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Zinc Complexes of 1-Propyl-2-(2-Tosylaminophenyl)-5-Aminobenzimidazole: Synthesis, Structure, and Luminescence Properties

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Abstract—1-Alkyl-2-(2-tosylaminophenyl)-5-aminobenzimidazole and related zinc complexes are synthesized. The structure of the complex with zinc pivalate is determined by X-ray diffraction analysis. The fluorescence with the anomalous Stokes shift of the benzimidazole ligand system in solution is transformed into the fluorescence with the normal Stokes shift upon complex formation due to blocking the mechanism of intramolecular proton transfer in the excited state or upon the transition to the crystalline state formed by zwitterionic forms that are generated due to the proton transfer from the sulfonamide group to the amino group.

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INTRODUCTION

The phenomenon of exited state intramolecular proton transfer (ESIPT) in systematic series of 2-(2-hydroxyphenyl)azoles is being actively studied for more than 40 years [1]. Interest in similar studies of aminoazoles demonstrating the anomalous Stokes shift due to the intramolecular proton transfer N–H···N in the excited state has recently increased [2]. The high efficiency of using these systems as fluorescent probes for the detection of traces of Zn^{2+} and other transition metal ions in solutions was also shown [3–7].

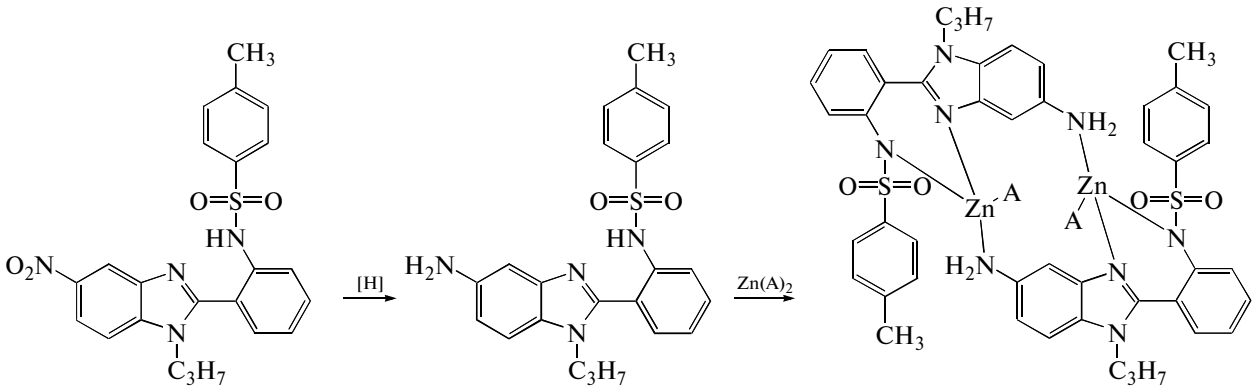
The synthesis and studies of the structure and the spectral and luminescence properties of 2-(2-tosylaminophenyl)benzimidazole have first been reported in [8]. The coordination compounds of transition metals were later synthesized on the basis of this compound [9]. We proposed a unique method for the synthesis of compounds of similar structures that made it possible to introduce the nitro group into position 5 of the benzimidazole system. Further this made it possible to obtain 1-alkyl-2-(2-tosylaminophenyl)-5-aminobenzimidazoles that demonstrate fluorescence with the anomalous Stokes shift. Before our studies, there were single publications on benzimidazoles bearing substituents in position 5 [10].

EXPERIMENTAL

1-Propyl-2-(2-tosylaminophenyl)-5-aminobenzimidazole (HL^2) and related zinc complexes were synthesized according to the following scheme.

Synthesis of 1-propyl-2-(2-tosylaminophenyl)-5-nitrobenzimidazole (HL^1). A boiling solution of 2-propylamino-5-nitroaniline (1.17 g, 6 mmol) [11] in 50% acetic acid (15 mL) was added by a hot solution of copper acetate (2.40 g, 12 mmol) in water (15 mL) and a hot solution of 2-tosylaminobenzaldehyde (1.65 g, 6 mmol) [12] in glacial acetic acid (6 mL). The resulting reaction mixture was refluxed for 1 h and cooled. The precipitate formed was filtered off, washed with water, and dried. The obtained copper salt was suspended in glacial acetic acid (10 mL) and treated with a solution of sodium thiosulfate (1.90 g, 12 mmol) in water (5 mL). In 30 min, the precipitate was filtered off, washed with water, and dried. Then the precipitate was dissolved in chloroform and passed through an alumina layer, and the solvent was distilled off. Yellow crystals (mp = 185–186°C) were obtained by recrystallization from acetic acid. The yield was 1.62 g (60%).

