

CONDENSED-MATTER
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Spectral and Luminescent Properties of N,N'-Bis(5-Bromosalicylidene)-1,3-Propylenediamine and Its Zinc Complex

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Received March 22, 2016

Abstract—Zn(II) complex with N,N'-bis(5-bromosalicylidene)-1,3-propylenediamine, which efficiently luminesce in the blue region of the visible spectrum, is synthesized for the first time. It is found that, at 293 K, azomethine and zinc complex fluoresce in both solution and the polycrystalline state. Fluorescence quantum yields of the compounds in diluted dimethylformamide and dimethylsulfoxide solutions are determined.

DOI: 10.1134/S0030400X16090216

INTRODUCTION

The development of methods of synthesis of new azomethines, which may serve as structural elements of luminescent complexes, is a topical problem. Growing interest in Zn(II) complexes with aromatic azomethine bases is explained by the need for new materials that can be used as emitting layers of efficient electroluminescent devices [1–3]. It is known that some Zn(II) complexes with aromatic azomethines of N₂O₂ type (derivatives of salicylic aldehyde) can efficiently fluoresce in the blue region of the visible spectrum. The luminescent properties of [Zn(Schiff)] complexes are determined mainly by the ligand nature, i.e., by the electronic character of substituents in its aryl fragments and by the conjugation length [4–6]. Thus, the structural features of coordinated azomethine and the intermolecular interaction character determine the difference of radiative transition energies in both polycrystalline samples and solutions of zinc complexes.

In the present work, we consider the spectral and luminescent properties of tetradentate aromatic

azomethine of the N₂O₂ type, i.e., of N,N'-bis(5-bromosalicylidene)-1,3-propylenediamine [H₂(5Br-salpn-1,3)] and its Zn(II) complex (Fig. 1).

EXPERIMENTAL

N,N'-Bis(5-bromosalicylidene)-1,3-propylenediamine was obtained by condensation of propylenediamine-1,3 (Merck, 99%) (0.1 mL, 1.24 mmol) and 5-bromosalicylic aldehyde (Aldrich, 98%) (0.5 g, 2.48 mmol, 15 mL of ethanol) in the presence of acetic acid as a catalyst. Heating and stirring of the solution obtained for 10 min led to the formation of lemon-yellow precipitate, which was filtered, washed with ethanol and diethyl ether, and dried at 70°C. The yield of the product was 85%. The melting temperature of the resulting material was 125–127°C. The IR spectrum, ν/cm^{-1} : $\nu(\text{C}=\text{N})$ 1634; $\nu(\text{C}=\text{C})$ of Ar fragments 1574, 1477, 1457, 1434; $\nu(\text{O}-\text{H})$ 3438, $\delta(\text{O}-\text{H})$ 1277. The ¹H NMR spectrum, δ , ppm (J, Hz): $-\text{N}=\text{CH}$ 8.51 s, $\text{N}-\text{CH}_2$ 3.63 t (6.78), CH_2 1.98 pentet (6.78), OH 13.55 s, in the aromatic ring 7.60 d (2.55), 7.40 dd (2.55, 8.82), 6.80 d (8.82). The ¹³C{¹H} NMR spec-

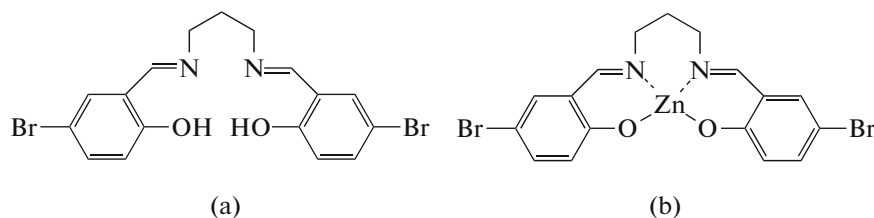


Fig. 1. Structural formulas of (a) H₂(5Br-salpn-1,3) azomethine and (b) [Zn(5Br-salpn-1,3)] complex.

