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Spectral and Luminescent Properties of N-(3-Methoxysalicylidene)-*o*-anisidine and Its Zinc Complex

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Abstract—The synthesis and the spectral and luminescent properties of N-(3-methoxysalicylidene)-*o*-anisidine and its Zn(II) complex are presented. It is found that Schiff base in solution has the *E(anti)*-configuration, and the zinc complex fluoresces in solution and the polycrystalline state at 77 and 293 K.

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INTRODUCTION

The complexes of transition metals with Schiff bases attract much attention of researchers owing to the development of methods of their synthesis and to the expansion of their application for creating new functional materials. In particular, some complexes of *d* elements with aromatic azomethines of N₂O₂, N₄, and NO types ([M(Schiff)]) exhibit luminescent [1] and catalytic [2] activities, sensor properties [3, 4], and ability to form stable polymers with electronic conductivity [5–8].

It is known that aromatic azomethines of the N₂O₂ type, salicylic aldehyde derivatives, and their zinc complexes are fluorescent materials that can efficiently luminesce in the visible blue region. These complexes can be used as emitting layers for creating highly efficient electroluminescent devices [9, 10].

Thus, the development of the methods of synthesis of new azomethine bases which can be used as structural elements of luminescent complexes is quite topical.

In the present work, we consider the spectral and luminescent properties of NO-type Schiff base—N-(3-methoxysalicylidene)-*o*-anisidine and its Zn(II) complex (Fig. 1).

EXPERIMENTAL

N-(3-methoxysalicylidene)-*o*-anisidine (L) was synthesized by condensation of 2-methoxyaniline (Aldrich, 99%) (0.93 mL, 8.25 mmol) and 2-hydroxy-3-methoxybenzaldehyde (Aldrich, 99%) (1.254 g, 8.25 mmol) in ethanol in the presence of a small amount of glacial acetic acid. The obtained red–orange solution was heated for 30 min. Upon cooling

the solution, we observed the formation of orange crystals, which were filtered, recrystallized from ethanol, and dried at a temperature of 50°C. The yield was 90%. The melting temperature of the synthesized compound was 78–79°C. The results of elemental analysis (chemical formula C₁₅H₁₄NO₃) are as follows (calculated/determined, %): C 70.04/70.14, H 5.84/5.79, N 5.48/5.52. The IR spectrum, ν/cm^{-1} : $\nu(\text{C}=\text{N})$ 1614; Ar ring vibrations 1585, 1479, 857, 744, 739, 640, 570; $\nu(\text{O}-\text{H})$ 3432, $\delta(\text{O}-\text{H})$ 1362, 1275; $\nu(\text{C}-\text{O})$ 1195, 1080, 1048. The NMR ¹H spectrum, δ , ppm (*J*, Hz): 3.87 s (3H, OC¹H₃), 3.92 s (3H, O²CH₃), 6.82 t (1H, *J* = 7.57), 6.90–7.05 m (4H), 7.18–7.28 m (2H), 8.68 s (1H, CH=N), 14.38 s (1H, OH). The NMR ¹³C{¹H} spectrum, δ , ppm: 55.86 (OC¹H₃), 56.13 (OC²H₃), 111.95, 114.30, 118.01, 119.10, 119.22, 120.93, 123.53, 128.09, 136.20, 148.78, 152.73, 153.09, 161.26 (CH=N). Based on the results of the ¹H–¹H NOESY experiment, N-(3-methoxysalicylidene)-*o*-anisidine in solution is found to have the *E(anti)*-configuration (Fig. 1).

To synthesize the [ZnL₂] complex, to the ethanol solution of N-(3-methoxysalicylidene)-*o*-anisidine

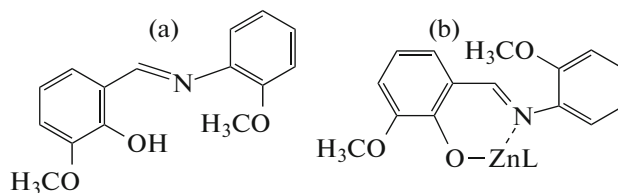


Fig. 1. Structural formulas of (a) Schiff base (L) and (b) [ZnL₂] complex.