For $C_{23}H_{22}N_4O_4S$			
anal. calcd., %:	C, 61.32;	H, 4.92;	N, 12.44.
Found, %:	C, 61.23;	H, 5.01;	N, 12.51.



(HL[1]) (HL[2]) (I)

Ia: A = CH_3COO^-
Ib: A = $(CH_3)(CH_3)_3CCOO^-$

Scheme 1.

IR, ν, cm^{-1}: 3147 w ν(NH), 1618 w, 1595 w, 1577 w (vibrations of benzimidazole ring), 1522 s $\nu(NO_2)$, 1334 v.s $\nu_{as}(SO_2)$, 1166 v.s $\nu_s(SO_2)$. ^{1}H NMR (DMSO-d_6), δ, ppm: 0.70 (3H, t, J = 7.3 Hz, $CH_2CH_2\underline{CH_3}$), 1.56 (2H, q, J = 7.4 Hz, $CH_2\underline{CH_2}CH_3$), 2.25 (3H, s, C_{Ar}–CH_3), 3.97 (2H, t, J = 7.5 Hz, $\underline{CH_2}CH_2CH_3$), 7.17 (2H, d, J = 8.1 Hz, C_{Ar}–H), 7.32–7.55 (6H, m, C_{Ar}–H), 7.91 (1H, d, J = 9.0 Hz, C_{Ar}–H), 8.23 (1H, dd, J = 8.9 Hz, J = 2.2 Hz, C_{Ar}–H), 8.59 (1H, d, J = 2.2 Hz, C_{Ar}–H), 10.07 (1H, s, NH).

Synthesis of 1-propyl-2-(2-tosylaminophenyl)-5-aminobenzimidazole (HL[2]). A solution of polysulfides, prepared of sodium sulfide nonahydrate (6.48 g, 27 mmol) and sulfur (0.87 g, 27 mmol) in water (15 mL), was added to a solution of 1-propyl-2-(2-tosylaminophenyl)-5-nitrobenzimidazole (6.08 g, 13.5 mmol) in ethanol (50 mL). The mixture was refluxed for 4 h. The alcohol layer was separated, and the solvent was filtered off. The residue was dissolved in 15% hydrochloric acid (90 mL) and filtered. The filtrate was treated with a 22% solution of ammonia to pH 7. The formed precipitate was filtered off, washed with water, and dried. Cream-colored crystals (mp = 140–141°C) were obtained by recrystallization from ethanol. The yield was 4.54 g (80%).

For $C_{23}H_{24}N_4O_2S$			
anal. calcd., %:	C, 65.69;	H, 5.75;	N, 13.32.
Found, %:	C, 65.59;	H, 5.82;	N, 13.39.

IR, ν, cm^{-1}: 3462 w $\nu_{as}(NH_2)$, 3440 w ν(NH), 3374 w $\nu_s(NH_2)$, 1629 w $\delta(NH_2)$, 1335 vs $\nu_{as}(SO_2)$, 1164 vs $\nu_s(SO_2)$. ^{1}H NMR (DMSO-d_6), δ, ppm: 0.82 (3H, t, J = 7.4 Hz, $CH_2CH_2\underline{CH_3}$), 1.64 (2H, q, J = 7.6 Hz, $CH_2\underline{CH_2}CH_3$), 2.27 (3H, s, C_{Ar}–CH_3), 3.67 (2H, t, J = 7.8 Hz, $\underline{CH_2}CH_2CH_3$), 4.84 (2H, br.s, NH_2), 6.71 (1H, dd, J = 8.6 Hz, J = 1.6 Hz, C_{Ar}–H), 6.91–6.93 (3H, m, C_{Ar}–H), 7.15–7.25 (4H, m, C_{Ar}–H), 7.39 (1H, d, J = 8.1 Hz, C_{Ar}–H), 7.42 (1H, d, J = 7.8 Hz, C_{Ar}–H), 7.61 (1H, d, J = 7.8 Hz, C_{Ar}–H), 10.15 (1H, br.s, NH).

Synthesis of bis(μ$_2$-(1-propyl-2-(2-tosylaminophenyl-κN)-5-aminobenzimidazolato-κ^{2}N,N')bis(acetato)-κO)dizincII) (Ia, A = CH_3COO^-). A hot solution of $Zn(CH_3COO)_2 \cdot 2H_2O$ (92 mg, 0.5 mmol) in methanol (6 mL) was poured to a hot solution of HL[2] (210 mg, 0.5 mmol) in methanol (4 mL), and the mixture was refluxed for 2 h. The solution was evaporated to a volume of 4 mL, and the formed precipitate was filtered off, washed with methanol, and dried. Colorless crystals (mp > 250°C) were obtained by recrystallization from acetonitrile. The yield was 158 mg (58%).

