

LETTERS
TO THE EDITOR

Spectral Luminescent Properties of 3-[5-(4-Methoxyphenyl)-1,3,4-oxadiazol-2-yl]acrylic Acid and Its Complex with Zn(II)

I. E. Mikhailov^{a,b*}, L. D. Popov^c, G. A. Dushenko^a,
Yu. V. Revinskii^b, and V. I. Minkin^a

^a Research Institute of Physical and Organic Chemistry, Southern Federal University,
pr. Stachki 194/2, Rostov-on-Don, 344090 Russia
*e-mail: mikhail@ipoc.sfedu.ru

^b Federal Research Center, Southern Science Center, Russian Academy of Sciences, Rostov-on-Don, Russia

^c Southern Federal University, Rostov-on-Don, Russia

Received December 14, 2017

Abstract—Zinc complex of (*E*)-3-[5-(4-methoxyphenyl)-1,3,4-oxadiazol-2-yl]acrylic acid has been prepared; its structure and composition have been elucidated by means of IR and ¹H as well as ¹³C NMR spectroscopy. Spectral luminescent properties of the ligand and the complex have been studied. Both compounds exhibit blue-violet luminescence ($\lambda_{\max}^{\text{fl}}$ 402–467 nm, ϕ 0.06–0.82) with low self-absorbance of the emitted light.

Keywords: 3-(5-aryl-1,3,4-oxadiazol-2-yl)acrylic acids, metal complexes, luminescence, quantum yield

DOI: 10.1134/S1070363218040369

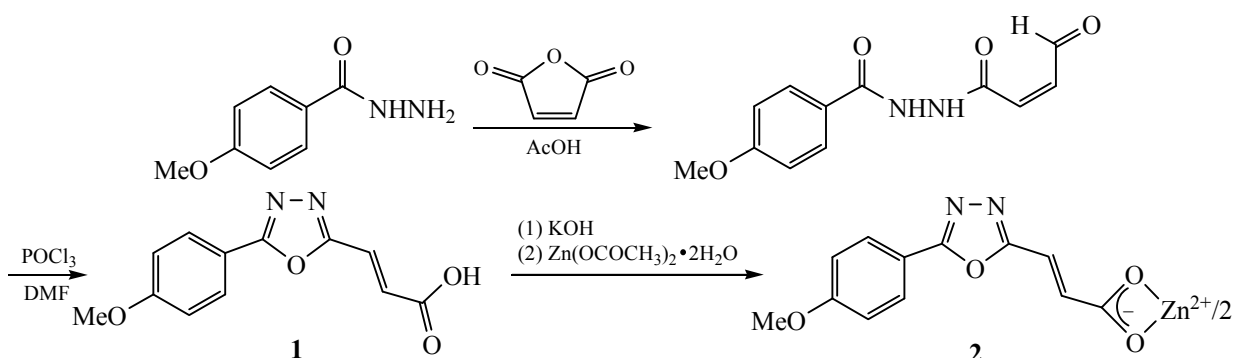
1,3,4-Oxadiazoles and their derivatives exhibit strong and diverse biological activity [1] as well as spectral luminescent properties enabling the preparation of fluorescent and phosphorescent luminophors [2–5], organic semiconductors, and other materials for modern optoelectronics [6] on their basis. Chelate complexes with oxadiazol ligands are widely used as metal complex luminophors [7, 8] as well as emission and electron-transport materials for organic and light emitting diodes (OLED) [9].

Starting from oxadiazolylpropionic [10] and oxadiazolylacrylic [10–12] acids, only a single metal com-

plex has been prepared [13]. Therefore, we prepared (*E*)-3-[5-(4-methoxyphenyl)-1,3,4-oxadiazol-2-yl]acrylic acid **1** (L) [12], refluxing of methanolic solution of which with 0.5 eq. of zinc acetate dihydrate in the presence of KOH gave the corresponding metal complex **L₂Zn 2** (Scheme 1).

Composition and structure of the zinc complex **2** were elucidated using the data of elemental analysis, and IR as well as ¹H and ¹³C NMR spectroscopy. The complex formation resulted in the disappearance of the bands of the O–H group (2617 and 2524 cm⁻¹) [12] of the ligand **1** due to the substitution of the proton with

Scheme 1.



the metal ion, and the band of the C=O group (1715 cm^{-1}) was shifted to longer wavelength (1612 cm^{-1}) due to the formation of the chelate structure.

