ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 9, pp. 1771–1776. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © E.V. Nosova, G.N. Lipunova, T.V. Stupina, P.A. Slepukhin, M.S. Valova, V.N. Charushin, 2014, published in Zhurnal Obshchei Khimii, 2014, Vol. 84, No. 9, pp. 1534–1539.

# Synthesis, Structure, and Photoluminescence Properties of Zn(II) Complexes with 2-Styryl Derivatives of 8-Hydroxyquinoline

**E. V. Nosova[a], G. N. Lipunova[b], T. V. Stupina[a], P. A. Slepukhin[b], M. S. Valova[b], and V. N. Charushin[b]**

[a] *Yeltsin Ural Federal University, ul. Mira 19, Yekaterinburg, 620002 Russia*
*e-mail: emily74@rambler.ru*

[b] *Postovskii Institute of Organic Synthesis, Ural Branch, Russian Academy of Sciences, Yekaterinburg, Russia*

Received March 27, 2014

**Abstract**—Novel Zn(II) complexes with 2-styryl-8-hydroxyquinoline were synthesized and characterized by $^{1}H$, $^{19}F$, and $^{13}C$ NMR spectroscopy and X-ray diffraction analysis. Photoluminescence properties of the ligands and complexes in solutions were studied. The effect of substituents in the quinoline and phenylethenyl fragments on spectral characteristics was discussed.

**Keywords:** 2-styryl-8-hydroxyquinoline, Zn(II) complexes, absorption spectra, emission spectra, X-ray diffraction analysis

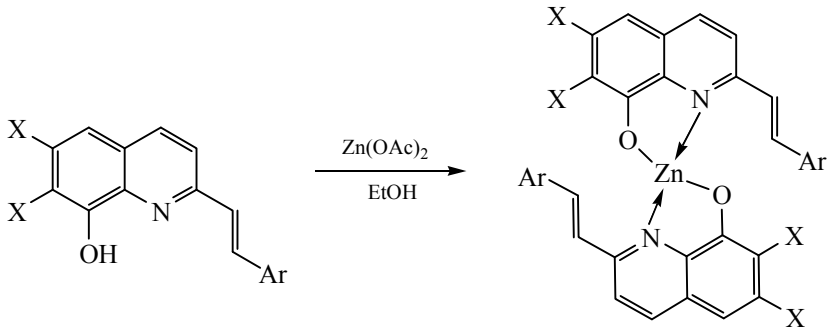
**DOI:** 10.1134/S1070363214090229

8-Hydroxyquinoline and its numerous derivatives and metal chelates fell under the scrutiny of researchers after an aluminum complex of 8-hydroxyquinoline ($AlQ_3$) having intense green luminescence, high thermal stability, and good electronic mobility had first been reported [1]. Some of them have found application in electroluminescence devices [2]. The zinc analog of $AlQ_3$ ($ZnQ_2$) was found to exhibit better characteristics [3], but both these complexes are sparingly soluble in ordinary organic solvents and, therefore, are hardly suitable for preparation of thin films. Some substituted 8-hydroxyquinolines, including fluorinated ones [4], have been reported, and the effect of substituents on the physicochemical and optical properties of 8-hydroquinoline have been studied. Owing to specific properties of fluorine atoms, metal complexes of fluorinated 8-hydroxyquinolines exhibit enhanced electronic mobility, low sublimation temperature, good stability in air, and broad band gap. Fluorine substitution in the 5 position results in a red shift of the luminescence maximum of the corresponding aluminum complex ($\lambda_{max}$ 547 nm vs 515 nm for the nonfluorinated analog) and an appreciable decrease in the luminescence intensity and quantum yield [4]. At the same time, the aluminum complex of 6-fluoro-8-hydroxyquinoline shows a blue shift ($\lambda_{max}$ 495 nm) and much increased intensity and quantum yield of luminescence. A 7-F substituent scarcely affects the luminescence properties.

Quinoline ligands are modified by extending the conjugation chain by introducing substituents, for example, styryl, into the 2 or 4 positions of the pyridine ring [3, 6–9]. The Al(III) and Zn(II) complexes of 2-styryl-8-hydroxyquinolines containing in the styryl fragment such substituents as methyl, chlorine, or methoxy, are readily soluble in ordinary organic solvents, thermally stable, and suitable for preparation of thin films. Solutions of these complexes in THF exhibit blue-green luminescence ($\lambda_{max}$ 513–576 nm) and an appreciable red shift with respect to the luminescence maxima of the $AlQ_3$ and $ZnQ_2$ complexes [3]. Even though 2-styryl(nitrostyryl)-8-hydroxyquinolines have also been reported [3, 10], their luminescent properties and zinc complexes have never been described. We previously synthesized 2-(4-methoxystyryl)-6,7-difluoro-8-hydroxyquinoline and its zinc complex and described their properties [5].