For $C_{50}H_{52}N_8O_8S_2Zn_2$			
anal. calcd., %:	C, 55.20;	H, 4.82;	N, 10.30.
Found, %:	C, 55.09;	H, 4.92;	N, 10.39.

IR, ν, cm^{-1}: 3373 w $\nu_{as}(NH_2)$, 3247 w $\nu_s(NH_2)$, 1629 w $\delta(NH_2)$, 1565 s (C=O), 1239 vs $\nu_{as}(SO_2)$, 1135 vs $\nu_s(SO_2)$.

Synthesis of bis(μ$_2$-(1-propyl-2-(2-tosylaminophenyl-κN)-5aminobenzimidatazolato-κ^{2}N,N')bis(pivalato-κO)dizonc(II) (Ib, A = $(CH_3)_3CCOO^-$). A hot solution of $[Zn((CH_3)_3CCOO)_2]_n$ (0.11 g, 0.4 mmol) [13] in acetonitrile (8 mL) was poured to a hot solution of HL[2] (0.17 g, 0.4 mmol) in acetonitrile (7 mL), and the mixture was stirred for 3 h at 60°C. The solution was concentrated under reduced pressure to a volume of 5 mL and cooled. The precipitate formed was filtered off, washed with benzene and hexane, and dried. Colorless crystals (mp > 250°C) were obtained by recrystallization from acetonitrile. The yield was 310 mg (66%).

Table 1. Crystallographic parameters and refinement details for structure **Ic**

Parameter	Value
Brutto–formula	$C_{61}H_{77}N_{10}O_{10.5}S_2Zn_2$
FW;	1313.19
T, K	173(2)
λ, Å	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
a, Å	11.4425(7)
b, Å	27.000(2)
c, Å	20.843(1)
β, deg	97.121(1)
V, Å^3	6389.7(7)
Z	4
ρ_{calcd}, g/cm^{-3}	1.365
μ, mm^{-1}	0.88
Number of reflections/measured/independent/with $I > 2\sigma(I)$	45352/14800/9373
R_{int}	0.093
$T_{min/max}$	0.420/0.746
θ Range, deg	2.11–27.79
Goodness-of-fit	1.001
R_1 ($I > 2\sigma(I)$)	0.079
wR_2 ($I > 2\sigma(I)$)	0.192
Residual electron density (min/max), e/Å^3	−1.012/1.550

For $C_{56}H_{64}N_8O_8S_2Zn_2$

anal. calcd., %:	C, 57.39;	H, 5.50;	N, 9.56.
Found, %:	C, 57.18;	H, 5.45;	N, 9.73.

IR, ν, cm^{-1}: 3366 w $\nu_{as}(NH_2)$, 3245 w $\nu_s(NH_2)$, 1630 w $\delta(NH_2)$, 1566 s ν(C=O), 1244 vs $\nu_{as}(SO_2)$, 1140 vs $\nu_s(SO_2)$.

^{1}H NMR spectra were recorded on a Varian Unity-300 instrument (300 MHz) in the mode of internal stabilization of the ^{2}H polar resonance line in DMSO-d_6. IR spectra were recorded on Varian Excalibur 3100 FT-IR and Perkin-Elmer Spectrum 65 instruments in KBr pellets.

X-ray diffraction analysis. Single crystals were grown from an acetonitrile–ethanol (2 : 1) mixture. The compound crystallizes as a solvate **Ib** · $2CH_3CN$ · $2H_2O$ · $0.5C_2H_5OH$ (**Ic**). An experimental material was obtained on a Bruker Smart CCD ApexII diffractometer (MoK_α, graphite monochromator, ω scan mode). The structure was solved by a direct method and refined by least squares using the SHELXS-97 [14] and SHELXL-97 [15] program packages in the anisotropic full-matrix approximation. Hydrogen atoms were refined isotropically in the riding model.

