-squared plane are more significant (approx. 0.16 Å), and the ligand is probably characterized better by conformational flexibility.

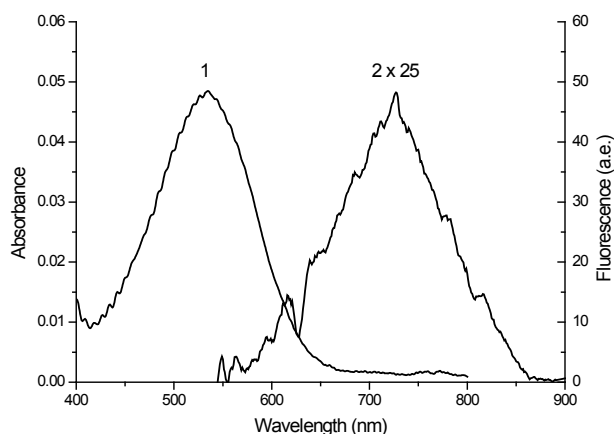


Figure 2: UV-vis spectra **5a** in CH_3CN (1) fluorescence emission ($\lambda_{\text{ex}}=530$) in CH_3CN (intensity of fluorescence is increased on 25).

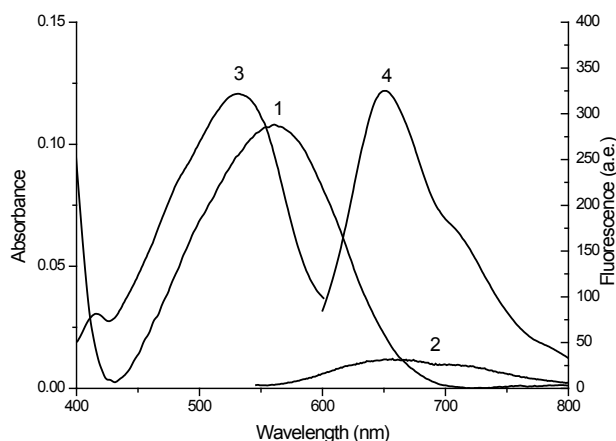


Figure 3: UV-vis spectra **5a** in 2-Me THF (1); fluorescence emission ($\lambda_{\text{ex}}=530$) in 2-Me THF at 297 K (2); fluorescence excitation ($\lambda_{\text{obs}}=650$); (3) and fluorescence emission ($\lambda_{\text{ex}}=530$); (4) in 2-Me THF at 77 K.

3.3 Fluorescent character of the ligands and the complexes

The Schiff bases **4a-d** and the Zn(II) complexes **5a-d** display low photoluminescence in acetonitrile solution at room temperature. Complex formations are accompanied by chelation of *o*-hydroxyazomethine, increasing the rigidity of the ligand and preventing photo-induced transfer of an electron, which leads to stronger emission [22-24]. The **5** complexes possess low red photoluminescence (for example, compound **5a**, Fig. 2).

Fluorescence of complex **5a** in 2-methyltetrahydrofuran solution at room temperature is also low, nevertheless at 77 K it increases considerably (Fig. 3). Complexes **5b-d** demonstrate the same increase in fluorescent intensity. Photophysical data for UV and FL spectra at 77 K are shown in Table 3.

Schiff bases bearing quinoxaline fragments (**4c,d**) show long-wave shift of absorption bands compared with analogs bearing quinoline fragments (**4a,b**). The **5** complexes **5** show considerable long-wave shift of absorption maximum compared with the corresponding ligands **4**.

The **5** complexes exhibit intense red photoluminescence with maxima at 616-715 nm. Emission spectra of difluoroderivatives **5b**, **5d** are characterized by blue shifts in comparison with non-fluorinated analogs **5a**, **5c** (Table 3). It should be noted that in such conditions, ligand **4d** demonstrates a weak orange luminescence (Table 3).

4 Conclusion

New Schiff bases as types of N,N,O-ligands were prepared, and their complex formations with zinc cations were studied. The complexes were characterized by elemental analysis, ^1H NMR spectra, and single crystal X-ray determination. Influence of structural factors on photophysical properties of ligands and complexes was shown; the fluorescent properties of the complexes indicate that they may have interesting applications.

Acknowledgement: This work was supported by the Russian Foundation for Basic Research (grant 14-03-00340), the Grants Council of the President of the Russian Federation (grant NSh-3656.2014.3) and Ural Division of Russian Academy of Sciences (project 12-P-3-1020).