In the present paper we present the synthesis, structure, and photoluminescent properties of novel

**Scheme 1.**




**I, III, V, VII** **II, IV, VI, VIII**

X = H, Ar = Ph (**I, II**), 4-$OMeC_6H_4$ (**III, IV**), 4-$NO_2C_6H_4$ (**V, VI**); X = F, Ar = 4-$OMeC_6H_4$ (**VII, VIII**).

Zn(II) complexes of 2-styryl-8-hydroxyquinoline derivatives.

Complexes **II**, **IV**, and **VI** were synthesized by heating compounds **I**, **III**, and **V** with Zn(II) acetate in a 2 : 1 molar ratio in ethanol or DMF (Scheme 1).

The $^1$H NMR spectra (DMSO-$d_6$) of compounds **I**, **III**, and **V** contain doublets of CH=CH protons at 7.23–7.62 and 8.01–8.23 ppm (*J* 16.0–16.2 Hz), which suggests their *trans* configuration. This suggestion is consistent with published data for compounds **I** [10] and **VII** [5]. According to [3], compound **III** is a *cis* isomer in $CDCl_3$ [3]. Chang et al. [10] published the $^1$H NMR spectrum of compound **V** in $CDCl_3$ but did not discuss its configuration.

The structure of complexes **II**, **IV**, and **VI** was studied by means of $^1$H and $^{13}$C NMR spectroscopy, IR spectroscopy, and mass spectrometry. The mass spectra and elemental analyses point to a $L_2Zn$ composition of the complexes. The $^1$H NMR spectra display no OH proton signal; the pyridine $H^4$ and $H^3$ proton signals are shifted downfield from those of ligands **I**, **III**, and **V**, whereas the benzene $H^5$ and $H^7$ signals are shifted upfield. Similar shifts were also observed in the $^1$H NMR spectra of complex **VIII** [5].

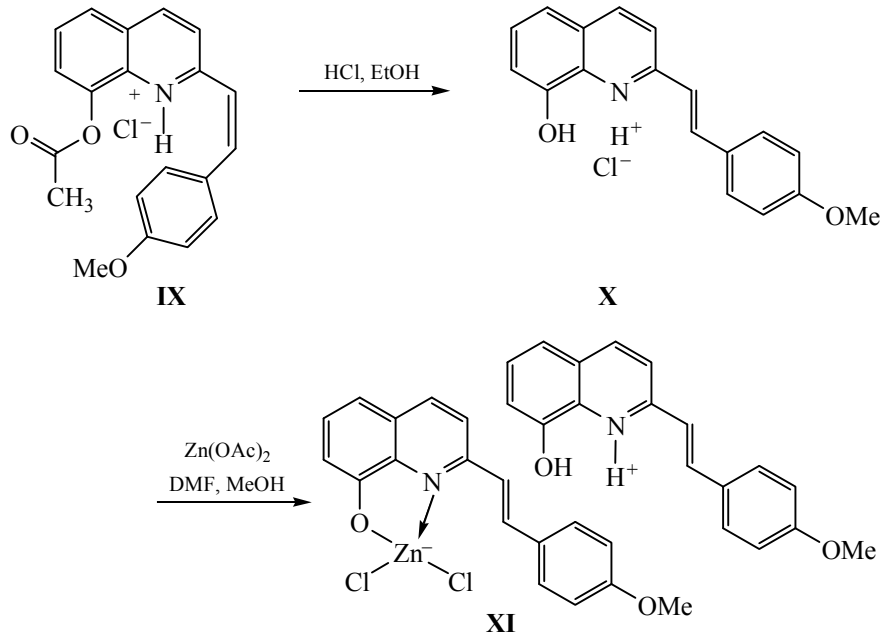
The *trans* configuration of the ligand is preserved in all the complexes, as evidenced by the observation in the $^1$H NMR spectra of vinyl doublets at 7.60–7.64 and 8.37–8.62 ppm (*J* 16.2–16.5 Hz). The IR spectra

