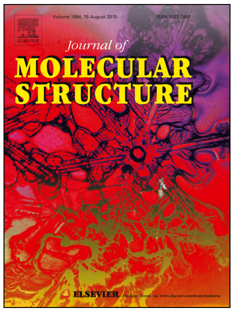

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Synthesis, structural and optical properties of 1-alkyl-2-(2’-tosylaminophenyl)-5-nitrobenzimidazoles and their zinc(II) complexes

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ABSTRACT

A series of novel benzimidazole derivatives 1-alkyl-2-(2’-tosylaminophenyl)-5-nitrobenzimidazoles with common formulae HL (**1-3**) (R = C_2H_5 (**1**); R = n-C_3H_7 (**2**); R = n-C_4H_9(**3**)) and their mononuclear zinc(II) complexes ZnL_2 (**4-6**) have been synthesized in a molar ratio Zn : HL = 1:2 in methanol solutions. Formulation of **1**-**6** is based upon satisfactory C, H, N, S elemental analyses, IR and ^1H , ^{13}C NMR spectroscopies, while the structures of **2**, **3**, **5**, **6** were determined by X-ray single-crystal diffraction. The optical properties of **1-6** were investigated.

Keywords: Benzimidazole, Zinc(II) complexes, N,N-chelating ligands, X-ray crystallography, optical

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1. Introduction

Benzimidazole and its derivatives constitute one of the most intensely studied classes of heterocycles due to their role in biological processes and their versatile application in both organic and coordination chemistries [1–3]. Many natural or synthetic compounds comprising benzimidazole moieties manifest different kinds of bioactivities, e.g. antibacterial [4, 5] or anticancer [6]. The interaction of metal ions with benzimidazole containing ligands allows to design the new metal-organic coordination compounds (frameworks) with various structural motifs and physical properties useful in catalysis, molecular absorption, molecular magnetism, nonlinear optics etc [2, 7–9].

Among the benzimidazole containing coordination compounds lately more attention was given to the zinc complexes of 2-(2'-hydroxyphenyl)benzimidazoles with N_2O_2 ligand environment due to their photoluminescence (PL) and electroluminescence properties(EL) and the possibility to use above complexes as emissive and electron-transport layers in the Organic light emitting diodes OLED [10-13], e.g. $Zn(BIZ)_2$ (BIZ = 1-Phenyl-2-(2'-hydroxyphenyl)benzimidazole) showed pure blue emission with a peak wavelength of around 450 nm and calculated Commission Internationale de l'Éclairage CIE color coordinates of around (0.17, 0.16) [12]. Besides, the replacement of tosyl amino group in the *ortho*-position of benzolic ring by hydroxy group allowed obtaining the zinc complexes with $\{ZnN_4\}$ coordination core. Based on the 2-(2'-tosylaminophenyl)benzimidazoles derivatives the very efficient selective fluorescent metal-ions (Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) sensors [14-16] were prepared.

Recently we have reported [17] the synthesis of 1-propyl-2-(2'-tosylaminophenyl)-5-aminobenzimidazole and its structurally characterized binuclear zinc(II) complex as well as their PL properties. Zinc complex having fluorescence in the solid phase is characterized by a broad band 400–600 nm with a maximum at 458 nm. The Stokes shift estimated from the excitation spectrum was 3940 cm^{-1} for the fluorescence of zinc complex.

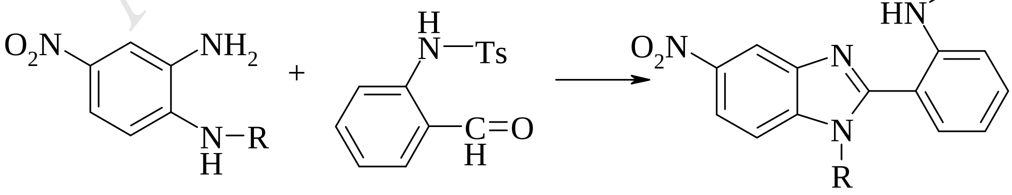
In this work we designed the novel N,N bidentate benzimidazole containing ligands 1-alkyl-2-(2'-tosylaminophenyl)-5-nitrobenzimidazoles (**1-3**) by condensation of corresponding 5-nitro-N-alkyl-*o*-phen**y**lendiamines and 2-tosylaminobenzaldeh**y**de and their zinc(II) complexes (**4-6**) in order to investigate the structural and optical features of these compounds.