Supplementary material: CCDC-996034 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at <http://www.ccdc.cam.ac.uk/const/retrieving.html> or from the Cambridge Crystallographic Data Center (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44(0)1223-336,033 or E-mail: deposit@ccdc.cam.ac.uk.

References

- [1] Lipunova G.N., Nosova E.V., Trashakhova T.V., Charushin V.N., *Rus. Chem. Rev.*, 2011, 80, 1115
- [2] Wang S.L., Lin J.M., *Chem. Phys. Lett.*, 2007, 444, 71
- [3] Barberis V.P., Mikroyannidis J.A., *Synth. Met.*, 2006, 156, 865
- [4] Cazaux L., Faher M., Picard C., Tisnes P., *Can. J. Chem.*, 1993, 71, 2007
- [5] Sano T., Nishio Y., Hamada Y., Takahashi H., Usuki T., Shibata K., *J. Mater. Chem.*, 2000, 10, 157
- [6] Pivovarov A.P., Kaplunov M.G., Yakuschenko I.K., Belov M.Yu., Nikolaeva G.V., Efimov O.N., *Rus. Chem. Bull.*, 2002, 51, 67
- [7] Kaplunov M.G., Yakuschenko I.K., Krasnikova S.S., Shamaev S.N., Pivovarov A.P., Efimov O.N., *Rus. Chem. Bull.*, 2004, 53, 2148
- [8] Kaplunov M.G., Yakuschenko I.K., Krasnikova S.S., Pivovarov A.P., Balashova I.O., *High Energy Chemistry*, 2008, 42, 563
- [9] Shavaleev N.M., Scopelliti R., Gumy F., Bunzil J.C.G., *Inorg. Chem.*, 2008, 47, 9055
- [10] Shi Y.W., Shi M.M., Huang J.C., Chen H.Z., Wang M., Lin M.D., Ma Y.G., Xu H., Yang B., *Chem. Commun.*, 2006, 1941
- [11] Trashakhova T.V., Nosova E.V., Slepukhin P.A., Valova M.S., Lipunova G.N., Charushin V.N., *Rus. Chem. Bull.*, 2011, 60, 2347
- [12] Mayadevi S., Yusuff K.K.M., *Synth. React. Inorg. Met.-Org. Chem.*, 1997, 27, 319
- [13] Sebastian M., Arun V., Robinson P.P., Varghese A.A., Abraham R., Suresh E., Yusuff K.K.M., *Polyhedron*, 2010, 3014
- [14] Nosova E.V., Trashakhova T.V., Ustyugov V.S., Mochul'skaya N.N., Valova M.S., Lipunova G.N., Charushin V.N., *Rus. Chem. Bull.*, 2011, 60, 942
- [15] Seyhan M., *Chem. Ber.*, 1952, 85, 436
- [16] Clark R.C., Reid J.S., *Acta Cryst. A*, 1995, 51, 887
- [17] Sheldrick G.M., *Acta Cryst. A*, 2008, 64, 112
- [18] Tang A., Lien E.J., Lai M.M.C., *J. Med. Chem.*, 1985, 28, 1103
- [19] Milton J., Wren S., Wang S., Folkes A., Chuckowree I., Hancox T., Miller W., Sohal S., *WO Pat*, 2004, 65389
- [20] Jarikote D.V., Li W., Jiang T., Eriksson L.A., Paul V., Murphy P.V., *Bioorg. Med. Chem.*, 2011, 19, 826
- [21] Chenard B.L., Welch W.M., Blake J.F., Batler T.W., Reinhold A., Ewing F.E., Menniti F.S., Pagnozzi M.J., *J. Med. Chem.*, 2001, 44, 1710
- [22] Metelitsa A.V., Burlov A.S., Borogkina I.G., Bren V.A., Garnovskii A.D., Minkin V.I., Bezuglyi S.O., *Russian Journal of Coordination Chemistry*, 2006, 32, 858
- [23] Chattopadhyay T., Mukherjee M., Banu K.S., Banerjee A., Suresh E., Zangtando E., Das D., *J. Coord. Chem.*, 2009, 62, 967
- [24] Basak S., Sen S., Banerjee S., Mitra S., Rosair G., Rodriguez M.T.G., *Polyhedron*, 2007, 26, 5104