Absorption and fluorescence data for compounds **II–X** and **XIII**[a]

| Comp. no. | X | Ar | $\lambda_{abs}$, nm | $\lambda_{fl}$, nm[b] | Stoke's shift, nm |
|---|---|---|---|---|---|
| **I** | H | $C_6H_5$ | 360 | 440 | 80 |
| **II** | H | $C_6H_5$ | 440 | 592 | 152 |
| **II**[c] | H | $C_6H_5$ | 428 | 602 | 174 |
| **III** | H | 4-$CH_3OC_6H_4$ | 320 | 430 | 110 |
| **IV** | H | 4-$CH_3OC_6H_4$ | 435 | 588 | 153 |
| **V** | H | 4-$NO_2C_6H_4$ | 357 | – | – |
| **VI**[c] | H | 4-$NO_2C_6H_4$ | 460 | 534 | 74 |
| **VII** | F | 4-$CH_3OC_6H_4$ | 352 | 455 | 103 |
| **VIII** | F | 4-$CH_3OC_6H_4$ | 420 | 560 | 140 |
| **XI** | H | 4-$CH_3OC_6H_4$ | 436 | 598 | 162 |

[a] The spectra were recorded in acetonitrile at 293 K. [b] Excitation at the absorption maximum. [c] The spectrum was recorded in DMF.

**Scheme 2.**




of complexes **II**, **IV**, and **VI** contain no bands at 3340–3375 (O–H) and 1330–1335 $cm^{-1}$ [δ(O–H)]. The long-wave band in the absorption spectra of complexes **II**, **IV**, and **VI** is shifted red by ~100 nm compared with the corresponding ligands (see table). The above evidence suggests that the metal chelate unit in complexes **II**, **IV**, and **VI**, like in **VIII**, has the composition $ZnN_2O_2$. According to **X**-ray diffraction data, the metal chelate units in the zinc complexes of 5,7-dihalo-8-hydroxyquinolines [11] and 5-nitro-8-hydroxyquinoline are composed of the same atoms [12].

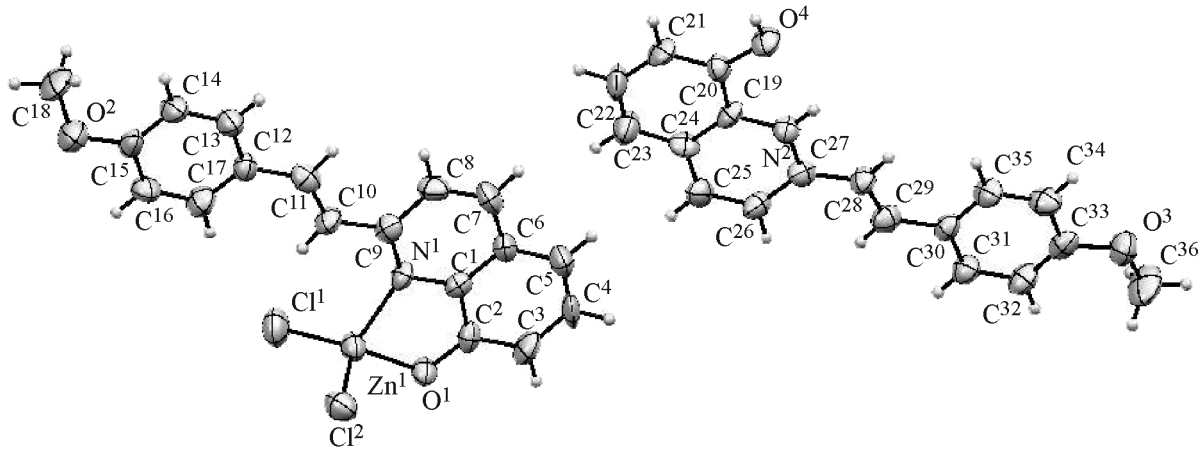
Synthesis at varied conditions was studied using the example of 2-[2-(4-methoxyphenyl)vinyl]-8-hydroxyquinoline (**III**). Hydrolysis of 8-acetoxy-2-(4-methoxystyryl)quinoline (**IX**) [3] gave hydrochloride **X** (Scheme 2). Treatment of its methanol solution with a minor addition of DMF (20 : 1) with methanolic zinc acetate at room temperature formed complex **XI**.