2. Experimental

2.1. Materials required and general methods

All starting materials and solvents were of reagent quality and were used as received. 2-alkylamino-5-nitroanilines and 2-tosylaminobenzaldeh**y**de were prepared according to the published methods [18-20]. C, H, N, S elemental analyses were carried out on a «Carlo Erba Instruments TCM 480». Melting points were determined on a Kofler table. The IR spectra of the ligands and complexes were recorded in the range 400-4000 cm^{-1} by means of a Varian Excalibur 3100 FT-IR spectrometer in KBr pellets. ^1H NMR spectra were measured on a Varian Unity 300 spectrometer at ambient temperature in DMSO-d_6 with the signal of residual ^2H of the solvent as the internal reference. ^{13}C NMR spectra (62.9 MHz) were registered on a Bruker DPX-250 spectrometer at ambient temperature in DMSO-d_6 with the TMS as internal standard.

2.2. Ligand synthesis



R = C_2H_5 (**1**), C_3H_7 (**2**), C_4H_9 (**3**);
Ts = $SO_2C_6H_4CH_3$-*p*

Scheme 1. Synthesis of the ligands (**1**-**3**)

A mixture of copper acetate monohydrate (12 mmol, 2.4 g) in 15 ml of H_2O, 2-tosylaminobenzaldehyde (6 mmol, 1.65 g) in 6 ml of glacial acetic acid and corresponding 2-alkylamino-5-nitroaniline (6 mmol) in 15 ml of 50 % of acetic acid was refluxed (Scheme 1). In *ca*. 1 h reaction mixture was cooled, the precipitate was filtered off, washed with water and dried in air. A copper salt was suspended in 10 ml of glacial acetic acid and treated with solution of sodium thiosulfate (12 mmol, 3.0 g) in 5 ml of water. In *ca*. 30 min the precipitate was collected by filtration, washed with water and dried in air. The precipitate was dissolved in chloroform and passed through the layer of Al_2O_3. After the evaporation to dryness and crystallization from DMF the precipitates of ligands 1-3 were obtained.

1-Ethyl-2-(2'-tosylaminophenyl)-5-nitrobenzimidazole (**1**)

Yield: 59 %, M.p. = 202 – 203 °C. Anal. Calc. for $C_{22}H_{20}N_4O_4S$: C, 60.54; H, 4.62; N, 12.84; S, 7.34. Found: C, 60.44; H, 4.70; N, 12.92; S, 7.28 %. IR (KBr, cm^{-1}): 3249 s ν(N-H), 1619 m-w, 1598 m-w and 1579 m-w ν(C=N and C=C of benzimidazole ring), 1332 vs $\nu_{as}(SO_2)$, 1164 vs $\nu_s(SO_2)$. ^{1}H NMR spectrum in DMSO-d_6, δ: 1.23 (t, 3 H, CH_2-CH_3, J = 7.2 Hz), 2.27 (s, 3 H, C_{Ar}-CH_3), 4.01 (q, 2 H, CH_2-CH_3, J = 7.2 Hz), 7.12 (d, 2 H, C_{Ar}-H, J = 8.1 Hz), 7.35-7.54 (m, 6 H, C_{Ar}-H), 7.90 (d, 1 H, C_{Ar}-H, J = 9.0 Hz), 8.24 (dd, 1 H, C_{Ar}-H, J = 8.9, J = 1.3 Hz), 8.61 (d, 1H, C_{Ar}-H, J = 1.5 Hz), 10.09 (s, 1H, N*H*). ^{13}C NMR (62,9 MHz, DMSO-d_6, TMS): δ 153.83, 143.27, 143.02, 141.47, 139.16, 136.45, 136.21, 131.38, 130.64, 129.40, 126.38, 125.32, 123.86, 122.14, 118.12, 115.26, 111.39, 39.86, 20.90, 14.62.