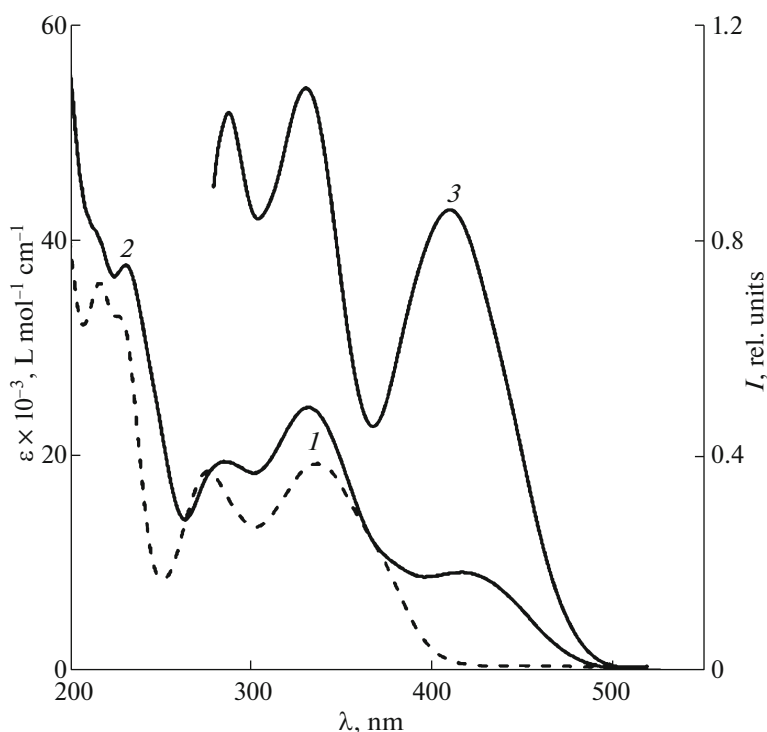


Fig. 2. Electronic absorption spectra of (1) Schiff base and (2) $[\text{ZnL}_2]$ complex in CH_3CN . (3) Luminescence excitation spectrum of $[\text{ZnL}_2]$ in CH_3CN , $\lambda_{\text{rec}} = 540 \text{ nm}$, $T = 293 \text{ K}$.

(0.445 g, 1.73 mmol), a saturated aqueous solution of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (0.189 g, 0.865 mmol) was added under stirring and heating. Cooling of the solution led to the formation of a yellow–orange precipitate. The yield was 60%. The results of the elemental analysis (chemical formula $\text{ZnC}_{30}\text{H}_{27}\text{N}_2\text{O}_6$), calculated/determined, %: C 62.39/63.44, H 4.85/4.99, N 4.85/4.92. The IR spectrum, ν/cm^{-1} : $\nu(\text{C}=\text{N})$ 1610; Ar ring vibrations 1585, 1494, 857, 744, 736, 637, 582; $\nu(\text{O}-\text{H})$ 3425, $\delta(\text{O}-\text{H})$ 1362, 1275; $\nu(\text{C}-\text{O})$ 1187, 1118, 1049. The NMR ^1H spectrum, δ , ppm (J , Hz): 3.44 s (3H, OC^1H_3), 3.75 s (3H, OC^2H_3), 3.88 s (3H, OC^3H_3), 3.93 s (3H, OC^4H_3), 6.47 t (1H, $J = 7.72$), 6.66 d (1H, $J = 8.18$), 6.70–6.80 m (3H), 6.82–6.90 m (2H), 6.92–7.10 m (5H), 7.20–7.28 m (2H), 8.27 s (1H, $\text{C}^1\text{H}=\text{N}$), 8.70 s (1H, $\text{C}^2\text{H}=\text{N}$), 14.48 s (1H, OH). The NMR $^{13}\text{C}\{^1\text{H}\}$, δ , ppm: 55.26 (OC^1H_3), 55.92 (OC^3H_3), 56.18 (OC^4H_3), 56.36 (OC^2H_3), 110.51, 112.01, 112.87, 114.34, 115.48, 118.04, 118.55, 119.18, 119.18, 119.28, 120.99, 121.16, 123.57, 127.10, 127.85, 128.12, 136.30, 137.87, 148.83, 151.31, 152.78, 153.13, 161.35 ($\text{C}^2\text{H}=\text{N}$), 164.00, 168.46 ($\text{C}^1\text{H}=\text{N}$).