Table 1. Characteristics of the electronic absorption spectra of H₂(5Br-salpn-1,3) and [Zn(5Br-salpn-1,3)] in various solvents

Compound	CH ₃ OH, Z =	C ₂ H ₅ OH, Z =	CH ₃ CN, Z =	DMSO, Z =	DMFA, Z =	CH ₂ Cl ₂ , Z =
	83.6 kcal mol ⁻¹	79.6 kcal mol ⁻¹	71.3 kcal mol ⁻¹	71.1 kcal mol ⁻¹	68.5 kcal mol ⁻¹	64.2 kcal mol ⁻¹
	λ _{max} , nm (logε)	λ _{max} , nm (logε)	λ _{max} , nm (logε)	λ _{max} , nm (logε)	λ _{max} , nm (logε)	λ _{max} , nm (logε)
H ₂ (5Br-salpn-1,3)	250 (4.52); [326] (4.08); 414 (3.54); 278 (3.83)	250 (4.45); [278] (3.74); 326 (3.99); 413 (3.34)	251 (4.39); 326 (4.01)	326 (3.87); 415 (3.03)	326 (1.71); 415 (2.89)	253 (4.55); 327 (4.17)
[Zn(5Br-salpn-1,3)]	Insoluble	Insoluble	Insoluble	370 (3.96)	370 (3.30)	Insoluble

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trum, δ, ppm: –N=CH 165.58, =N–CH₂ 56.38, CH₂ 31.65, in the aromatic ring 120.78, 160.72, 119.57, 135.24, 109.57, 133.96.

To synthesize the [Zn(5Br-salpn-1,3)] complex, to a solution of H₂(5Br-salpn-1,3) in ethanol (0.5 g, 1.14 mmol, 15 mL of ethanol), a saturated aqueous solution of Zn(CH₃COO)₂ · 2H₂O (0.22 g, 1.14 mmol) was added with heating and stirring. The formed light-yellow precipitate was filtered and washed with hot ethanol. The complex was dried in vacuum over phosphorus pentoxide. The yield of the product was 83%. The IR spectrum, ν/cm⁻¹: ν(C=N) 1626; ν(C=C) of Ar fragments 1590, 1529, 1462. The ¹H NMR spectrum, δ, ppm (J, Hz): –N=CH 8.19 s, =N–CH₂ 3.66 t (5.00), CH₂ 1.93 m, in the aromatic ring 7.26 d (2.65), 7.15 dd (2.65, 9.03), 6.48 d (9.03). The ¹³C{¹H} NMR spectrum, δ, ppm: –N=CH 168.95, =N–CH₂ 60.42, CH₂ 29.87, in the aromatic ring 120.76, 170.49, 125.13, 135.84, 102.17, 136.81.

The electronic absorption spectra at 293 K were recorded within the range of 200–900 nm on a Shimadzu UV 2550 PC spectrophotometer. To study the effect of the solvent polarity on the position and intensity of absorption bands, we used solvents with different spectroscopic polarity parameters Z [7], namely, acetonitrile, dichloromethane, ethanol, methanol, DMFA, and DMSO.

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

The ¹H and ¹³C{¹H} NMR, ¹H–¹³C HMQC, and ¹H–¹HNOESY spectra were recorded on a Jeol JNM-ECX400A spectrometer with working frequencies of 399.78 (¹H) and 100.53 MHz (¹³C) in dimethylsulfoxide-*d*₆. As an internal standard, we used signals of residual protons of the nondeuterated solvent. The signals of protons and carbon atoms of =N–CH₂ and –CH=N– groups were identified based on analysis of the ¹H–¹³C HMQC spectra.

The photoluminescence spectra of polycrystalline samples, as well as of solutions of azomethine and Zn(II) complex in dimethylformamide (DMFA) and dimethyl sulfoxide (DMSO), were measured at 293 K using a Fluorat-02-Panorama spectrometer. The relative quantum yields of luminescence (Φ_{rel}) were determined using the method described in [8]. As a standard, we used an alkaline aqueous solution of fluorescein (λ_{max} = 515 nm, Φ_{lum} = 0.85 at 293 K). The accuracy of Φ_{rel} determination was 20%.

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 azomethine H₂(5Br-salpn-1,3) in methanol, ethanol, acetonitrile, dichloromethane, DMFA, and DMSO are caused by the spin-allowed transitions of different orbital nature (Fig. 2; the main parameters are listed in Table 1).

The absorption bands with maxima in the region of 220 and 250 nm, the positions of which are almost independent of the Z parameter of the solvent, belong to the intraligand transitions of the π–π* type in aryl fragments.