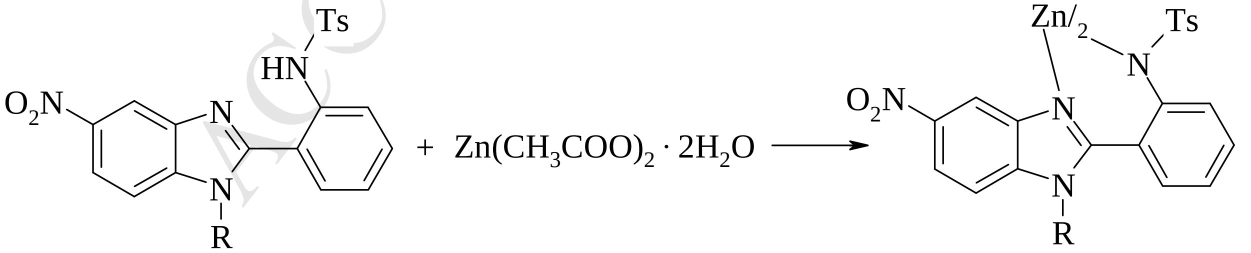
1-Propyl-2-(2'-tosylaminophenyl)-5-nitrobenzimidazole (**2**)

Yield: 60 %. M.p. = 185–186 °C. Anal. Calc. for $C_{23}H_{22}N_4O_4S$: C, 61.32; H, 4.92; N, 12.44; S, 7.11. Found: C, 61.23; H, 5.01; N, 12.51; S, 7.24 %. IR (KBr, cm^{-1}): 3247 s ν(N-H), 1618 m-w, 1595 m-w and 1577 m-w ν(C=N and C=C of benzimidazole ring), 1334 vs $\nu_{as}(SO_2)$, 1166 vs $\nu_s(SO_2)$. ^{1}H NMR spectrum in DMSO-*d*$_6$, δ: 0.70 (t, 3 H, $\mathrm{CH_2CH_2C}\mathit{H_3}$, J = 7.3 Hz), 1.56 (q, 2 H, $\mathrm{CH_2C}\mathit{H_2}\mathrm{CH_3}$, J = 7.4 Hz), 2.25 (s, 3 H, $\mathrm{C_{Ar}}$-C$\mathit{H_3}$), 3.97 (t, 2 H, $\mathrm{C}\mathit{H_2}\mathrm{CH_2CH_3}$, J = 7.5 Hz), 7.17 (d, 2H, $\mathrm{C_{Ar}}$–H, J = 8.1 Hz), 7.32-7.55 (m, 6 H, $\mathrm{C_{Ar}}$-H), 7.91 (d, 1 H, $\mathrm{C_{Ar}}$-H, J = 9.0 Hz), 8.23 (dd, 1 H, $\mathrm{C_{Ar}}$-H, J = 8.9, J = 2.2 Hz), 8.59 (d, 1H, $\mathrm{C_{Ar}}$-H, J = 2.2 Hz), 10.07 (s, 1H, N*H*). ^{13}C NMR (62,9 MHz, DMSO-*d*$_6$, TMS): δ 154.15, 143.33, 142.95, 141.50, 139.61, 136.68, 136.17, 131.40, 130.96, 129.50, 126.46, 125.13, 123.15, 122.13, 118.07, 115.27, 111.62, 46.22, 22.41, 20.92, 10.92.

