

CONDENSED-MATTER
SPECTROSCOPY

Fluorescence of Zinc Complex with N,N'-Bis(5-Bromosalicylidene)Ethylenediamine

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Abstract—A Zn(II) complex with N,N'-bis(5-bromosalicylidene)ethylenediamine exhibiting intense visible blue luminescence is synthesized. It is found that the zinc complex fluoresces at 293 K in both polycrystalline form and in solutions ($\lambda_{\text{max}} = 440$ and 450 nm, respectively); the relative fluorescence quantum yields of the complex are determined in dilute ethanol, dimethylformamide, and dimethylsulfoxide solutions.

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INTRODUCTION

It is known that Zn(II) complexes with aromatic azomethines of N₂O₂ and NO types (Schiff bases), salicylic aldehyde derivatives, can exhibit intense fluorescence in the visible spectral range and can be used as emitting layers for creating efficient electroluminescent devices [1–3]. The luminescent properties of [Zn(Schiff)] complexes in solutions and polycrystalline form are related to the radiative transitions between the levels of the organic ligand and are determined by its structural features, i.e., by the electronic character of substituents in aryl fragments, the diamine-bridge nature, and the length of the π -conjugation system [4–6].

In the present work, we consider the spectral and luminescent properties of tetradentate aromatic azomethine of the N₂O₂ type—N,N'-bis(5-bromosalicylidene)ethylenediamine—and its Zn(II) complex, i.e., H₂(5Br-salen) and [Zn(5Br-salen)] (Fig. 1).

EXPERIMENTAL

The elemental analysis of the compounds was performed on a Eurovector EA3000 analyzer. The IR spectra (KBr pellets) were recorded on a Shimadzu

IR-Prestige 21 Fourier-transform spectrometer in the range of 4000–400 cm⁻¹.

Synthesis of H₂(5Br-salen). Azomethine was obtained by condensation of bromosalicylic aldehyde (Aldrich, 98%) (0.47 g, 2.34 mmol, 15 mL of ethanol) and ethylenediamine (Merck, 99%) (0.08 mL, 1.17 mmol) under conditions of general acid catalysis with glacial acetic acid. Heating and mixing of the obtained solution for 5 min results in the formation of bright yellow crystals. The targeted compound was filtered, washed with ethanol, and dried in air at 70°C. The yield was 90%. The results of elemental analysis (chemical formula C₁₆H₁₄N₂O₂Br₂) are as follows (calculated/determined, %): C 45.07/44.92, H 3.29/3.23, N 6.57/6.64. The IR spectrum, ν/cm^{-1} : $\nu(\text{C}=\text{N})$ 1635; $\nu(\text{C}=\text{C})$ of Ar fragments 1568, 1476, 1448.

Synthesis of [Zn(5Br-salen)]. To synthesize the complex, we added with stirring saturated aqueous solution Zn(CH₃COO)₂ · 2H₂O (0.21 g, 0.94 mmol) to boiling solution of H₂(5Br-salen) in ethanol (0.40 g, 0.94 mmol, 40 mL of ethanol). The formed white precipitate was filtered and repeatedly washed with hot ethanol. The complex was dried in air at 70°C and then in vacuum over phosphorus pentoxide. The yield

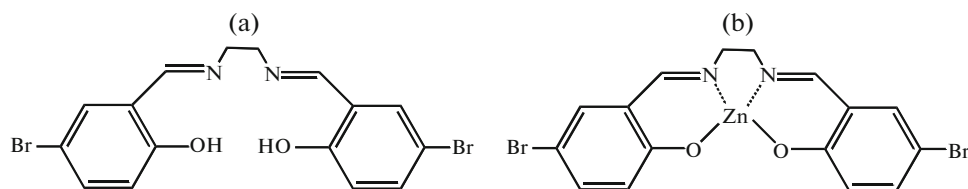


Fig. 1. Structural formulas of (a) H₂(5Br-salen) azomethine base and (b) [Zn(5Br-salen)] complex.

Table 1. Characteristics of the electronic-absorption spectra of H₂(5Br-salen) and [Zn(5Br-salen)] in different solvents

Compound	C ₂ H ₅ OH, Z = 79.6 kcal mol ⁻¹	DMSO, Z = 71.1 kcal mol ⁻¹	DMF, Z = 68.5 kcal mol ⁻¹	CH ₂ Cl ₂ , Z = 64.2 kcal mol ⁻¹
	λ _{max} , nm (logε)	λ _{max} , nm (logε)	λ _{max} , nm (logε)	λ _{max} , nm (logε)
H ₂ (5Br-salen)	220 (4.76); [250] (4.27); [279] (3.49); 328 (3.86); 415 (3.13)	326 (4.15); 418 (3.07)	327 (3.72); 417 (3.72)	[253] (4.27); 328 (3.92)
[Zn(5Br-salen)]	230 (4.53); [242] (4.52); [261] (4.06); 360 (3.79)	[265] (4.38); 365 (4.19)	[265] (4.48); 367 (4.23)	Insoluble

[] shoulder.

was 85%. The results of elemental analysis (chemical formula C₁₆H₁₂N₂O₂Br₂Zn) are as follows (calculated/determined, %): C 39.23/38.95, H 2.45/2.57, N 5.72/5.85. IR spectrum, ν/cm⁻¹: ν(C=N) 1647; ν(C=C) of Ar fragments 1589, 1477, 1526, 1435.