The absorption band peaking at 325 nm is assigned to the n–π* and π–π* transitions in the azomethine fragments –HC=N– [9]. In highly nucleophilic solvents (alcohols, DMFA, and DMSO) [10], the electronic absorption spectra of azomethine are characterized by the existence of an additional absorption band with a moderate intensity and a peak at 415 nm, which belongs to the n–π* transitions in bipolar keto-amine structures [9, 11]. In the solvents mentioned, additional polarization of hydroxy groups may occur, which is favorable for partial transformation of benzenoid fragments of azomethine into quinoid fragments.

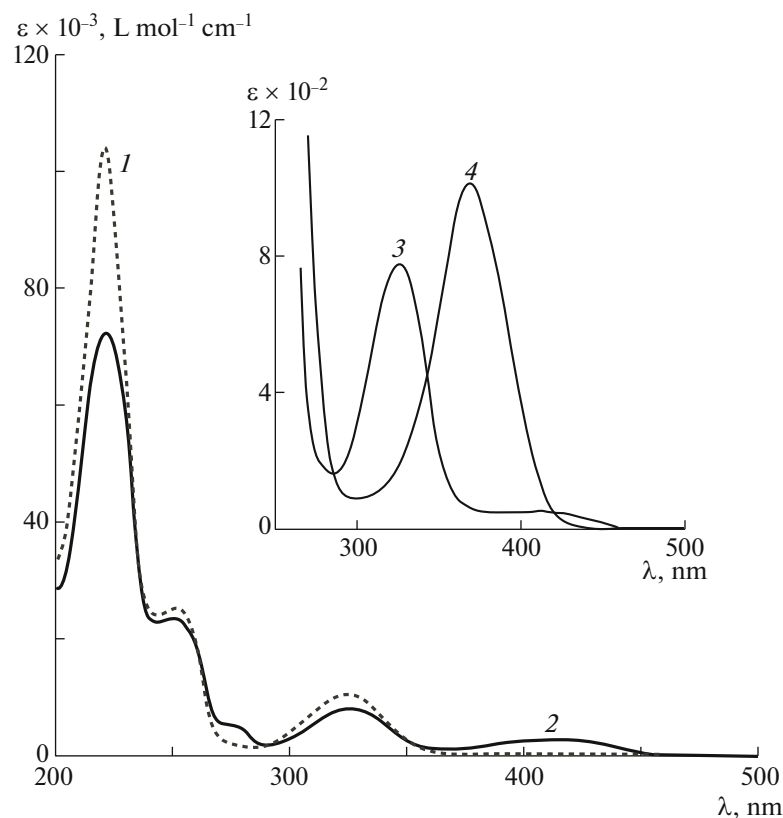


Fig. 2. Electronic absorption spectra of $\text{H}_2(5\text{Br-salpn-1,3})$ azomethine in (1) CH_3CN , (2) CH_3OH , and (3) DMFA, as well as of (4) the $[\text{Zn}(5\text{Br-salpn-1,3})]$ complex in DMFA.