The solvate alcohol molecule is disordered, and the site occupancy of its atoms is 1/2. The main crystallographic and experimental characteristics of compound **Ic** are presented in Table 1. Selected interatomic spacings and bond angles are listed in Table 2. The Cif file containing the full information on structure **Ic** was deposited with the Cambridge Crystallographic Data Centre (969846; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The structure of coordination compound **Ic** in the crystal state (Fig. 1) was unambiguously determined by X-ray diffraction analysis. In complex **Ib**, two Zn atoms are linked by two bridging 1-propyl-2-(2-tosylaminophenyl)-5-aminobenzimidazole ligands. Each ligand L is tridentate-chelating (3N). Each zinc atom is supplemented to a distorted tetrahedral coordination by the monodentate pivalate group (Zn–O 1.928, 1.934(4) Å). A weak interaction between the Zn atoms and the second oxygen atoms of the pivalate groups (Zn···O 2.748, 2.800(4) Å) should be mentioned.

The six-membered metallocycles ZnN_2C_3 are nonplanar and inflected along the N···N line by 141.4(4)° and 145.9(3)°. Among other features of complex **Ib**, one should mention its *cis* structure: noncrystallographic symmetry C_2. The pivalate groups are arranged at one side from the Zn···Zn line (torsion angle OZnZnO is 35°). Figure 1 shows that the benzene fragments of the ligands are almost in the screened conformation: the dihedral angle between their medium planes is 155.1°, and the value of one of the short intramolecular C···C contacts is 3.04 Å. The Zn(1) and Zn(2) atoms are remote from each other by 6.902(1) Å. The O(2) and O(6) oxygen atoms of the carboxy groups of the pivalate anions that are not involved in coordination are at a distance of 4.682(8) Å.

The absorption spectrum of HL[2] in acetonitrile (Fig. 2) is characterized by the long-wavelength with a maximum at 341 nm (ε = 9350 L mol^{-1} cm^{-1}). The UV irradiation of the solution at the long-wavelength absorption band induces an intense fluorescence with

Table 2. Selected interatomic spacings (Å) and bond angles (deg) in complex **Ib**

Bond	*d*, Å	Bond	*d*, Å
Zn(1)–N(1)	2.020(4)	Zn(2)–N(5)	2.004(4)
Zn(1)–N(2)	2.013(4)	Zn(2)–N(7)	2.023(4)
Zn(1)–N(8)	2.071(4)	Zn(2)–N(4)	2.060(4)
Zn(1)–O(1)	1.928(4)	Zn(2)–O(5)	1.934(4)
Angle	ω, deg	Angle	ω, deg
N(2)Zn(1)N(1)	93.52(16)	N(5)Zn(2)N(7)	94.27(17)
N(1)Zn(1)N(8)	112.09(18)	N(5)Zn(2)N(4)	111.07(18)
O(1)Zn(1)N(8)	113.90(18)	O(5)Zn(2)N(4)	105.96(17)
N(2)Zn(1)N(8)	109.31(17)	N(7)Zn(2)N(4)	110.15(16)
O(1)Zn(1)N(1)	109.56(16)	O(5)Zn(2)N(5)	109.35(17)
O(1)Zn(1)N(2)	116.77(17)	O(5)Zn(2)N(7)	125.36(17)

the band maximum at 478 nm and a quantum yield of 0.18.

The anomalously high Stokes shift of fluorescence being 8405 cm^{-1} is caused by the intramolecular proton transfer N–H···N in the excited state to form a quinoid tautometer that demonstrates the radiative deactivation of the electron excitation energy. Compounds HL^2 in the solid phase (crystalline powder) also possess intense fluorescence (Fig. 3), but its maximum is hypsochromically shifted to 440 nm. In addition, zinc complex **Ib** having fluorescence in the solid phase (Fig. 3) is characterized by a broad band at 400–600 nm with a maximum at 458 nm. The Stokes shift estimated from the excitation spectra was 3940 and 4300 cm^{-1} for the fluorescence of complex **Ib** and ligand HL^2, respectively.

Evidently, a substantial decrease in the Stokes shift of fluorescence is caused by blocking the mechanism of intramolecular proton transfer N–H···N due to the replacement of the sulfonamide proton by the zinc ion. At the same time, the absence of ESIPT fluorescence of ligand HL^2 in the solid phase can be caused by its existence in the crystalline state as zwitterions formed due to the proton transfer from the sulfonamide group to the more basic amino group in position 5 of the benzimidazole fragment.