1-Butyl-2-(2’-tosylaminophenyl)-5-nitrobenzimidazole (**3**)

Yield: 67 %. M.p. = 177–178 °C. Anal. Calc. for $C_{24}H_{24}N_4O_4S$: C, 62.05; H, 5.21; N, 12.06; S, 6.90. Found: C, 62.00; H, 5.29; N, 12.13; S, 7.04 %. IR (KBr, cm^{-1}): 3250 s ν(N-H), 1617 m-w, 1594 m-w and 1577 m-w ν(C=N and C=C of benzimidazole ring), 1334 vs ν_{as}(SO$_2$), 1165 vs ν_s(SO$_2$). ^{1}H NMR spectrum in DMSO-*d*$_6$, δ: 0.81 (t, 3 H, $\mathrm{CH_2CH_2CH_2}\mathit{CH_3}$, J = 7.3 Hz), 1.20 (q, 2 H, $\mathrm{CH_2CH_2}\mathit{CH_2}\mathrm{CH_3}$, J = 7.6 Hz), 1.60 (t, 2 H, $\mathrm{CH_2}\mathit{CH_2}\mathrm{CH_2CH_3}$, J = 7.5), 3.99 (t, 2 H, $\mathit{CH_2CH_2}\mathrm{CH_2CH_3}$, J = 7.7 Hz), 7.09 (d, 2H, $\mathrm{C_{Ar}}$–H, J = 8.1 Hz), 7.26 (m, 1H, $\mathrm{C_{Ar}}$–H),7.43-7.48 (m, 5 H, $\mathrm{C_{Ar}}$-H), 7.76 (d, 1 H, $\mathrm{C_{Ar}}$-H, J = 8.9 Hz), 8.21 (dd, 1 H, $\mathrm{C_{Ar}}$-H, J = 9.0, J = 2.1 Hz), 8.59 (s, 1H, $\mathrm{C_{Ar}}$-H), 10.04 (s, 1H, N*H*). ^{13}C NMR (62,9 MHz, DMSO-d^6, TMS): δ 154.16, 143.32, 142.95, 141.56, 139.55, 136.74, 136.18, 131.42, 131.02, 129.51, 126.47, 125.08, 123.07, 122.07, 118.09, 115.29, 111.57, 44.35, 30.91, 20.93, 19.20, 13.16.

2.3. Synthesis of complexes



R = C_2H_5 (**4**), C_3H_7 (**5**), C_4H_9 (**6**)

Scheme 2. Synthesis of the complexes (**4-6**)

A hot solution of zinc acetate dihydrate (0.5 mmol, 110 mg) in 5 ml of methanol was added to a hot solution containing 1 mmol of corresponding ligand in 50 ml of methanol (Scheme 2). In *ca*. 2 h. of refluxing the reaction mixtures were cooled, the precipitates were filtered off and washed many times with methanol and then crystallized from a methanol - chloroform 1:1.

Bis-[1-ethyl-2-(2’-tosylaminophenyl)-5-nitrobenzimidazolato]zinc(II) (**4**)

Yield: 67 %. M.p. > 250 °C.Anal. Calc. for $C_{44}H_{38}N_8O_8S_2Zn$: C, 56.44; H, 4.09; N, 11.97; S, 6.84. Found: C, 56.39; H, 4.15; N, 12.05; S, 7.01 %. IR (KBr, cm^{-1}): 1617 vw, 1597 m-w and 1561 m-w *ν*(C=N and C=C of benzimidazole ring), 1239 vs $\nu_{as}(SO_2)$, 1144 vs $\nu_s(SO_2)$. ^{1}H NMR spectrum in DMSO-*d*$_6$, δ: 1.31 (t, 3 H, CH_2CH_3, J = 6.6 Hz), 2.20 (s, 3 H, C_{Ar}–H), 4.44 (br s, 2 H, CH_2), 7.00-7.79 (m, 9 H, C_{Ar}-H), 7.94-8.03 (m, 2H, C_{Ar}-H). ^{13}C NMR (62,9 MHz, DMSO-*d*$_6$, TMS): δ 156.49, 145.17, 143.06, 141.45, 140.14, 138.09, 137.63, 132.27, 130.76, 129.09, 126.13, 123.39, 121.62, 118.78, 117.05, 112.72, 112.52, 41.92, 20.78, 14.27.