The electronic-absorption spectra of solutions of azomethine and its Zn(II) complex were recorded at 293 K within the range of 200–700 nm on a Shimadzu UV 2550 PC spectrophotometer.

The luminescence spectra of polycrystalline samples, as well as of solutions of the Zn(II) complex in ethanol, DMF, and DMSO, were measured at 293 K using a Flyuorat-02-Panorama spectrofluorimeter. The relative luminescence quantum yields (Φ_{rel}) were calculated by the Parker formula [7]

$$\Phi_{\text{rel}} = \Phi_{\text{st}} \frac{(1 - 10^{-D_{\text{st}}}) S_x n_x^2}{(1 - 10^{-D_x}) S_{\text{st}} n_{\text{st}}^2},$$

where Φ_{st} is the luminescence quantum yield of the standard, S_x and S_{st} are the areas under the curves of the real luminescence spectra of the sample and the standard, D_x and D_{st} are the optical densities of the solutions at the excitation wavelength, and n_x and n_{st} are the refractive indices of the solutions.

As a standard, we used an aqueous solution of fluorescein in 0.1 M NaOH (λ_{max} = 520 nm, Φ_{st} = 0.85 at 293 K [8]). The accuracy of Φ_{rel} determination was 20%.

RESULTS AND DISCUSSION

The electronic-absorption spectra of solutions of azomethine H₂(5Br-salen) in ethanol, dichloromethane, DMF, and DMSO are formed by spin-allowed transitions of different orbital natures (the main parameters of the spectra are listed in Table 1).

The intense absorption bands of H₂(5Br-salen) solutions with maxima in the regions of 220, 250, and

280 nm, the positions of which are independent of the spectroscopic solvent polarity parameter Z [9], correspond to the intraligand transitions of the π–π* type in aryl fragments. The band peaking around 330 nm is caused by the n–π* and π–π* transitions in azomethine groups –HC=N– [10].

The electronic-absorption spectra of azomethine solutions in alcohols, DMSO, and DMF exhibit an additional band with a maximum at 415 nm. This band corresponds to the n–π* transitions in quinoid fragments of azomethine [10, 11], which are formed upon intramolecular proton transfer between the nitrogen atom and the oxygen of the hydroxyl group. It is obvious that the formation of keto-enol structures is most probable in the aforementioned solvents, which are characterized by a high nucleophilicity [12].

The [Zn(5Br-salen)] complex is soluble in ethanol, DMF, and DMSO and almost insoluble in dichloromethane, chloroform, acetone, and acetonitrile. The low solubility of the complex may be caused by the formation of stacking dimers with Zn–O–Zn intermolecular bonds [13]. These structures appear due to the accepting of the electron density of the complexing agent of one monomeric unit of the complex by phenolic oxygen of another unit. Presumably, the coordination of molecules of solvents with a high donor number (nucleophilicity) by Zn(II) ions leads to destruction of dimers.

The electronic-absorption spectrum of the [Zn(5Br-salen)] solution in C₂H₅OH exhibits bands peaking at 230, 242, and 260 nm, which are assigned to the π–π* transitions in the aryl fragments of coordinated azomethine. In ethanol, DMF, and DMSO, one also observes an intermediate-intensity band with a maximum in the region of 360 nm, which corresponds to the π–π* transitions in azomethine groups. The absence of [Zn(5Br-salen)] absorption in the region of 450 nm typical for H₂(5Br-salen) is