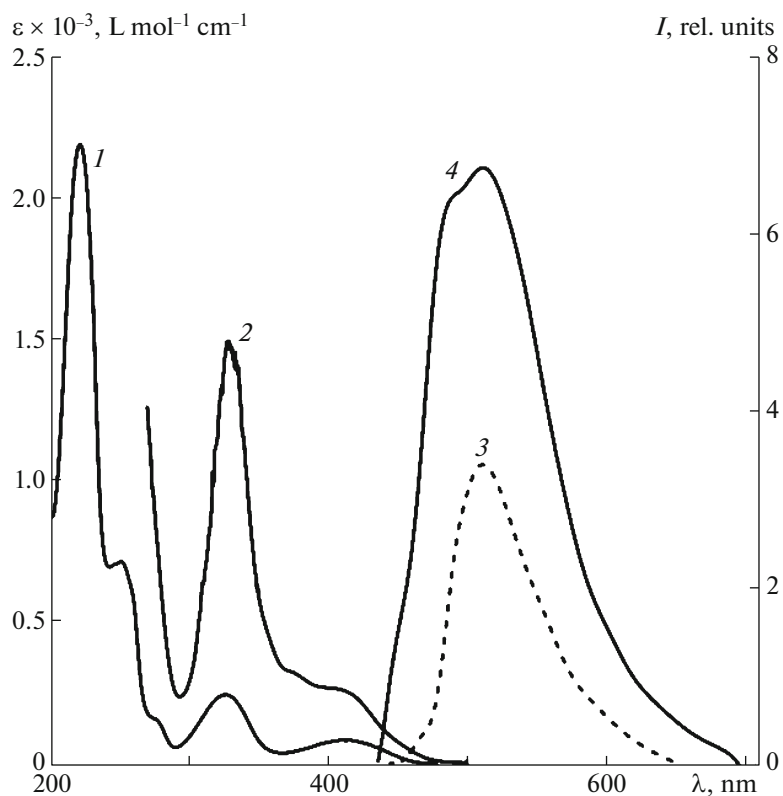


Fig. 3. (1) Absorption spectrum of $\text{H}_2(5\text{Br-salpn-1,3})$ and (2) its luminescence excitation spectrum (solutions in CH_3OH , $\lambda_{\text{rec}} = 510 \text{ nm}$, $T = 293 \text{ K}$). (3, 4) Luminescence spectra ($\lambda_{\text{exc}} = 340 \text{ nm}$) of (3) polycrystalline $\text{H}_2(5\text{Br-salpn-1,3})$ 293 K and (4) its solution in CH_3OH ($C = 5 \times 10^{-3} \text{ M}$, 293 K).

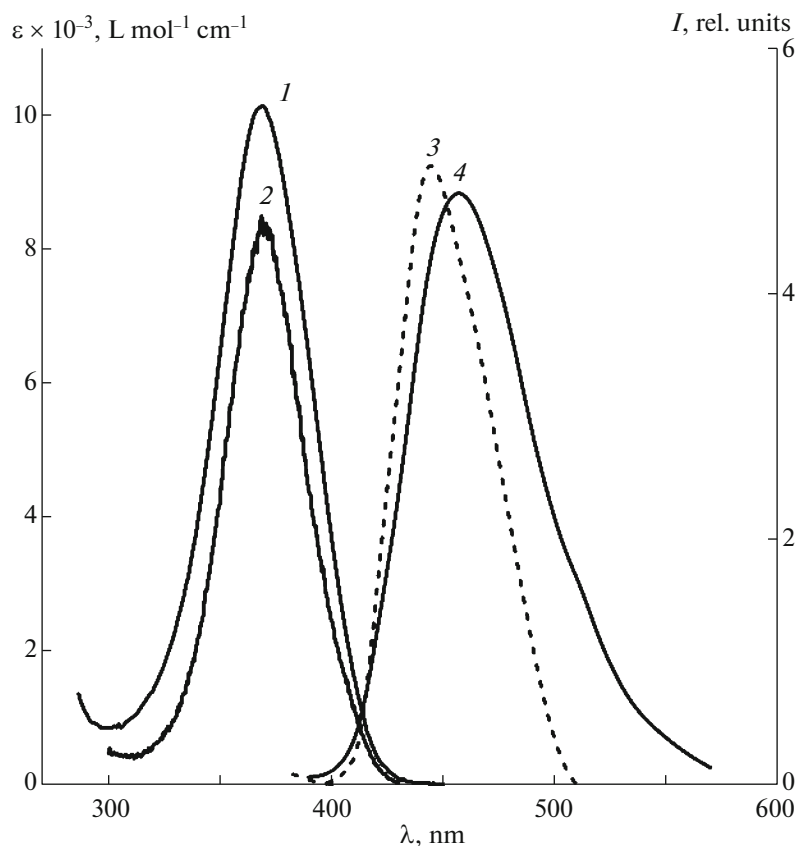


Fig. 4. (1) Absorption and (2) luminescence excitation ($\lambda_{\text{rec}} = 460$ nm) spectra of $[\text{Zn}(\text{5Br-salpn-1,3})]$ complex in DMFA at $T = 293$ K. (3, 4) Luminescence spectra ($\lambda_{\text{exc}} = 370$ nm, 293 K) of (3) polycrystalline $[\text{Zn}(\text{5Br-salpn-1,3})]$ and (4) its solution in DMFA ($C = 5 \times 10^{-5}$ M).

In contrast to $\text{H}_2(\text{5Br-salpn-1,3})$, the corresponding Zn(II) complex is soluble only in DMFA and DMSO. It is known that the low solubility of $[\text{Zn}(\text{Schiff})]$ complexes is caused by the intermolecular Zn–O–Zn interaction, which leads to the formation of dimeric structures in the crystalline state [12]. Such structures with the intermolecular bonds M–O–M (M = Cu, Ni, Zn) appear because the electron density of the metal center of one monomeric fragment of the complex is accepted by the phenyl oxygen of another fragment [13–15].