Bis-[1-propyl-2-(2’-tosylaminophenyl)-5-nitrobenzimidazolato]zinc(II) (**5**)

Yield: 64 %. M.p. > 250 °C.Anal. Calc. for $C_{46}H_{42}N_8O_8S_2Zn$: C, 57.29; H, 4.39; N, 11.62; S, 6.65. Found: C, 57.19; H, 4.48; N, 11.73; S, 6.92 %. IR (KBr, cm^{-1}): 1617 vw, 1597 m-w and 1566 m-w *ν*(C=N and C=C of benzimidazole ring), 1236 vs $\nu_{as}(SO_2)$, 1135 vs $\nu_s(SO_2)$. ^{1}H NMR spectrum in DMSO-*d*$_6$, δ: 0.65 (t, 3 H, CH_2CH_2CH3, J = 7.3 Hz), 1.59 (q, 2 H, CH_2CH_2CH3 J = 7.1 Hz), 2.21 (s, 3 H, C_{Ar}-H), 4.49 (br s, 2 H, CH_2CH_2CH3), 7.02 (d, 2 H, C_{Ar}-H, J = 7.8 Hz), 7.15 (br s, 2 H, C_{Ar}-H), 7.47 (d, 3 H, C_{Ar}-H , J = 7.5 Hz), 7.87 (br s, 1 H, C_{Ar}-H), 8.06 (q, 2 H, C_{Ar}-H, J = 8.2 Hz). ^{13}C NMR (62,9 MHz, DMSO-*d*$_6$, TMS): δ 157.08, 145.07, 143.08, 141.44, 140.09, 138.36, 137.48, 132.31, 131.01, 129.06, 126.20, 122.66, 121.28, 118.81, 116.77, 113.15, 112.77, 48.11, 21.98, 20.77, 10.65.

Bis-[1-butyl-2-(2’-tosylaminophenyl)-5-nitrobenzimidazolato]zinc(II) (**6**)

Yield: 68 %. M.p. > 250 °C.Anal. Calc. for $C_{48}H_{46}N_8O_8S_2Zn$: C, 58.09; H, 4.67; N, 11.29; S, 6.23. Found: C, 58.02; H, 4.72; N, 11.36; S, 6.17 %. IR (KBr, cm^{-1}): 1620 vw, 1597 m-w and 1567 m-w *ν*(C=N and C=C of benzimidazole ring), 1236 vs $\nu_{as}(SO_2)$, 1138 vs $\nu_s(SO_2)$. ^{1}H NMR spectrum in

DMSO-d_6, δ: 0.66 (t, 3 H, $CH_2CH_2CH_2\mathit{CH3}$, J = 7.2 Hz), 1.10 (q, 2 H, $CH_2CH_2\mathit{CH_2}CH_3$ J = 7.1 Hz), 1.57 (br s, 2 H, $CH_2CH_2\mathit{CH_2}CH3$), 2.21 (s, 3 H, C_{Ar}-H), 4.53 (br s, 2 H, $\mathit{CH_2}CH_2CH_2CH3$), 7.02 (d, 2 H, C_{Ar}-H, J = 7.5 Hz), 7.14 (br s, 2 H, C_{Ar}-H), 7.49 (d, 3 H, C_{Ar}-H), 7.72 (br s, 1 H, C_{Ar}-H), 8.01-8.03 (m, 2 H, C_{Ar}-H). ^{13}C NMR (62,9 MHz, DMSO-d_6, TMS): δ 157.37, 145.50, 143.53, 141.89, 140.52, 138.69, 137.88, 132.78, 131.44, 129.52, 126.69, 122.96, 121.65, 119.26, 116.99, 113.56, 113.05, 46.51, 30.88, 21.22, 19.41, 13.39.

2.4. *Crystal structure determination*

The X-ray data sets for ligands and complexes **2**, **3**, **5** and **6** were collected on a Bruker APEX II diffractometer equipped with a CCD camera and a graphite-monochromated MoK$_\alpha$ radiation source (λ = 0.71073 Å) [21]. Semiempirical absorption correction for all compounds was applied [22]. The structures was solved by direct methods and using Fourier techniques and were refined by the full-matrix least squares against F^2 with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms of the carbon-containing ligands were positioned geometrically and refined using the riding model. All calculations were carried out with the use of the SHELX97 program package [23]. Disordered solvent molecules in **6**, which could not be localised, were removed by SQUEEZE [24]. The crystallographic parameters and the refinement statistics are given in Table 1.