The $^1H$ NMR spectrum of this compound, unlike what we observed in the spectrum of complex **IV**, displayed double sets of quinoline, methoxyphenyl, and vinyl proton signals and only one OH proton signal. Elemental analysis showed that complex **XI** contained chlorine. The presence in the $^1H$ NMR spectra (DMSO) of hydrochloride **X** and complex **XI** of a doublet of the CH=CH fragment at 7.90 and 8.23 ppm (*J* 16.0 Hz) points to the preservation of the *trans* configuration. The structure of complex **XI** was determined by **X**-ray diffraction analysis (see figure).

According to **X**-ray diffraction data, complex **XI** $\{LH^+[ZnLCl_2]^-\}$ crystallizes in a centrosymmetric space group. The Zn atom in the $ZnLCl_2^-$ anion has a pseudotetrahedral configuration with close Zn–Cl bond lengths. The stereochemical parameters for the anionic and cationic forms of the organic ligand are quite close to each other. Both molecules are planar and have the quinoline and aryl moieties *trans* with respect to the HC=CH bond. The bond lengths and angles do not deviate considerably from normal values. The molecular packing features hydrogen bonding between OH groups of the cationic form and O atoms of the metal chelate unit of the anionic complex.

Excitation of solutions of compounds **I**–**VIII** and **XI** in MeCN at their absorption maxima induces a blue, green, or yellow-green photoluminescence. The extinction maxima of the ligands are at 430–455 nm and those of complexes **II**, **IV**, **VIII**, and **XI**, at 560–598 nm (see table). Because of the poor solubility of complex **VI**, its emission spectrum was measured for a DMF solution and shows a maximum at $\lambda_{max}$ 534 nm.

The luminescent properties of both 2-styryl-substituted 8-hydroxyquinolines and their complexes are affected by substituents in the quinoline and aryl fragments. Fluorine substitution in the 6 and 7 positions of the quinoline fragment shifts red the emission band in the spectra of ligands **III** and **V**, whereas the respective bands in the spectra of complexes **IV** and **VIII** undergoes a blue shift. Introduction of the




General view of a molecule of complex **XI**.

electron-donor methoxy group in the aryl fragment causes a slight (10 nm) blue shift of the emission band in the spectra of both ligands **I** and **III** and complexes **II** and **IV**. The electron-acceptor nitro group in the styryl fragment produces a considerable blue shift in the spectra of complexes **II** and **VI**. The spectrum of mixed-ligand complex **XI** having the metal coordinated in the same way as in complex **IV** shows a red shift of the emission band by 10 nm. The complexes exhibit larger Stoke's shifts compared to the ligands (see table).

## EXPERIMENTAL

The $^1$H NMR spectra in DMSO-$d_6$ and $CDCl_3$ were measured on a Bruker DRX-400 spectrometer at 400.13 MHz. The $^{19}$F NMR spectra in DMSO-$d_6$ were obtained on a Bruker Avance 400 spectrometer at 376.45 MHz. The internal standards were TMS ($^1$H) or hexafluorobenzene ($^{19}$F, $\delta_F$ 162.9 ppm). The mass spectra were run on a Shimadzu GCMS-QP2010 Ultra in the electron ionization mode. The IR spectra (4000–400 cm$^{-1}$) were obtained on a Bruker Alpha FTIR spectrometer equipped with an attenuated total reflectance attachment with a SeZn crystal. The UV spectra and fluorescence spectra in MeCN ($c = 10^{-4}$ M) were run on a Shimadzu UV-2401PC spectrophotometer and a Varian Eclipse spectrofluorimeter. The melting points were measured on a Stuart SMP3 instrument.

The **X**-ray diffraction analysis was performed on an Xcalibur S automated diffractometer (CCD detector, Mo$K_\alpha$ radiation, ω scanning). The structures were solved by a direct method using SHELXS-97 [13] and refined by anisotropic least-squares (for H atoms) using the same software suit. Hydrogen atoms were located geometrically (riding model).

**Crystals of complex XI** as thin needles were grown from a supersaturated solution in DMF. Crystal data: *a* 18.1681(15), *b* 12.3495(9), *c* 14.4452(9) Å, β 107.430(7)°, *V* 3092.2(4) Å$^3$, space group *P*2(1)/*c*, monoclinic, $C_{36}H_{30}Cl_2N_2O_4Zn$, crystal dimensions 0.25 × 0.07 × 0.01 mm, *Z* 4, $d_{calc}$ 1.484 g/cm$^3$. Intensities of 24436 reflections, 6214 reflections were unique ($R_{int}$ 0.1078) and 2185 had $I > 2\sigma(I)$. Data collection range 2.71° < θ < 26.38°, completeness 98.1%. An analytical absorption correction was applied (μ 1.011 mm$^{-1}$, $T_{min}$ 0.798, $T_{max}$ 0.970). The final divergence indices were as follows: $wR_2$ 0.0786 and $R_1$ 0.0498 for reflections with $I > 2\sigma(I)$ and $wR_2$ 0.0878 and $R_1$ 0.1954 for all reflections, *S* 1.009. All atomic coordinates and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Center (CCDC 10009943).