The coordination of DMFA and DMSO molecules to Zn(II) ions presumably leads to disruption of the Zn–O–Zn molecular bonds and formation of well-soluble forms of the composition $[\text{Zn}(\text{5Br-salpn-1,3})(\text{DMF})]$ or $[\text{Zn}(\text{5Br-salpn-1,3})(\text{DMSO})]$.

The electronic absorption spectra of solutions of $[\text{Zn}(\text{5Br-salpn-1,3})]$ in DMFA and DMSO exhibit only one moderate-intensity band with a peak in the region of 370 nm, which corresponds to the π – π^* transition in the azomethine group. The absence of the 415-nm absorption band, which is characteristic for $\text{H}_2(\text{5Br-salpn-1,3})$, is explained by the distortion of

the quinoid form of azomethine upon the formation of the $[\text{ZnN}_2\text{O}_2]$ coordination site.

At 293 K, the compounds under study luminesce both in the crystalline state and in diluted DMFA and DMSO solutions. According to the literature [1, 16], photoluminescence of aromatic azomethines and $[\text{Zn}(\text{Schiff})]$ complexes occurs due to the radiative decay of short-lived ($\tau < 1$ μs) singlet excited electronic states of the $^1(\pi^*-\pi)$ type.

The fluorescence spectra of a solid sample of $\text{H}_2(\text{5Br-salpn-1,3})$ and its solution in methanol show weakly structured bands (Fig. 3). The similarity of the luminescence spectra (band shapes and peak positions) points to a weak π – π interaction between the aryl fragments of azomethine in both the crystalline state and solution (Fig. 3, curves 3, 4).

The highly intense fluorescence band of solid $[\text{Zn}(\text{5Br-salpn-1,3})]$ with $\lambda_{\text{max}} = 445$ nm (Fig. 4, curve 3) is hypsochromically shifted with respect to the emission band of $\text{H}_2(\text{5Br-salpn-1,3})$. Such a shift was observed in [17–19] and is explained by photo-stimulated intramolecular proton transfer resulting in the formation of the quinoid form of $\text{H}_2(\text{Schiff})$ in the

Table 2. Some characteristics of the photoluminescence of azomethine and its Zn(II) complex

State/solvent	λ_{\max} , nm	Φ_{rel}
H ₂ (5Br-salpn-1,3)*	510	—
H ₂ (5Br-salpn-1,3)/DMFA	470	0.013
H ₂ (5Br-salpn-1,3)/DMSO	470	0.012
[Zn(5Br-salpn-1,3)]*	445	—
[Zn(5Br-salpn-1,3)]/DMFA	460	0.060
[Zn(5Br-salpn-1,3)]/DMSO	460	0.055

* Polycrystalline samples.

luminescent excited electronic state, which is characterized by a smaller energy difference between the HOMO and LUMO compared to the corresponding Zn(II) complexes.

It should be noted that crystalline azomethines contain only a small amount of the quinoid form, which appears independently of the proton phototransfer. In particular, the X-ray photoelectron spectra of H₂(Schiff) usually contain additional low-intensity lines corresponding to quinoid oxygen and to nitrogen with localized and delocalized positive charges [20]. The formation of [Zn(Schiff)] complexes leads to distortion of tautomers, which is accompanied by an increase in the energy difference of the radiative transition.

The studied Zn(II) complex exhibits intense luminescence in diluted DMFA and DMSO solutions. The fluorescence band maximum is bathochromically shifted from 445 to 460 nm in comparison with the solid complex. This is probably related to a decrease in the effective charge of the complexing agent due to the disruption of the Zn–O–Zn bonds and the coordination of solvent molecules.

The H₂(5Br-salpn-1,3) and [Zn(5Br-salpn-1,3)] solutions are characterized by the absence of a dependence of the profiles and peak positions of emission bands on the exciting light energy. The similarity of the absorption and luminescence excitation spectra (Figs. 3, 4, curves 1, 2) points to the existence of only one energetically lowest luminescent singlet state of the ¹($\pi^*-\pi$) type for each of the compounds studied; the probability of internal conversion from the highest excited electronic state to the lowest state is close to unity.

The relative quantum yields of luminescence Φ_{rel} for solutions of the compounds in DMFA and DMSO are determined (Table 2).

Thus, we have studied the spectral and luminescent properties of aromatic azomethine and its Zn(II) complex, which fluoresce in the blue spectral region.

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Translated by M. Basieva