The electronic absorption spectra (EASs) at 293 K were recorded within the range of 200–900 nm on a Shimadzu UV 2550 PC spectrophotometer. To study the effect of solvent polarity on the position and efficiency of absorption bands, we used solvents with different spectroscopic polarity parameters Z [11],

namely, acetonitrile, dichloromethane, ethanol, and methanol.

The vibrational transmission spectra of the Schiff base and the complex were recorded within the range of 400–4000 cm^{-1} (KBr pellets) on a Shimadzu IR-Prestige 21 Fourier transform spectrometer.

The NMR ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^1\text{H}-^{13}\text{C}$ HMQC, $^1\text{H}-^1\text{H}$ NOESY spectra were recorded on a Jeol JNM-ECX400A spectrometer with working frequencies of 399.78 (^1H) and 100.53 (^{13}C) MHz in chloroform- d as a solvent. As an internal standard, we used the signals of residual protons of the non-deuterated solvent. The signals of protons and carbon atoms of the $-\text{OCH}_3$ and $-\text{CH}=\text{N}-$ groups were identified based on the analysis of the $^1\text{H}-^{13}\text{C}$ HMQC spectra.

The luminescence spectra of the polycrystalline samples, as well as of the solutions of Schiff base and Zn(II) complex, were measured at 293 and 77 K using a Flyuorat-02-Panorama spectrofluorimeter.

The physicochemical investigations were performed using the equipment of the Center of Collective Use at the Faculty of Chemistry of the Herzen State Pedagogical University.

RESULTS AND DISCUSSION

The electronic absorption spectra of N-(3-methoxysalicylidene)-*o*-anisidine in methanol, etha-

Characteristics of the electronic absorption spectra of Schiff base (L) and $[ZnL_2]$ complex in different solvents

Substance	CH ₃ OH, $Z = 83.6 \text{ kcal mol}^{-1}$	C ₂ H ₅ OH, $Z = 79.6 \text{ kcal mol}^{-1}$	CH ₃ CN, $Z = 71.3 \text{ kcal mol}^{-1}$	CH ₂ Cl ₂ , $Z = 64.2 \text{ kcal mol}^{-1}$
	λ_{max} , nm (log ϵ)	λ_{max} , nm (log ϵ)	λ_{max} , nm (log ϵ)	λ_{max} , nm (log ϵ)
(L)	212 (4.55), 228 (4.46), 277 (4.17), 339 (4.32), 462 (3.71)	216(4.27), 230(4.21), 282 (3.98), 345 (4.15), [371] (3.98), 465 (3.49)	217 (4.56), 229 (4.52), 276 (4.27), 338 (4.49), [371](4.05), 468(2.71)	231 (4.53), 277 (4.28), 338(4.30),[374](4.06), 472 (2.69)
$[ZnL_2]$	236 (4.75), [288] (4.44), 333 (4.57), 413 (4.24)	[219] (4.77), [229] (4.72), 277 (4.41), 338 (4.47), 425 (3.85)	[216] (4.61), 232 (4.57), 287 (4.27), 334 (4.39), 420 (3.99)	219 (4.65), [232] (4.63), 279 (4.36), 341 (4.42)

[] shoulder.

sol, acetonitrile, and dichloromethane, have the following series of spin-allowed transitions of different orbital nature (Fig. 2; the main parameters are listed in the table).

Intraligand (IL) transitions in aryl fragments of the $\pi-\pi^*$ type with maxima at $\lambda < 300 \text{ nm}$, the positions of which are almost independent of the solvent polarity.

The absorption bands with maxima within the range of 340–360 nm are assigned to the $n-\pi^*$ and $\pi-\pi^*$ transition in the Schiff base fragments $-\text{HC}=\text{N}-$ [12]. In the most polar solvents (CH₃OH, C₂H₅OH), additional absorption bands appear with moderate

intensities and maxima at $\lambda > 400 \text{ nm}$, which correspond to the $n-\pi^*$ transitions in bipolar keto-amine structures [12, 13]. The appearance of these absorption bands is probably related to a partial transformation of benzenoid fragments of Schiff base into quinoid fragments due to the formation of the intramolecular hydrogen bond between the hydroxyl oxygen and the aminogroup nitrogen. In polar solvents, additional hydroxyl group polarization is possible, which is favorable for the tautomeric transition.

