PHOTONICS

Spectral and Luminescent Properties of *N***,***N'***-Bis(salicylidene)-1,4- Butylenediamine,** *N***,***N'***-Bis(5-bromosalicylidene)-1,4- Butylenediamine, and Their Complexes with Zinc(II)**

A. N. Borisov*a***, *, M. V. Puzyk***^a* **, E. A. Posadskaya***a***, L. P. Ardasheva***a***, and V. N. Pak***^a*

a Russian State Pedagogical University, St. Petersburg, 191186 Russia ******e-mail: alexey-borisov@mail.ru* Received October 10, 2019; revised October 22, 2019; accepted October 22, 2019

Abstract—The spectral and luminescent properties of N_2O_2 -type aromatic azomethines, *N*,*N*'-bis(salicylidene)-1,4-butylenediamine, *N*,*N*'-bis(5-bromosalicylidene)-1,4-butylenediamine, and their complexes with $Zn(II)$, have been studied. All compounds at 293 K fluoresce in solutions and in a polycrystalline state. An increase in the fluorescence intensity of the azomethines in alcohol solutions occurs upon their conversion to the quinoid form. The main photoluminescent parameters of solutions of the compounds in DMF and DMSO have been determined. Depending on the presence of bromoaryl substituents in the structure of the ligands and the solvent properties, the zinc complexes fluoresce with quantum yields up to 50%.

Keywords: luminescence, azomethine bases, Zn(II) complexes **DOI:** 10.1134/S0018143920020034

Coordination compounds of transition metals with azomethine bases (Schiff bases) attract the attention of researchers and are considered as precursors for the creation of new functional materials. In particular, complexes of some *d* elements with aromatic azomethines of N_2O_2 -, NO-, and N_4 -types ([M(Schiff)]) possess luminescent [1, 2], catalytic [3], and sensory properties [4], as well as the ability to form stable conductive polymers [5].

It is known that some complexes of Zn(II) with aromatic azomethines (Schiff bases), derivatives of salicylic aldehyde, intensively fluoresce in the visible spectral region and can be used to create the emission layer of electroluminescent devices [6]. The spectral and luminescent properties of [Zn(Schiff)] complexes are mainly determined by the nature of the coordinated azomethine base: the electronic character of substituents in the aryl fragments, the structure of the diamine bridge, and the extension of the π -conjugation system [7, 8]. Hence, the structural features of the ligand environment, as well as the nature of the intermolecular interaction, determine the energy of the radiative transition and the luminescence efficiency of the zinc complexes in a polycrystalline form and solutions.

This work considers the electronic absorption and emission properties of tetradentate aromatic azomethines of N_2O_2 -type *N,N*'-bis(salicylidene)-1,4-butylenediamine $(H_2(salbn-1,4))$ and *N*,*N*⁻bis(5-bromosalicylidene)-1,4-butylenediamine $(H_2(5Br-salbn-$ 1,4)), and their complexes with Zn(II) (Scheme 1).

Scheme 1. Structures of (a) azomethines and (b) their complexes with $Zn(II): X = H(H_2(salbn-1,4)$ and $[Zn(salbn-1,4)]$; $X = Br(H_2(5Br-salbn-1, 4)$ and $[Zn(5Br-salbn-1, 4)]$.

The choice of azomethine bases for the synthesis of the Zn(II) complexes is due to the limiting character of the diamine fragment $-(CH₂)₄$, which limits the length of the internal conjugation system and favors the tetrahedral structure of the coordination site $[ZnN_2O_2]$. The luminescent properties of azomethines H_2 (salbn-1,4) and H_2 (5Br-salbn-1,4) and the corresponding zinc complexes have not been studied previously.

EXPERIMENTAL

The synthesis of azomethines H_2 (salbn-1,4) and $H₂(5Br-salbn-1,4)$ was carried out under the conditions of general acid catalysis with glacial acetic acid.

