

Research Article

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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 ($HL = 6,7$ -difluoroquinoxaline- and $6,7$ -difluoroquinolinicarboxalidin-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, Zink (II) complex, Fluorescence

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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 azometine 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-difluoroquinoxaline-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

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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-d₆): 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-d₆): δ 8.16 (1H, dd, H-5, ³J 10.6, ⁴J 8.2 Hz), 8.24 (1H, dd, H-8, ³J 10.5, ⁴J 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-ylmethylen)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-d₆): 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-ylmethylen)amino]phenol (4a): yield 78%, mp 113-115°C. ¹H NMR (DMSO-d₆): 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-ylmethylen)amino]phenol (4b): yield 74%, mp 173-175°C. ¹H NMR (DMSO-d₆): 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-ylmethylen)amino]phenol (4c): yield 69%, mp 236-238°C. ¹H NMR (DMSO-d₆): 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-difluoroquinolin-2-ylmethylen)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 (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-ylmethylen)amino]phenol (5a): yield 81%, mp > 300°C. ^1H NMR (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-ylmethylen)amino]phenol (5b): yield 73%, mp > 300 °C. ^1H NMR (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%.

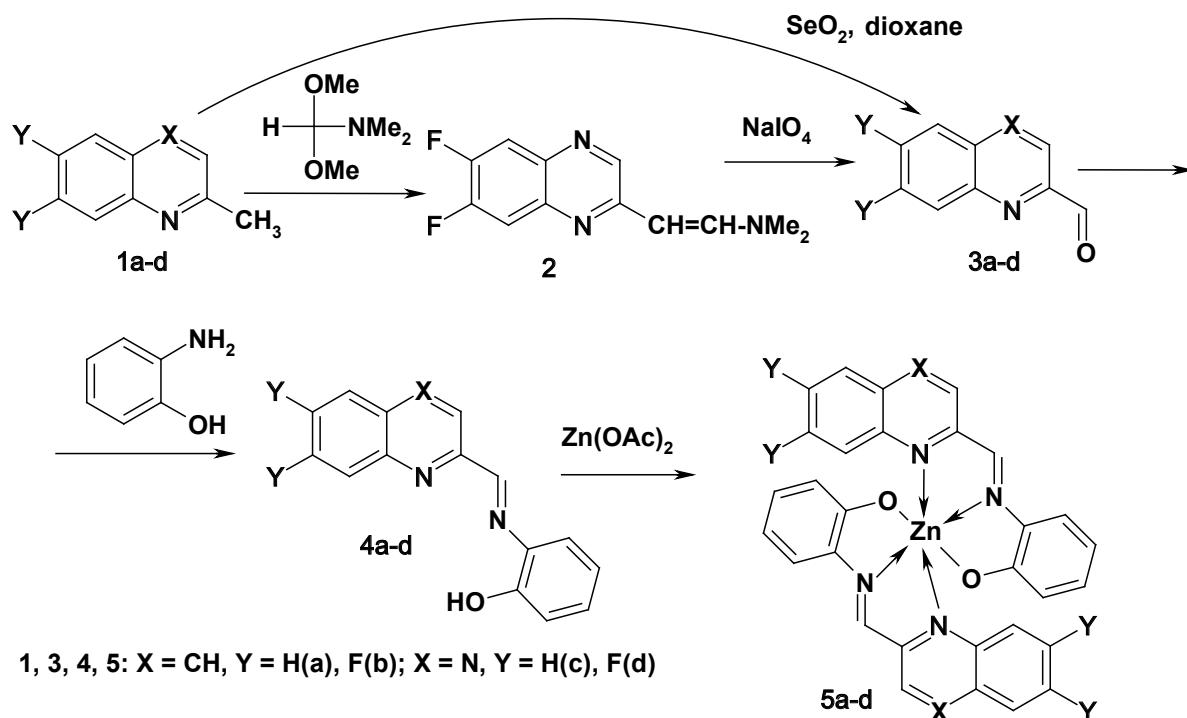
Zn(II) Complex of [2-(quinolin-2-ylmethylen)amino]phenol (5c): yield 77%, mp > 300°C. ^1H NMR (DMSO- d_6): δ 6.40 (1H, m, H-6'), 6.45 (1H, m, H-4'), 7.05 (1H, m, H-5'), 7.50 (1H, m, H-3'), 7.56 (1H, m, H-8), 7.69 (1H, m, H-7), 7.82 (1H, m, H-5), 8.01 (1H, m, H-6), 9.44 (1H, s, H-3), 9.48 (1H, s, CH=N). 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
Rw [$I \geq 2\sigma(I)$]	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 Xcalibur S CCD 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 (\AA) and angles ($^\circ$) for **5a**.