The complexation leads to a small shift of the IL absorption bands corresponding to the $\pi-\pi^*$ transitions in aryl fragments. In acetonitrile and alcoholic solutions, the $[ZnL_2]$ complex has an additional absorption band in the region of 420 nm, the position of which only slightly depends on parameter Z of the solvent. This band presumably belongs to the $\pi-\pi^*$ transition in the quinoid form of the complex [14], which is stabilized in polar solvents.

According to data from the literature, the photoluminescence of $[Zn(\text{Schiff})]$ complexes has an IL nature and is caused by a singlet electronically excited state (EES) of the $^1(\pi^*-\pi)$ type. In addition, the fluorescent properties of zinc complexes are sensitive to the electronic nature of substituents, which determine the difference in the radiative transition energy and the character of the intermolecular interaction in both polycrystalline form and solutions [10, 15].

In contrast to the Zn(II) complex, the initial Schiff base in polycrystalline form and in solution luminesce at neither room nor liquid nitrogen temperature.

The $[ZnL_2]$ complex exhibits intense luminescence in the polycrystalline form and in diluted acetonitrile solution at 77 and 293 K (Fig. 3) with the maximum in the region of 540 nm. At 77 K, the vibrationally structured fluorescence spectrum of the complex is characterized by the main progression with a frequency of $\sim 580 \text{ cm}^{-1}$, which corresponds to the deformation vibrations of aryl fragments (Fig. 3, curve 3).

The similarity of the fluorescence spectra points to the absence of association (stacking interaction) in both the polycrystalline sample and solution. This is

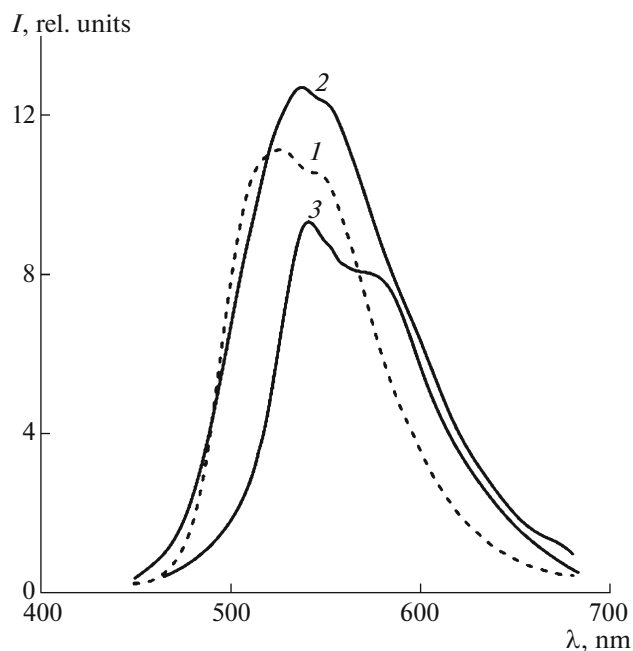


Fig. 3. Luminescence spectra of $[ZnL_2]$ complex ($\lambda_{\text{exc}} = 410 \text{ nm}$) for (1) polycrystalline sample, 293 K; (2) solution in CH₃CN, $C = 1.3 \times 10^{-5} \text{ M}$, 293 K; and (3) solution in CH₃CN, 77 K.

probably caused by the distorted tetrahedral structure of the complex and by the existence of bulky methoxy substituents in its ligand environment.

The solution of $[\text{ZnL}_2]$ in CH_3CN is characterized by the absence of dependences of both the profile and peak position (540 nm) of the absorption band on the excitation energy. The presence of only one energetically lowest luminescent singlet state is confirmed by the similarity of the absorption and luminescence excitation spectra of the complex (Fig. 2, curves 2 and 3). This attests that the luminescence occurs from one and the same lowest EES of the IL type, while the probability of internal conversion from the highest EESs to the lowest state is close to unity.

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