Synthesis of H₂(salbn-1,4). *N,N*'-bis(salicylidene)-1,4-butylenediamine was obtained by the condensation reaction of butylenediamine-1,4 (Merck, 99%, 0.149 g, 1.69 mmol) and salicylic aldehyde (0.412 g, 3.38 mmol, in 10 mL of ethanol). After heating and stirring the resulting solution for 15 min, a lemon yellow precipitate was formed. The compound was filtered, washed with cold ethyl alcohol and ether, and dried. The results of elemental analysis (gross formula $C_{18}H_{20}N_2O_2$, calculated/found, %: C 72.97/72.84, H 6.76/6.85, N 9.46/9.54. IR spectrum, v/cm^{-1} : $v(C = N)$ 1632, $v(Ar-O)$ 1285, $v(O-H)$ 2864. The yield was 86%.

Synthesis of H₂(5Br-salbn-1,4). N , N -bis(5-bromosalicylidene)-1,4-butylenediamine was obtained by the condensation reaction of butylenediamine-1,4 (Merck, 99%, 0.039 g, 0.44 mmol) and 5-bromosalicylic aldehyde (Aldrich, 98%, 0.18 g, 0.88 mmol, in 15 mL of ethanol). Upon mixing the reactants, a yellow solution was formed, which was then heated for 10 min. The yellow precipitate formed was filtered off, washed with ethanol and ether, and dried. The gross formula is $C_{18}H_{18}N_2O_2Br_2$. The results of elemental analysis, calculated/found, %: С 47.58/47.46, Н 3.96/4.02, N 6.17/6.15. IR spectrum, ν/cm−1: ν(С=N) 1633, ν(Ar−O) 1281, ν(O−H) 2864. The yield was 80%.

Synthesis of $[Zn(salbn-1,4)] \cdot H_2O$ **.** To obtain the complex, a saturated aqueous solution of a saturated aqueous solution of $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.17 g, 0.77 mmol) was added to a solution of $H₂(salbn-1,4)$ in ethanol (0.23 g, 0.77 mmol, in 10 mL of alcohol). The resulting mixture was stirred and heated. The pale yellow precipitate formed was filtered off, washed with hot ethanol, and dried. The gross formula is $C_{18}H_{20}N_2O_3Zn$. The results of elemental analysis, calculated/found, %: С 57.19/57.06, Н 5.30/5.42, N 7.41/7.50. IR spectrum, v/cm^{-1} : $v(C=N)$ 1628, $v(Ar-O)$ 1278, $v(H₂O)$ 3550−3350. The yield was 73%.

Synthesis of $[Zn(5Br-salbn-1,4)]$ **· H₂O.** A saturated aqueous solution of $Zn(CH_3COO)$, $2H_2O (0.13 g)$ 0.59 mmol) was added to a solution of $H_2(5Br-salbn-$

1,4) (0.27 g, 0.59 mmol, in 15 mL of ethanol) with stirring and heating. A pale yellow precipitate was formed, which was filtered off, washed with hot ethyl alcohol, and dried. The gross formula is $C_{18}H_{18}N_2O_3Br_2Zn$. The results of elemental analysis, calculated/found, %: С 40.34/40.26, Н 3.36/3.49, N 5.23/5.32. IR spectrum, v/cm^{-1} : $v(C=N)$ 1623, $v(Ar-O)$ 1280, $v(H₂O)$ 3650−3350. The yield was 68%.

The IR transmission spectra of azomethines and Zn(II) complexes were measured in the range of $4000-400$ cm⁻¹ (tablets with KBr) on a Shimadzu IR-Prestige 21 IR Fourier spectrometer.