Table 1

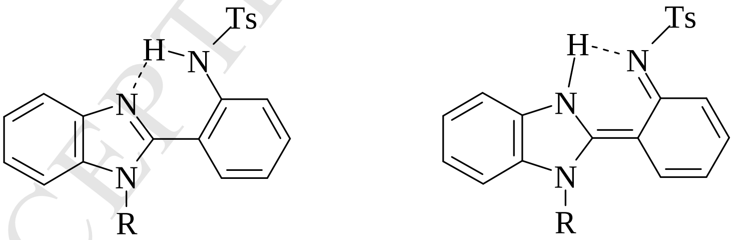
2.5. *UV-vis spectra*

Electronic absorption spectra were recorded on a Varian Cary 100 spectrophotometer. Fluorescence measurements were performed on a Varian Cary Eclipse spectrofluorimeter. Spectral grade DMSO from Sigma-Aldrich was used for the preparation of solutions.

3. Results and Discussion

3.1. Ligand tautomerism

According to the literature data [14, 18] the enamine tautomeric *E* form of ligand **1-3** is more stable in the solid state comparing with sulfonimino form *I* (Scheme 3). This fact was unambiguosly confirmed by the X-ray diffraction analisis data for the ligands **1** [18], **2** and **3**. Thus, the distribution of double N(3)–C(13), N(2)–C(14) (1.322(3)Å и 1.319(2)Å) and single N(2)–C(13), N(3)–C(14) (1.380(3)Å и 1.380(2)Å) bonds in **2** and **3** is in a good agreement with earlier structurally characterized 2-(2'-tosylamino)benzimidazoles (R = Et(**1**), Ph) that confirms the realization of enamine tautomeric E form of **2** and **3**. Moreover, *E* form is stabilized by the intramolecular H-bond between nitrogen atom N(3) of benzimidazole moiety and hydrogen atom of tosylated amino group: N(1)…N(3) 2.804(3), N(3)…H 2.08 Å, N(1)–H–N(3) 139.7(2)^o for 2, N(1)…N(2) 2.809(2), N(3)…H 2.17 Å, N(1)–H–N(3) 134.0(2)^o for 3 (Figs. 1 and 2).



E (enamine form) ***I*** (sulfonimino form)

Scheme 3. Tautomeric forms of **HL**

3.2. Spectroscopic properties

^{1}H NMR spectra (run in DMSO-d^6) of ligands **1-3** display the resonance lines in the field 10.04–10.07 ppm assigned to the tosylated amino protons, whereas IR spectra of "free" ligands **1-3** exhibit the stretching vibration bands in the range 3140–3150 cm^{-1} attributable to ν(N–H) of tosylamino group. The IR spectra of the complexes **4-6** in comparison with the IR spectra of uncoordinated compounds (**1-3**) do not exhibit the stretching vibration bands in the range 3140–3150 cm^{-1} attributable to ν(N–H) of the tosylated amino group and show a frequency shift (98–30 cm^{-1}) of stretching valence bands ν_{as} and ν_s of sulfo group. The ^{1}H NMR spectra of the Zn(II) complexes **4-6** in (run in dmso-*d*^{6}) did not display any resonance assigned to the tosylated amino proton. Thus, both NMR and IR data favor a {ZnN4} coordination core for the zinc(II) complexes **4-6** with participation of one deprotonated amide nitrogen atom and the endocyclic nitrogen atom of benzimidazole ring of each ligand.