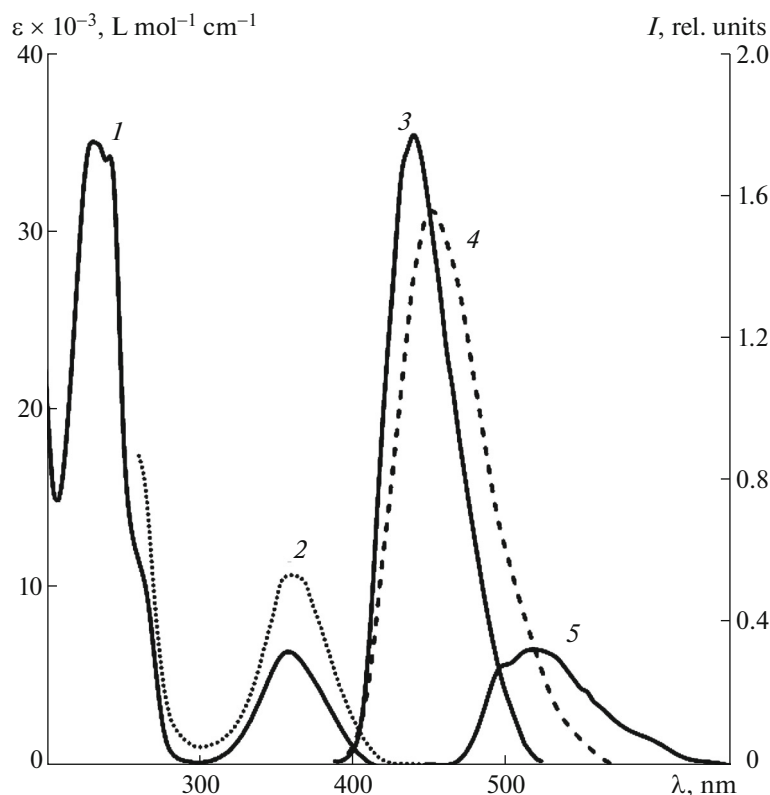


Fig. 2. (1) Absorption and (2) luminescence-excitation spectra of $[\text{Zn}(5\text{Br-salen})]$ complex ($\lambda_{\text{rec}} = 495 \text{ nm}$, 293 K, solvent $\text{C}_2\text{H}_5\text{OH}$). (3–4) Luminescence spectra of $[\text{Zn}(5\text{Br-salen})]$ ($\lambda_{\text{exc}} = 340 \text{ nm}$, 293 K) for (3) a polycrystalline sample and (4) a solution in $\text{C}_2\text{H}_5\text{OH}$, $C = 5 \times 10^{-5} \text{ M}$. (5) Luminescence spectrum ($\lambda_{\text{exc}} = 340 \text{ nm}$, 293 K) of polycrystalline $\text{H}_2(5\text{Br-salen})$.

explained by destruction of the quinoid form of azomethine upon complexation.

At 293 K, $\text{H}_2(5\text{Br-salen})$ and $[\text{Zn}(5\text{Br-salen})]$ luminesce in the polycrystalline form and in dilute solutions. According to [14], the photoluminescence of aromatic azomethines (Schiff bases) and corresponding $[\text{Zn}(\text{Schiff})]$ complexes is caused by radiative decay of short-lived singlet excited electronic states of the $^1(\pi^*-\pi)$ type.

The fluorescence spectra of $\text{H}_2(5\text{Br-salen})$ in ethanol, DMF, and DMSO, as well as in the polycrystalline form (Fig. 2, curve 5), at 293 K are characterized by the presence of a low-intensity weakly structured band. The emission-band maximum in solid samples is bathochromically shifted with respect to dilute solutions from 450 to 520 nm. Such a decrease in the radiative transition energy indicates the existence of intermolecular interaction of the $\pi-\pi$ type between aryl fragments of azomethine $\text{H}_2(5\text{Br-salen})$ in the polycrystalline state.

The $[\text{Zn}(5\text{Br-salen})]$ complex exhibits intense luminescence in dilute solutions in ethanol, DMF, and DMSO. Compared to the polycrystalline sample, the fluorescence maxima of the complex solutions are bathochromically shifted from 440 to 450 nm (Fig. 2,

curves 3 and 4). The decrease in the radiative transition energy in this case is probably related to a decrease in the effective charge of zinc ions upon destruction of stacking dimers and coordination of solvent molecules.

The position and profile of the fluorescence band of $[\text{Zn}(5\text{Br-salen})]$ solutions do not depend on the exciting light energy. The luminescence excitation spectra of the complex agree well with the spin-allowed optical transitions in the absorption spectrum (Fig. 2, curves 1 and 2). This confirms the assignment of the complex luminescence to radiative transitions from the single energy-lowest excited state of the $^1(\pi^*-\pi)$ type. The probability of internal conversion from the highest excited states to the lowest state is close to unity.

The values of relative luminescence quantum yields Φ_{rel} for the complex solutions in ethanol, DMF, and DMSO are presented in Table 2. These values show that complexation leads to a considerable increase in the fluorescence quantum yield. This is obviously related to a more rigid structure of azomethine in the coordinated state and to a decrease in the probability of nonradiative decay of the excited state.

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

Compound/solvent	λ_{\max} , nm	Φ_{rel}
H ₂ (5Br-salen)*	520	–
H ₂ (5Br-salen)/DMF	450	0.03
H ₂ (5Br-salen)/DMSO	450	0.01
H ₂ (5Br-salen)/C ₂ H ₅ OH	450	0.01
[Zn(5Br-salen)]*	440	–
[Zn(5Br-salen)]/DMF	453	0.08
[Zn(5Br-salen)]/DMSO	452	0.07
[Zn(5Br-salen)]/C ₂ H ₅ OH	450	0.06

* Polycrystalline samples.

Thus, we have studied the spectral and luminescent properties of the Zn(II) complex with N,N'-bis(5-bromosalicylidene)ethylenediamine, which exhibits fluorescence in the blue spectral range.

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