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

The luminescence spectra of polycrystalline samples, as well as solutions of Zn(II) complex in ethanol, DMF, and DMSO at 293 K, were obtained using a Flyuorat-02-Panorama spectrofluorimeter. The relative luminescence quantum yields (Φ_{rel}) were calculated using the Parker formula [9]:

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

where Φ_{st} is the luminescence quantum yield of the standard; S_x and S_{st} are the areas under the curves of the true luminescence spectra of the sample and the standard, respectively; A_x and A_{st} are the absorbances of solutions at an excitation wavelength; and n_x and n_{st} are the refractive indices of solutions. An aqueous solution of fluorescein in 0.1 M NaOH (λ_{max} = 520 nm, $\Phi_{st} = 0.85$ at 293 K [10]) was used as a standard. The accuracy of Φ_{rel} determination was 10%.

RESULTS AND DISCUSSION

Electronic absorption spectra of solutions of $H₂(salbn-1,4)$ and $H₂(5Br-salbn-1,4)$ in ethanol, dichloromethane, DMF, and DMSO are due to spinallowed transitions of different orbital nature. Table 1 presents the main parameters of the spectra.

The high-intensity absorption bands with maximums in the range of 215–220 and 250–250 nm correspond to $\pi \pi^*$ transitions in the aryl groups of azomethines [11]; their position is practically not affected by a change in the spectroscopic solvent polarity parameter *Z* (Table 1, Fig. 2). The band with a maximum in the region of 315 nm (326 nm for $H_2(5Br-salbn-1,4)$) is due to $\pi \pi^*$ transitions in the azomethine groups [12].

In solvents with high *Z* values (alcohols) and high nucleophilicity (DMF, DMSO), an additional broad band of medium intensity with a maximum in the region of 400 nm appears in EAS of azomethines, which corresponds to *n*π* transitions in bipolar keto-

Compound	C_2H_5OH , $Z = 79.6$ kcal mol ⁻¹	DMSO, $Z = 71.1$ kcal mol ⁻¹	DMF, $Z = 68.5$ kcal mol ⁻¹	CH_2Cl_2 $Z = 64.2$ kcal mol ⁻¹
	λ_{max} , nm (log ε)	λ_{max} , nm (log ε)	λ_{max} , nm (log ε)	λ_{max} , nm (log ε)
$H2(salbn-1,4)$	215(4.60); 255(4.28); $[278]$ (3.79); 313 (3.79); 402(3.40)	315 (3.78); [375] (2.90); [403] (3.42)	315(3.87); $[375]$ (3.63) ; 415(3.33)	255(4.36); 315(3.90)
$H2(5Br-salbn-1,4)$	220(4.74); 250(4.26); $[277]$ (3.5) ; 326 (3.79) ; 409 (3.34)	326(3.89); 415(3.04)	326(3.58); 415(2.36)	224(4.83); 253(4.31); 326 (3.92)
$[Zn(salbn-1,4)]$		$[259]$ (4.38); [325] (3.25) ; 366 (3.72)	[272] (4.00); [321] (3.45) ; 367 (3.80)	
$[Zn(5Br-salbn-1,4)]$		$[269]$ (4.10); 374 (3.90)	$[268]$ (4.10); 373 (3.91)	

Table 1. Characteristics of EAS of azomethines and Zn(II) complexes in different solvents

"[$]$ " Shoulder.
" $\sum_{n=1}^{\infty}$ " Solubility

Solubility less than 0.05 mg/mL.

imine structures—quinoid forms [13, 14]. This band is absent in acetonitrile and dichloromethane.

In contrast to azomethines, the zinc complexes are soluble only in DMF and DMSO and have very limited solubility in ethanol $(\leq 0.1 \text{ mg/mL})$. The low solubility of such complexes is explained by the formation of cluster structures at the expense of intermolecular donor–acceptor bonds Zn–O–Zn [15]. The solving action of DMF and DMSO is obviously due to coordination of solvent molecules, coupled with destruction of intermolecular bonds.

Upon complexation, the position of the bands corresponding to $\pi \pi^*$ transitions in the aryl groups remains practically unchanged. At the same time, the formation of the coordination site leads to the destruction of keto-imine structures and, hence, disappearance of the "quinoid" band, as well as an insignificant bathochromic shift of the "azomethine" band.