The signal of the OH group (observed in the spectrum of the ligand **1** at 13.18 ppm [12]) in the ^1H NMR spectrum of complex **2** (DMSO- d_6) disappeared, the signals of the olefinic protons were shifted upfield (the weaker-field signal was shifted by 0.26 ppm, and the stronger-field signal was shifted by 0.19 ppm), allowing their assignment to the proton in position 2 of the acrylate fragment, located closer to the coordination site. The constants of the spin-spin interaction of the protons at the double bond $-\text{CH}=\text{CH}-$ in the ligand **1** and its complex **2** ($^3J = 16.2$ and 17.0 Hz) evidenced the *E*-configuration of the compounds. As far as the ^{13}C NMR spectra are concerned, the complex formation resulted in the downfield shift of the signals of the C=O group (by 3.07 ppm) and the C^2 atom of the unsaturated fragment (by 6.35 ppm), whereas the signal of the C^3 atom was shifted upfield by 3.83 ppm.

The electronic absorption spectra of compounds **1** and **2** contained the long-wave bands (assigned to the $\pi \rightarrow \pi^*$ transitions in the conjugated 1,3,4-oxadiazol and aryl fragments) with maximum at 301–318 nm. Whereas the effect of the polarity of the solvent in the position of the absorption bands in the electronic absorption spectra of compounds **1** and **2** was not revealed, their luminescence spectra were affected by the medium polarity. Compounds **1** and **2** exhibited strong luminescence in the short-wave part of the visible spectral range ($\lambda_{\text{max}}^{\text{fl}}$ 402–467 nm, ϕ 0.06–0.82), showing the bathochromic shift by 30–65 nm and significant decrease in the quantum yield of luminescence in strongly polar solvent (DMSO) (**1**, $\lambda_{\text{max}}^{\text{fl}}$ 467 nm, ϕ 0.12; **2**, $\lambda_{\text{max}}^{\text{fl}}$ 434 nm, ϕ 0.06). In polar solvents, the acid **1** emitted longer-wave light with higher quantum yield (acetonitrile, $\lambda_{\text{max}}^{\text{fl}}$ 463 nm, ϕ 0.81) as compared to the zinc complex **2** ($\lambda_{\text{max}}^{\text{fl}}$ 438 nm, ϕ 0.16). Since the luminescence bands of compounds **1** and **2** exhibited strong Stokes shift in nonpolar solvents ($6770\text{--}7644\text{ cm}^{-1}$) and anomalously strong Stokes shift in polar solvents ($8616\text{--}11487\text{ cm}^{-1}$), their self-absorption of the emitted light was low.

The described features showed that (*E*)-3-[5-(4-methoxyphenyl)-1,3,4-oxadiazol-2-yl]acrylic acid **1** and its zinc complex **2** belonged to the group of demanded luminophors with low self-absorbance of the emitted light.

(E)-3-[5-(4-Methoxyphenyl)-1,3,4-oxadiazol-2-yl]-acrylic acid (1) was prepared as described in [12], via

acylation of hydrazide of *o*-methoxybenzoic acid with maleic anhydride, followed by cyclization of the formed aroylhydrazinyloxobutenoic acid under the action of POCl_3 in DMF. Yield 56%, colorless crystals, mp $238\text{--}240^\circ\text{C}$ (toluene) (mp $237\text{--}239^\circ\text{C}$ [12]). Data of IR and ^1H NMR spectroscopy coincided with the reference data [12]. Electronic spectrum, λ_{max} , nm [$\epsilon \times 10^{-4}\text{ L mol}^{-1}\text{ cm}^{-1}$, λ_{ex} 300 nm]: toluene, 316 [2.01], $\lambda_{\text{max}}^{\text{fl}}$ (ϕ) 402 (0.45); dioxane, 311 [2.83], $\lambda_{\text{max}}^{\text{fl}}$ (ϕ) 408 (0.67); acetonitrile, 266 [2.94], 284 [2.79], 292 [2.84], 312 [2.87], $\lambda_{\text{max}}^{\text{fl}}$ (ϕ) 463 (0.81); DMSO, 304 [2.78], $\lambda_{\text{max}}^{\text{fl}}$ (ϕ) 467 (0.12). ^{13}C NMR spectrum (DMSO- d_6), δ_{C} , ppm: 56.00 (OCH₃), 115.34 ($2\text{C}_{\text{Ar}}^{3,5}$), 115.55 ($\text{C}^{\text{ipso},1}$), 124.63 ($=\text{C}^3$), 129.33 ($=\text{C}^2$), 129.35 ($2\text{C}_{\text{Ar}}^{2,6}$), 162.21 ($\text{C}^{\text{ipso},4}$), 162.91 (C_{Het}), 164.86 (C_{Het}), 166.40 ($\text{C}=\text{O}$).