Compounds **VII** and **VIII** were synthesized by the procedure in [5], compounds **I** and **V**, by the procedure in [10], and compounds **III** and **IV**, by the procedure in [3].

**2-[*(E)*-2-Phenylvinyl]quinolin-8-ol (I).** IR spectrum, ν, cm$^{-1}$: 3391.79 (O−H), 1693.87, 1633.42, 1593.74, 1503.56, 1460.76, 1440.45, 1367.75 [δ(O−H)], 1226.22 (C−OH), 1155.43, 953.60 (*trans*-CH=CH), 829.34, 744.05, 719.37. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 7.03 m (1H, H$^5$), 7.28 m (1H, H$^7$), 7.30–7.34 m (2H, H$^{3'}$, H$^{5'}$), 7.37 m (1H, H$^{4'}$), 7.39 d (1H, CH=, *J* 16.2 Hz), 7.41 m (1H, H$^6$), 7.68 m (2H, H$^{2'}$, H$^{6'}$), 7.70 m (1H, H$^3$), 8.07 d (1H, CH=, *J* 16.2 Hz), 8.20 d (1H, H$^4$, *J* 8.5 Hz), 9.19 br.s (1H, OH). $^{13}$C NMR spectrum (DMSO-$d_6$), $\delta_C$, ppm: 111.26 (C$^5$), 117.60 (C$^7$), 120.99

($C^6$), 127.09 ($C^{4'}$), 127.19 ($C^{3'}$, $C^{5'}$), 127.72 ($C^{1'}$), 128.02 (CH=), 128.63 (CH=), 128.94 ($C^{2'}$, $C^{6'}$), 134.34 ($C^3$), 136.53 ($C^{4a}$, $C^4$), 138.18 ($C^2$), 152.99 ($C^{8a}$), 153.42 ($C^8$). Mass spectrum, *m*/*z* ($I_{rel}$, %): 247 (76) $[M]^+$, 246 (100), 217 (13), 114 (18).

**Zinc complex of 2-[(*E*)-2-phenylvinyl]quinolin-8-ol (II).** A hot solution of 0.2 mmol of zinc acetate in ethanol was added to a hot solution of 0.4 mmol of compound **I** in 20 mL of ethanol. The reaction mixture was heated under reflux for 6 h, and the precipitate that formed was filtered off and dried. Yield 45%, mp >250°C. IR spectrum, ν, $cm^{-1}$: 1628.80, 1597.71, 1551.66, 1504.07, 1453.67, 1434.15, 1374.64, 1333.00, 1274.15, 1204.84, 1100.86, 966.62 (*trans*-CH=CH), 828.48, 744.09, 566.46. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 6.96 m (2H, $H^5$, $H^7$), 7.32 m (1H, $H^{4'}$), 7.41 m (2H, $H^{3'}$, $H^{5'}$), 7.64 d (1H, CH=, *J* 16.5 Hz), 7.66 m (1H, $H^6$), 7.73 m (2H, $H^{2'}$, $H^{6'}$), 8.10 d (1H, $H^3$, *J* 7.9 Hz), 8.31 d (1H, $H^4$, *J* 7.9 Hz), 8.62 d (1H, CH=, *J* 16.5 Hz). $^{13}$C NMR spectrum (DMSO-$d_6$), $\delta_C$, ppm: 100.00 ($C^5$), 110.61 ($C^7$), 112.94 ($C^6$), 118.29 (CH=), 127.55 ($C^{3'}$, $C^{5'}$), 128.82 ($C^{1'}$), 129.16 ($C^{2'}$, $C^{6'}$), 129.35 (CH=), 130.12 ($C^{4'}$), 134.52 ($C^3$), 137.15 ($C^{4a}$), 138.76 ($C^4$), 139.96 ($C^2$), 152.50 ($C^{8a}$), 162.79 ($C^8$). Mass spectrum, *m*/*z* ($I_{rel}$, %): 558 (20) $[M]^+$, 556 (27), 248 (13), 247 (72), 246 (100), 217 (20), 114 (19). Found, %: C 73.25; H 4.35; N 5.00, Zn 11.63. $C_{34}H_{24}N_2O_2Zn$. Calculated, %: C 73.19; H 4.34; N 5.02; Zn 11.72. *M* 557.95.