Compared to azomethines, an additional band of medium intensity with a maximum at 367 nm appears in EAS of the complexes. In the literature [16], information is available about its assignment to ligand-tometal charge transfer (**LMCT**), which is consistent with the tetrahedral structure of the coordination site. The LMCT bands, as a rule, shift bathochromically with increasing the solvent parameter $Z[17]$; however, due to the low solubility of the complexes, this feature could not be verified.

At 293 K, the studied compounds luminesce in polycrystalline form and in solutions. According to the literature data [18], photoluminescence of aromatic azomethines (Schiff bases) and the corresponding complexes [Zn(Schiff)] is due to radiative degradation of short-lived (τ < 1 µs) singlet electronically excited states of $(\pi^* - \pi)$ type.

Apparently, the necessary condition for fluorescence of azomethine bases is the presence of aryl-type hydroxy groups in their structure. We showed in our experiments that azomethines—derivatives of benzaldehyde, 3-methoxybenzaldehyde, and 2-aminobenzaldehyde, not containing aryl hydroxy groups, do not luminesce in the solid form and in solutions.

Fluorescence is characteristic of aromatic azomethines of the N_2O_2 type in the quinoid form, which is formed upon excitation as a result of photoinduced proton transfer to the nitrogen atom of the imino group [19]. However, when considering the photochemical mechanism of the formation of the luminescent tautomer, it should be kept in mind that crystalline azomethines initially contain an insignificant amount of the quinoid form not associated with photoinduced proton transfer. In particular, in the X-ray photoelectron spectra of azomethines of the N_2O_2 type, low-intensity components are always present corresponding to quinoid oxygen and nitrogen with localized and delocalized positive charge [20], which disappear upon complexation.

At 293 K, the luminescence spectra of polycrystalline samples of H_2 (salbn-1,4) and H_2 (5Br-salbn-1,4) represent broad unstructured bands with maximums at 493 and 510 nm, respectively (Fig. 2, curves *1*, *2*). The observed bathochromic shift in the fluorescence

Fig. 1. Electronic absorption spectra of H₂(salbn-1,4) in (*1*) CH₃CN, (*2*) C₂H₃OH, (*3*) CH₂Cl₂, (*4*) DMF, and (*5*) DMSO. $C =$ 0.1 mg/mL, 293 K.

maximum of $H₂(5Br-salbn-1,4)$ is due to the participation of bromoaryl substituents in the conjugation of *p* orbitals, which reduces the energy of the radiative transition. Unlike azomethines, the fluorescence bands of solid samples of the complexes are multicomponent: 422, 475, and 518 nm for $[Zn(salbn-1,4)]$ and 443, 495, and 515 nm for [Zn(5Br-salbn-1,4)] (Fig. 2, curves *3*, *4*). Presumably, the first two components of the emission bands of the complexes have a vibrational nature and correspond to stretching vibrations of C=C bonds in aryl groups, and the additional splitting of the radiative level is due to specificity of intermolecular interaction in the crystalline state.

Since luminescence of azomethines is due to the presence of the quinoid form, it should be expected that an increase in its content will increase the intensity of emission bands. To convert azomethines to the quinoid (salt) form, we used deprotonation of aryl hydroxy groups with alkali in an alcohol solution. Obviously, this excludes the possibility of the formation of a luminescent tautomer as a result of photoinduced proton transfer.