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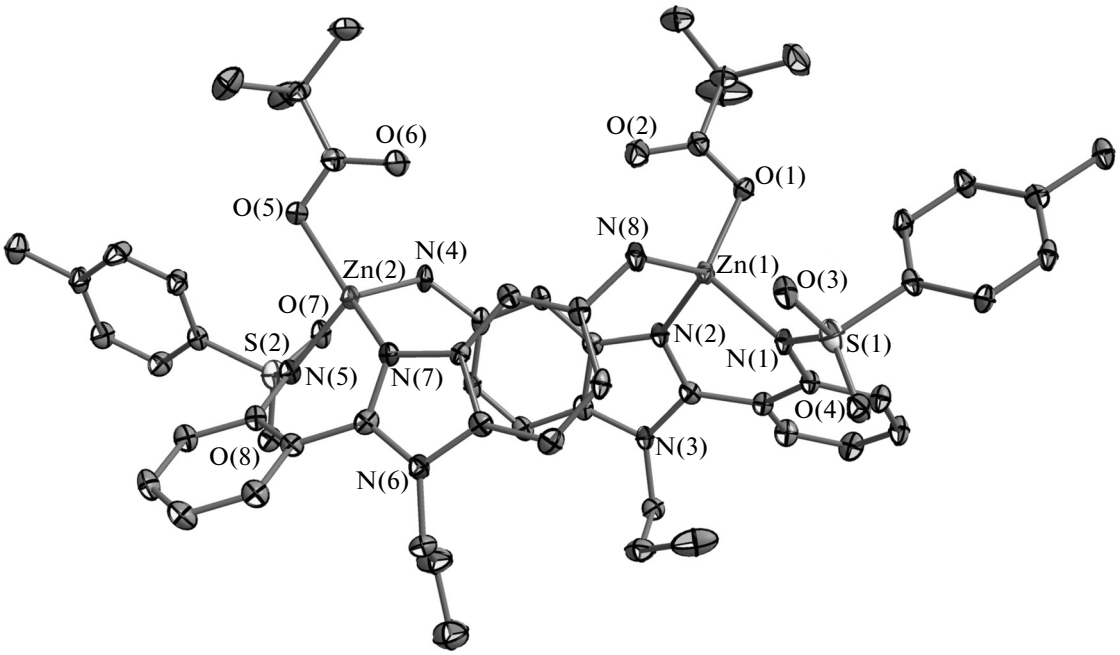

Fig. 1. Molecular structure of complex **Ib** (hydrogen atoms and solvate molecules are omitted, thermal ellipsoids with 30% probability).

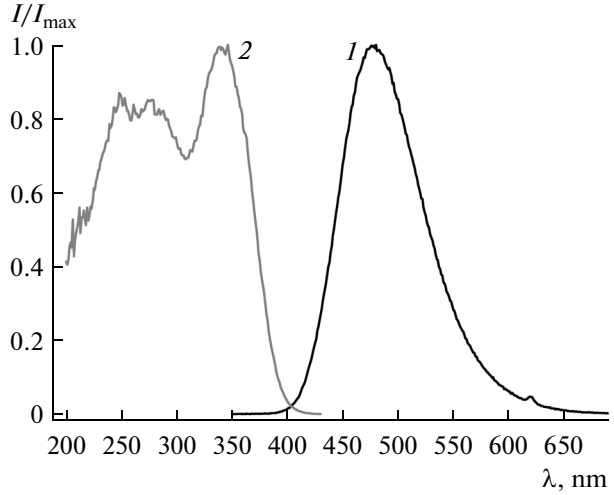

Fig. 2. Fluorescence (*1*) emission and (*2*) excitation spectra of compound HL^2 in acetonitrile.

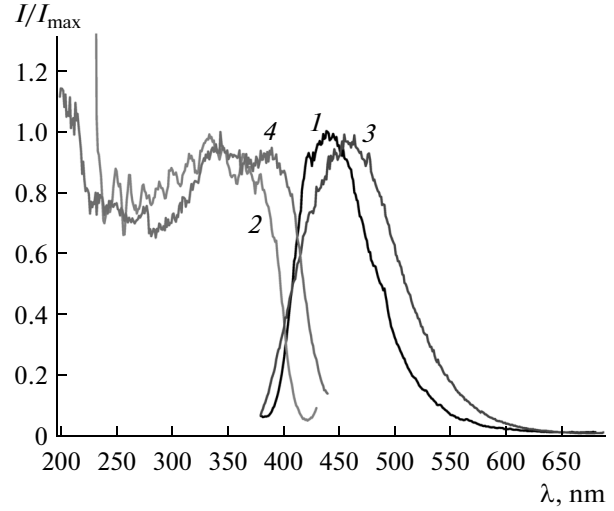

Fig. 3. Fluorescence (*1*) emission and (*2*) excitation spectra of compound HL^2 and the fluorescence (*3*) emission and (*4*) excitation spectra of complex **Ib** in the solid phase.

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