Zinc(II) bis{(E)-3-[5-(4-methoxyphenyl)-1,3,4-oxadiazol-2-yl]acrylate} (2). A mixture of 0.002 mol of compound **1** and 0.002 mol of KOH in 20 mL of methanol was refluxed during 15 min, then 0.001 mol of $\text{Zn}(\text{OCOCH}_3)_2 \cdot 2\text{H}_2\text{O}$ in 10 mL of methanol was added, and the mixture was refluxed during 5 h. The precipitate formed after cooling down to ambient was filtered off, washed with hot methanol (2×15 mL), and dried in air. Yield 75%, colorless crystals, mp $> 300^\circ\text{C}$. IR spectrum, ν , cm^{-1} : 3407 (H_2O), 1651 ($\text{C}=\text{C}$), 1614 (COO^-), 1574 ($\text{C}=\text{C}_{\text{Ar}}$), 1510, 1505 ($\text{C}=\text{N}$), 1277, 1196, 1126 ($\text{C}-\text{O}-\text{C}$), 972 [$\delta(\text{trans-CH}=\text{CH})$], 822 [$\delta(\text{C}-\text{H}_{\text{Ar}})$]. ^1H NMR spectrum (DMSO- d_6), δ , ppm: 3.38 s (4H, $2\text{H}_2\text{O}$), 3.82 s (3H, OCH₃), 6.97 d (1H, $=\text{CH}^3$, 3J 17.0 Hz), 7.09 d ($2\text{H}_{\text{Ar}}^{3,5}$, 3J 8.3 Hz), 7.18 d (1H, $=\text{CH}^2$, 3J 17.0 Hz), 7.96 d ($2\text{H}_{\text{Ar}}^{2,6}$, 3J 8.3 Hz). ^{13}C NMR spectrum (DMSO- d_6), δ_{C} , ppm: 55.97 (OCH₃), 115.30 ($2\text{C}_{\text{Ar}}^{3,5}$), 115.81 ($\text{C}^{\text{ipso},1}$), 120.80 ($=\text{C}^3$), 129.12 ($2\text{C}_{\text{Ar}}^{2,6}$), 135.68 ($=\text{C}^2$), 162.70 ($\text{C}^{\text{ipso},4}$), 163.01 (C_{Het}), 164.36 (C_{Het}), 169.47 ($\text{C}=\text{O}$). Electronic spectrum, λ_{max} , nm [$\epsilon \times 10^{-4}\text{ L mol}^{-1}\text{ cm}^{-1}$, λ_{ex} 300 nm]: dioxane, 313 [2.77], $\lambda_{\text{max}}^{\text{fl}}$ (ϕ) 408 (0.82); acetonitrile, 276 [2.89], 318 [2.92], $\lambda_{\text{max}}^{\text{fl}}$ (ϕ) 438 (0.16); DMSO, 301 [3.34], $\lambda_{\text{max}}^{\text{fl}}$ (ϕ) 444 (0.06). Found, %: C 48.39; H 3.82; N 9.53. $\text{C}_{24}\text{H}_{18}\text{N}_4\text{O}_8\text{Zn} \cdot 2\text{H}_2\text{O}$. Calculated, %: C 48.71; H 3.75; N 9.47.