As an example, Fig. 3 shows the dynamics of changes in the EAS of an ethanol solution of azomethine H_2 (salbn-1,4) upon the gradual addition of alkali. The concentration of NaOH in alcohol was chosen so as to minimize the effect of dilution, and the total amount of NaOH added was equivalent to deprotonation of both hydroxy groups. The gradual increase in the absorption in the region of 400 nm corresponding to *n*π* transition in the quinoid form unambiguously indicates an increase in its concentration. The decrease in the intensity of the bands with maximums at 215 and 255 nm indicates a decrease in the aromaticity of the system, and the decrease in the intensity of the $\pi \pi^*$ transition band in the imino group (λ_{max} = 313 nm) indicates the participation of this group in stabilization of the anion formed. The changes in EAS of azomethine that occur upon its deprotonation are in good agreement with Scheme 2 of delocalization of the negative charge in the anions formed:

Fig. 2. Luminescence spectra of polycrystalline samples at 293 K of (*1*) H₂(salbn-1,4), (*2*) H₂(5Br-salbn-1,4), (*3*) [Zn(salbn-1,4), (*a*) [Zn(salbn-1,4), (*a*) [Zn(salbn-1,4), (*a*) [Zn(salbn-1,4), (*a*) [Zn(sal 1,4)], and (4) $[Zn(5Br-salbn-1,4)]$. $\lambda_{ex} = (1, 2)$ 420 and (3, 4) 337 nm.

Scheme 2. Stabilization of the anion of azomethine base in an alcohol solution upon an addition of alkali $(X = H$ or Br).

The addition of alkali causes not only changes in EAS of alcohol solutions of azomethines, but also a predictable increase in the intensity of the excitation and luminescence spectra (Fig. 3, inset).

The studied zinc complexes intensively luminesce in dilute solutions in DMF and DMSO. Compared to solid samples, the fluorescence spectra of solutions lose their multicomponent character, which is probably due to destruction of the cluster structures, a decrease in the degree of $\pi\pi$ stacking interaction, and coordination of solvent molecules.

For solutions of the complexes, the positions of the maximums and the shape of the emitting bands are independent of the energy of the excitation light, and the fluorescence excitation spectra of the complexes are in good agreement with the spin-allowed optical transitions in EAS (Fig. 4, curves *1*, *2*). This confirms the assignment of luminescence of the studied com-

Fig. 3. Dynamics of changes in EAS, excitation, and luminescence spectra (inset) of H_2 (salbn-1,4) in ethanol solution ($C =$ 0.05 mg/mL) upon the addition in 0.2-mL portions of 1.0×10^{-3} M NaOH solution in C₂H₅OH.

plexes to radiative transitions from the lowest-energy electronically excited state of the $(\pi^* - \pi)$ type. The probability of internal conversion from the higher to lowest electronically excited state is close to unity.

The values of the luminescence quantum yields Φ_{rel} for dilute solutions of the azomethines and the complexes are given in Table 2. It follows from the data that passing to $Zn(II)$ complexes leads to a significant increase in the average value of Φ_{rel} : in the case of a solution of [Zn(salbn-1,4)] in DMSO, up to 52%. The decrease in the efficiency of nonradiative processes on passing to [Zn(Schiff)] complexes is due to the more "rigid" structure of azomethines in the coordinated state.

On the other hand, the conformational "flexibility" of the aliphatic diamine bridge favors the tetrahedral structure of the coordination site $[ZnN_2O_2]$. This, in turn, hinders the stacking interaction of complex molecules and the appearance of additional $\pi\pi$ states responsible for nonradiative deactivation of electronically excited states. The decrease in the values of Φ_{rel} in the case of bromo-substituted azomethine and the complex is due to the fact that the presence of heavy bromine atoms increases the rate of the processes of nonradiative energy degradation.

CONCLUSIONS

In this work, the spectral and luminescent properties of the azomethine bases H_2 (salbn-1,4) and $H₂(5Br-salbn-1,4)$ and their complexes with zinc have been studied. It has been found that the conversion of the azomethines to the salt (quinoid) form leads to a significant increase in the fluorescence quantum yield. The high luminescence quantum yields in the blue-violet spectral region of solutions of the Zn(II) complexes (\sim 50%) are determined by the nature of the ligand environment and the solvent.