**2-[*(E)*-2-(4-Methoxyphenyl)vinyl]quinolin-8-ol (III).** IR spectrum, ν, $cm^{-1}$: 3374.92 (O–H), 1758.67, 1606.78, 1573.52, 1510.96, 1455.37, 1419.26, 1334.35 [δ(O−H)], 1236.31 (C−OH), 1174.56, 951.01 (*trans*-CH=CH), 830.76, 767.65, 715.64, 715.64. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 3.83 s (3H, $CH_3O$), 6.96 d (2H, $H^{3'}$, $H^{5'}$, *J* 8.7 Hz), 7.04 m (1H, $H^5$), 7.26 d (1H, CH=, *J* 16.1 Hz), 7.29 m (1H, $H^7$), 7.34 t (1H, $H^6$, *J* 7.9 Hz), 7.63 d (2H, $H^{2'}$, $H^{6'}$, *J* 8.7 Hz), 7.68 d (1H, $H^3$, *J* 8.6 Hz), 8.01 d (1H, CH=, *J* 16.1 Hz), 8.18 d (1H, $H^4$, *J* 8.6 Hz), 9.14 br.s (1H, OH). $^{13}$C NMR spectrum (DMSO-$d_6$), $\delta_C$, ppm: 55.68 ($OCH_3$), 111.59 ($C^5$), 114.86 ($C^{3'}$, $C^{5'}$), 118.01 ($C^7$), 121.25 ($C^6$), 126.12 (CH=), 127.24 (CH=), 127.97 ($C^{1'}$), 129.10 ($C^{2'}$, $C^{6'}$), 129.57 ($C^{4a}$), 134.57 ($C^3$), 136.84 ($C^4$), 138.60 ($C^{8a}$), 153.31 ($C^2$), 154.25 ($C^{4'}$), 160.22 ($C^8$). Mass spectrum, *m*/*z* ($I_{rel}$, %): 277 (92) $[M]^+$, 276 (100), 262 (11), 234 (14), 233 (31), 204 (11), 117 (10), 89 (11).

**Zinc complex of 2-[*(E)*-2-(4-methoxyphenyl)vinyl]-quinolin-8-ol (IV).** IR spectrum, ν, $cm^{-1}$: 1758.67, 1595.48, 1562.36, 1510.96, 1455.37, 1419.26, 1367.10, 1334.35, 1271.01, 1199.55, 1098.71, 951.01 (*trans*-CH=CH), 830.76, 767.65, 569.24. $^1$H NMR spectrum (DMSO-$d_6$, δ, ppm: 3.82 s (3H, $CH_3O$), 6.9–7.0 m (4H, $H^{3'}$, $H^{5'}$, $H^5$, $H^7$), 7.40 m (1H, $H^6$), 7.57–7.62 m (3H, CH=, $H^{2'}$, $H^{6'}$), 8.03 m (1H, $H^3$), 8.26 m (1H, $H^4$), 8.39 d (1H, CH=, *J* 16.2 Hz). Mass spectrum, *m*/*z* ($I_{rel}$, %): 618 (2) $[M]^+$, 278 (19), 277 (100), 276 (99), 262 (13), 234 (10), 233 (27), 89 (10).