IR spectra were recorded in Vaseline oil using a Varian Excalibur 3100 FT-IR spectrometer. ^1H (250.13 MHz) and ^{13}C (62.90 MHz) NMR spectra were recorded using a Bruker DPX-250 instrument. Absorption and fluorescence spectra were recorded using a Cary Scan 100 spectrophotometer and a Cary Eclipse spectrofluorimeter, respectively. Quantum yield of fluorescence was determined with respect to a solution of anthracene in acetonitrile as the reference [14].

ACKNOWLEDGMENTS

This study was financially supported by the Russian Foundation for Basic Research (project no. 16-03-00095a).

REFERENCES

1. Bostrom, J., Hogner, A., Llinas, A., Wellner, E., and Plowright, A.T., *J. Med. Chem.*, 2012, vol. 55, no. 5, p. 1817. doi 10.1021/jm2013248
2. Beldovskaya, A.D., Dushenko, G.A., Vikrishchuk, N.I., Popov, L.D., Revinskii, Yu.V., Mikhailov, I.E., and Minkin, V.I., *Russ. J. Org. Chem.*, 2013, vol. 49, no. 12, p. 1861. doi 10.1134/S1070428013120312
3. Mikhailov, I.E., Artyushkina, Yu.M., Burov, O.N., Dushenko, G.A., Revinskii, Yu.V., and Minkin, V.I., *Russ. J. Gen. Chem.*, 2016, vol. 86, no. 2, p. 406. doi 10.1134/S1070363216020341
4. Mikhailov, I.E., Artyushkina, Yu.M., Dushenko, G.A., Mikhailova O.I., Revinskii, Yu.V., Burov O.N., and Minkin, V.I., *Russ. J. Org. Chem.*, 2016, vol. 52, no. 11, p. 1700. doi 10.1134/S1070428016110270
5. Artyushkina, Yu.M., Mikhailov, I.E., Burov, O.N., Dushenko, G.A., Mikhailova, O.I., Revinskii, Yu.V., and Minkin, V.I., *Russ. J. Gen. Chem.*, 2016, vol. 86, no. 12, p. 2702. doi 10.1134/S1070363216120239
6. Lee, W.Ch., Kim, O.Y., and Lee, J.Y., *J. Ind. Eng. Chem.*, 2014, vol. 20, no. 4, p. 1198. doi 10.1016/j.jiec.2013.09.036
7. Beldovskaya, A.D., Dushenko, G.A., Vikrishchuk, N.I., Popov, L.D., Revinskii, Yu.V., Mikhailov, I.E., and Minkin, V.I., *Russ. J. Gen. Chem.*, 2014, vol. 84, no. 1, p. 171. doi 10.1134/S1070363214010290
8. Mikhailov, I.E., Vikrishchuk, N.I., Popov, L.D., Dushenko, G.A., Beldovskaya, A.D., Revinskii, Yu.V., and Minkin, V.I., *Russ. J. Gen. Chem.*, 2016, vol. 86, no. 5, p. 1054. doi 10.1134/S1070363216050121
9. Deng, R., Li, L., Song, M., Zhao, Sh., Zhou, L., and Yao, Sh., *CrystEng Comm.*, 2016, vol. 18, no. 23, p. 4382. doi 10.1039/c6ce00066e
10. Gutov, O.V., *Cryst. Growth Des.*, 2013, vol. 13, no. 9, p. 3953. doi 10.1021/cg400649h
11. Detert, H. and Schollmeier, D., *Synthesis*, 1999, no. 6, p. 999. doi 10.1055/s-1999-3511
12. Rozhkov, S.S., Ovchinnikov, K.L., Krasovskaya, G.G., Danilova, A.S., and Kolobov, A.V., *Russ. J. Org. Chem.*, 2015, vol. 51, p. 982. doi 10.1134/S1070428015070155
13. Kokunov, Yu.V., Gorbunova, Yu.E., Popov, L.D., Kovalev, V.V., Razgonyaeva, G.A., Kozyukhin, S.A., and Borodkin, S.A., *Russ. J. Coord. Chem.*, 2016, vol. 42, no. 6, p. 361. doi 10.7868/S0132344X16060037
14. Beldovskaya, A.D., Dushenko, G.A., Vikrishchuk, N.I., Popov, L.D., Revinskii, Y.V., and Mikhailov, I.E., *Russ. J. Gen. Chem.*, 2013, vol. 83, no. 11, p. 2075. doi 10.1134/S1070363213110200