HIGH ENERGY CHEMISTRY Vol. 54 No. 2 2020

Fig. 4. (*1*) Luminescence excitation and (*2*) absorption spectra of a solution of [Zn(salbn-1,4)] in DMSO (293 K). Luminescence spectra $(\lambda_{ex} = 370 \text{ nm}, 293 \text{ K})$ of $[Zn(\text{salbn-1,4})]$ in (*4*) DMSO ($C = 2.5 \times 10^{-5}$ M) and (*5*) ethanol (saturated solution), and (3) fluorescein in 0.1 M NaOH/H₂O.

REFERENCES

- 1. Wang, S., *Coord. Chem. Rev*., 2001, vol. 251, no. 1, p. 79.
- 2. Ardasheva, L.P. and Shagisultanova, G.A., *Russ. J. Inorg. Chem*., 1998, vol. 43, no. 1, p. 85.
- 3. Canali, L., Sherrington, D.C., and Deleuze, H., *React. Funct. Polym*., 1999, vol. 40, no. 2, p. 155.
- 4. Shahrokhian, S. and Fotouhi, L., *Sens. Actuators, B*, 2007, vol. 123, no. 2, p. 942.
- 5. Shagisultanova, G.A., *Teor. Eksp. Khim*., 1991, vol. 3, p. 330.
- 6. Evans, R.C., Douglas, P., and Winscom, C.J., *Coord. Chem. Rev*., 2006, vol. 250, nos. 15–16, p. 2093.

HIGH ENERGY CHEMISTRY Vol. 54 No. 2 2020

- 7. Wong, W.-Y., Lu, G.-L., Liu, L., Shi, J.-X., and Lin, J., *Eur. J. Inorg. Chem*., 2004, no. 10, p. 2066.
- 8. Zheng, S.-L., Zhang, J.-P., Chen, X.-M., Huang, Z.-L., Lin, Z.-Y., and Wong, W.-T., *Chem.-Eur. J.*, 2003, vol. 9, no. 16, p. 3888.
- 9. Calvert, J.G. and Pitts, J.N., *Photochemistry*, New York: Wiley, 1966.
- 10. Becker, H.G.O., von, Becker, H.G.O., von (Ed.), *Einführung in die Photochemie*, Berlin: Wissenschaften, 1976.
- 11. Estiu, G.L., Jubert, A.H., Costamagna, J., and Vargas, J., *J. Mol. Struct*., 1996, vol. 367, p. 97.
- 12. Alexander, P.V. and Sleet, R.J., *Aust. J. Chem*., 1970, vol. 23, no. 6, p. 1183.
- 13. Alexander, P.V. and Sleet, R.J., *Aust. J. Chem*., 1970, vol. 23, no. 6, p. 1183–1190.
- 14. Estiu, G.L., Jubert, A.H., Costamagna, J., and Vargas, J., *J. Mol. Struct*., 1996, vol. 367, p. 97.
- 15. Ma, C.T.Z., Lo, A., Abdolmaleki, A., and Maclachlan, M.J., *Org. Lett*., 2004, vol. 6, no. 21, p. 3841.
- 16. Temel, H., Cakir, U., Otludil, B., and Ugras, I., *Synth. React. Inorg. Met.-Org. Chem*., 2001, vol. 31, no. 8, p. 1323.
- 17. Lever, A., *Inorganic Electronic Spectroscopy*, Amsterdam: Elsevier, 1984.
- 18. Garnovskii, D.A., Burlov, A.S., Vasil'chenko, I.S., Uraev, A.I., and Korshunova, E.V., *Vestn. Yuzhn. Nauchn. Tsentra RAN*, 2014, vol. 10, no. 3, p. 35.
- 19. Tong, Y.-P., Zheng, S.-L., and Chen, X.-M., *Eur. J. Inorg. Chem*., 2005, no. 18, p. 3734.
- 20. Shagisultanova, G.A., Shchukarev, A.V., and Semenistaya, T.V., *Russ. J. Inorg. Chem*., 2005, vol. 50, no. 6, pp. 912.

Translated by A. Tatikolov