**2-[*(E)*-2-(4-Nitrophenyl)vinyl]quinolin-8-ol (V).** IR spectrum, ν, $cm^{-1}$: 3347.34 (O−H), 1588.93, 1558.19, 1503.42, 1462.07, 1434.40, 1331.43 [δ(O−H)], 1229.69 (C−OH), 1176.01, 1156.79, 1105.19, 1084.90, 978.46 (*trans*-CH=CH), 842.72, 747.95. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 7.03 d (1H, $H^5$, *J* 7.3 Hz), 7.28 d (1H, $H^7$, *J* 7.3 Hz), 7.35 t (1H, $H^6$, *J* 7.6 Hz), 7.62 d (1H, CH=, *J* 16.2 Hz), 7.71 d (1H, $H^3$, *J* 8.5 Hz), 7.91 d (2H, $H^{2'}$, $H^{6'}$, *J* 8.4 Hz), 8.22 d (2H, $H^{3'}$, $H^{5'}$, *J* 8.4 Hz), 8.23 d (1H, CH=, *J* 16.2 Hz), 8.26 d (1H, $H^4$, *J* 8.5 Hz), 9.32 s (1H, OH). $^{13}$C NMR spectrum (DMSO-$d_6$), $\delta_C$, ppm: 111.81 ($C^5$), 118.05 ($C^{3'}$, $C^{5'}$), 121.91 ($C^7$), 124.60 ($C^6$), 128.08 (CH=), 128.45 (CH=), 132.44 ($C^{2'}$, $C^{6'}$), 132.80 ($C^3$), 137.17 ($C^4$), 138.67 ($C^{1'}$), 143.72 ($C^{4a}$, $C^{8a}$), 147.21 ($C^2$), 152.93 ($C^8$), 153.59 ($C^{4'}$). Mass spectrum, *m*/*z* ($I_{rel}$, %): 292 (100) $[M]^+$, 291 (72), 276 (11), 246 (18), 245 (64), 244 (26), 233 (14), 228 (18), 217 (22), 216 (16), 117 (16), 114 (10), 89 (16).

**Zinc complex of 2-[*(E)*-2-(4-nitrophenyl)vinyl]-quinolin-8-ol (VI).** A hot solution of 0.23 mmol of zinc acetate in 2 mL of water was added to a hot solution of 0.46 mmol of compound **V** in 5 mL of DMF. The reaction mixture was heated under reflux for 3 h, cooled, and allowed to stand for 1 day at room temperature. The precipitate that formed was filtered off, washed with cold ethanol, and dried. Yield 56%, mp >250°C. IR spectrum, ν, $cm^{-1}$: 1593.48, 1552.36, 1515.67, 1445.99, 1434.12, 1411.97, 1373.70, 1336.94, 1270.91, 1183.13, 1100.99, 969.57 (*trans*-CH=CH), 835.96, 746.14, 577.51. $^{13}$C NMR spectrum (DMSO-$d_6$), δ, ppm: 100.00 ($C^5$), 116.23 ($C^7$), 118.55 ($C^6$), 124.43 ($C^{3'}$, $C^{5'}$), 128.26 ($C^{2'}$, $C^{6'}$), 129.26 ($C^{1'}$), 132.36 (CH=), 138.99 (CH=), 144.37 ($C^{4a}$, $C^{8a}$), 147.53 ($C^2$), 167.71 ($C^3$), 169.59 ($C^8$), 184.54 ($C^4$), 196.42 ($C^{4'}$). Found, %: C 63.10; H 8.60; N 8.70; Zn 9.98. $C_{34}H_{22}N_4O_6Zn$. Calculated, %: C 63.03; H 3.42; N 8.65; Zn 10.09. *M* 647.95.

**8-Hydroxy-2-[*(E)*-2-(4-methoxyphenyl)vinyl]quinolinium chloride (X).** 8-Acetoxy-2-[(*E*)-2-(4-methoxy-

phenyl)vinyl]quinolinium chloride (**IX**) [3] (2.81 mmol) was dissolved in 15 mL of ethanol, 2.5 mL of conc. HCl was then added, the mixture was heated under reflux for 1.5 h, cooled to room temperature, and the precipitate that formed was filtered off. Yield 57%, mp 120–122°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 3.88 s (3H, MeO), 5.16 br.s (1H, $HN^+$), 6.65 m (1H, $H^7$), 7.04 d (2H, $H^{3'}$, $H^{5'}$, *J* 8.8 Hz), 7.18 m (1H, $H^5$), 7.57 d (2H, $H^{2'}$, $H^{6'}$, *J* 8.8 Hz), 7.69 m (1H, $H^6$), 7.90 d (1H, CH=, *J* 16.0 Hz), 8.23 d (1H, CH=, *J* 16.0 Hz), 8.45 m (1H, $H^3$), 8.83 d (1H, $H^4$, *J* 8.3 Hz), 12.1 br.s (1H, OH). Found, %: C 68.70; H 5.45; N 4.40. $C_{18}H_{17}ClNO_3$. Calculated, %: C 68.68; H, 5.44; N 4.45. *M* 314.49.