Bond	Length (\AA)	Angle	($^\circ$)
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)

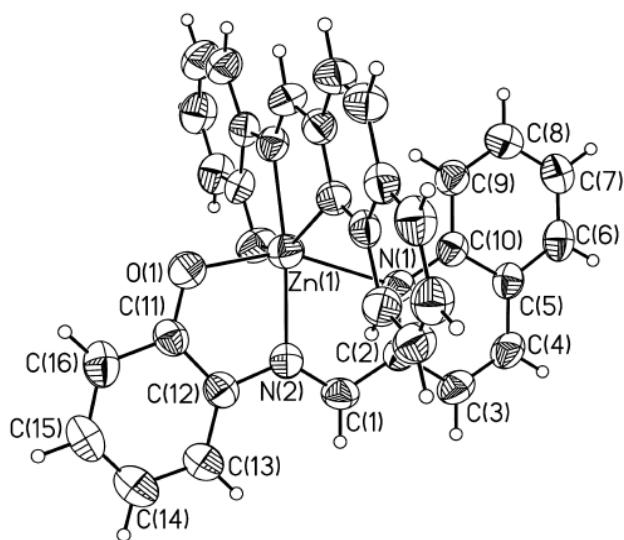


Figure 1: The structure of **5a** showing the atom-numbering scheme (crystallographic independent non-hydrogen atoms are numbered).

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_s , 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)

*Excitation 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-methylderivatives **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-methylderivative **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.

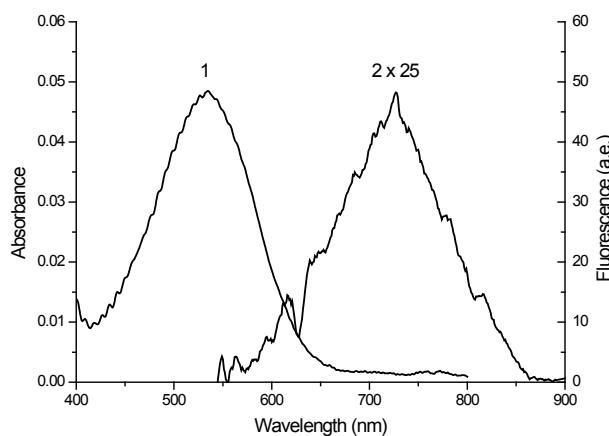


Figure 2: UV-vis spectra **5a** in CH_3CN (1) fluorescence emission ($\lambda_{\text{ex}}=530$) in CH_3CN (intensity of fluorescence is increased on 25).

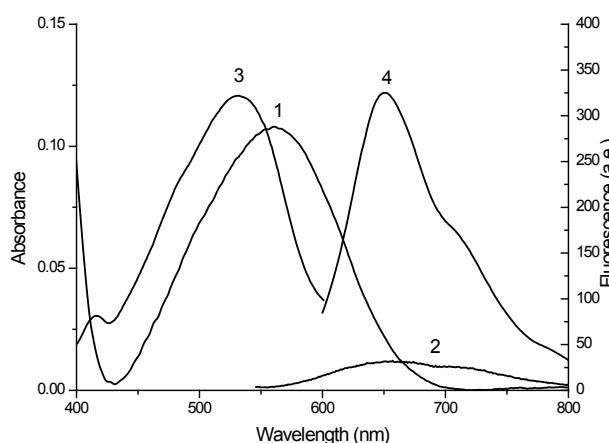


Figure 3: UV-vis spectra **5a** in 2-Me THF (1); fluorescence emission ($\lambda_{\text{ex}}=530$) in 2-Me THF at 297 K (2); fluorescence excitation ($\lambda_{\text{obs}}=650$) (3) and fluorescence emission ($\lambda_{\text{ex}}=530$) (4) in 2-Me THF at 77 K.

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 chelatation 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.

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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.

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