**Zinc complex XI.** Compound **X** (0.36 mmol) was dissolved in a mixture of 10 mL of methanol and 0.5 mL of DMF, the mixture was stirred for 10 min and then heated to 50°C. A solution of 0.2 mmol of zinc acetate in 2 mL of methanol was added to the mixture dropwise, after which is was stirred at room temperature for 6 h and concentrated in a vacuum. A yellow precipitate formed and was filtered off and washed with ethanol. Yield 42%, mp >300°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 3.36 s (6H, 2MeO), 6.22 br.s (1H, $HN^+$), 6.43–6.56 m (6H, $2H^{3'}$, $2H^{5'}$, $2H^7$), 6.70–6.85 m (3H, 2 CH=, $H^5$), 6.92 m (1H, $H^5$), 7.05–7.20 m (6H, $2H^{2'}$, $2H^{6'}$, $2H^6$), 7.55–7.70 m (4H, CH=, $2H^3$, $H^4$), 7.79 d (1H, $H^4$, *J* 8.3 Hz), 7.90 d (1H, CH=, *J* 16.0 Hz), 8.6 br.s (1H, OH). Found, %: C 59.35; H 4.45; N 3.90; Zn 9.38. $C_{36}H_{30}Cl_2N_2O_4Zn$. Calculated, %: C 62.58; H 4.39; N 4.05; Zn 9.46. *M* 690.94.

## ACKNOWLEDGMENTS

The work was financially supported by the Russian Foundation for Basic Research (project no. 14-03-00340), Ural Branch of the Russian Academy of Sciences (project no. 12-P-1020), and Grant Council of the President of the Russian Federation (grant NSh-3656.2014.3).

## REFERENCES

1. Tang, C. and Vanslyke, S., *Appl. Phys. Lett*., 1987, vol. 51, p. 913. DOI: 10.1063/1.98799.
2. Lipunova, G.N., Nosova, E.V., Trashakhova, T.V., and Charushin, V.N., *Russ. Chem. Rev*., 2011, vol. 80, p. 1115. DOI: 10.1070/RC2011v080n11ABEH004234.
3. Barberis, V.P. and Mikroyannidis, J.A., *Synth. Met*., 2006, vol. 156, p. 865. DOI: 10.1016/j.synthmet.2006.-05.007.
4. Shi, Y.W., Shi, M.M., Huang, J.C., Chen, H.Z., Wang, M., Lin, M.D., Ma, Y.G., Xu, H., and Yang, B., *Chem. Commun*., 2006, no. 18, p. 1941. DOI: 10.1039/B516757D.
5. Nosova, E.V., Stupina, T.V., Lipunova, G.N., and Charushin, V.N., *J. Fluorine Chem*., 2013, vol. 150, p. 36. DOI: 10.1016/j. jfluchem.2013.03.005.
6. Huo, Y.P. and Zhu, S.Z., *Tetrahedron,* 2010, vol. 66, p. 8635. DOI: 10.1016/j.tet.2010.09.039.
7. Ouyanga, X.H., Zeng, H., Ding, G., Jiang, W., and Li, J., *Synth. Met.,* 2009, vol. 159, p. 2063. DOI: 10.1016/j.synthmet. 2009.07.026.
8. Wang, G., Zeng, G., Zeng, H., Liu, P., Wang, R., Zhang, Z., and Xiong, Y., *Tetrahedron*, 2009, vol. 65, p. 6325. DOI: 10.1016/j.tet.2009.06.025.
9. Omar, W.A.E. and Hormi, O.E.O., *Tetrahedron*, 2009, vol. 65, p. 4422. DOI: 10.1016/j.tet.2009.03.028.
10. Chang, F.S., Tzeng, C.C., Chen, Y.L., Chen, W., and Wang, C., *Bioorg. Med. Chem*., 2010, vol. 18, p. 124. DOI: 10.1016/j.bmc.2009.11.012.15.
11. Liu, Y., Wei, J., Chen, Z., Liu, M., Gu, Y., Huang, K., Li, Z., and Liang, H., *Eur. J. Med. Chem*., 2013, vol. 69, p. 554. DOI: 10.1016/j.ejmech.2013.08.033.
12. Hu, Y., Qu, J., Yi, Y., Gao, H., and Cui, J., *J. Coord. Chem*., 2013, vol. 66, p. 18. DOI: 10.1080/00958972.-2012.744972.
13. Sheldrick, G.M., *Acta Crystallogr., Sect. A*, 2008, vol. 64, p. 112. DOI: 10.1107/S0108767307043930.