*3.3 Structural description of **2**, **3**, **5**,and **6***

The crystal structures of the ligands **2** and **3** (Figs. 1 and 2) are similar to the earlier described for **1** [18]. The phenyl rings C(8)–C(12)C(23) (in **2**) and C(8)–C(13) (in **3**) is not coplanar to benzimidazole ring and the torsion angles N(3)C(13)C(23)C(8) and N(2)C(14)C(13)C(8) are 39.1 and 38.7^o for **2** and **3**, respectively.

Fig. 1

Fig. 2

The mutual disposition of the benzimidazole and phenyl (C(1)–C(6)) rings within the **3** allowed assuming the presence of π-π stacking with the centroid distance 3.577 Å and the dihedral angle 7.3° (Fig. 2). This type of intramolecular interaction was not observed for **2**.

X-Ray diffraction analysis revealed that the coordination environment of the central atom in compounds **5** and **6** is formed by four nitrogen atoms of two monodeprotonated chelating ligands

(Figs. 3 and 4). In the crystal of **5** the molecule of complex stands in the local position, while in **6** on the C_2 axis. In both complexes the zinc atom is arrounded by four nitrogen atoms in distorted tetrahedral environment: (Zn(1)–N(2) 1.965(2), Zn(1)–N(5) 1.970(2), Zn(1)–N(1) 2.022(2), Zn(1)–N(6) 2.036(2) Å for **5** and Zn(1)–N(1) 2.0060(16), Zn(1)–N(2) 2.0459(15) Å for **6**. Both deprotonated ligands form the non-planar six-membered metallocycles where C(8), C(13) and C(14) atoms deviate from the average Zn(1)N(1)N(2) plane by 0.57, 0.59 and 0.06 Å, whilst C(31), C(36) and C(37) atoms deviate by 0.89, 0.98 and 0.17 Å for **5**. In the **6** structure the same features were observed, *i.e.* the C(8), C(13) and C(14) atoms deviate from the plane Zn(1)N(1)N(2) by 0.65, 0.75 and 0.11 Å. The mutual disposition of benzimidazole and phenyl rings (C(8)–C(13) and C(31)–C(36) in **5**, C(8)–C(13) and C(31)–C(36) in **6**) as well as in ligands are not coplanar (the dihedral angles are equal 43.4 and 43.6^o for **5** and 37.5^o for **6**). Selected bond lenghts and bond angles are summerised in Table 2.

Fig. 3

Fig. 4

Table 2

In the crystal structure of **6**, molecular packing is stabilized by weak π-π stacking intramolecular interactions: distances between centers of symmentrical C(15)–C(20) benzene rings (symmentry code: – *x*, 1 – *y*, – *z*)) is 3.967 Å (Fig. 5).

Fig. 5

3.4 UV-vis and luminescent spectra

Spectral absorption and PL properties of the ligands **1-3** with different alkyl substituents (R = Et, Pr, Bu) at N_1-atom of benzimidazole moiety as well as their zinc(II) complexes 4-**6** were studied at ambient temperature in DMSO solutions. These results are presented in the **table 3**. UV-vis absorption spectra of **1-6** are depicted on the Fig. 6.

Table 3

Fig. 6

The UV-vis absorption spectra of 1-alkyl-2-(2'-tosylaminophenyl)-5-nitrobenzimidazoles **1-3** **(table 3,** Fig. 6) in DMSO exhibit almost similar long-wave absorption bands with maxima at 326 nm for **1, 2** and 327 nm for **3** and molar extinction coefficients 13850, 14480 и 13450 $M^{-1} \cdot cm^{-1}$, respectively. In comparison with ligands **1-3** the complexes **4-6** demonstrate practically identical optical properties. In the UV-vis spectra of complexes **4-6** the low hypsochromic shift (2-3 nm) with the maxima of long wave absorption bands till λ_{max} = 324 nm (**4-6**) and simultaneous increasing of their intensities were observed (ε = 27600 – 28500 $M^{-1} \cdot cm^{-1}$) (**table 3**, fig. 6). Double increasing of intensity of absorption for **4-6** comparing with **1-3** confirms the ZnL_2 composition for complexes **4-6**. Regardless the variation of alkyl substituents the solutions of **1-6** in DMSO did not show any fluorescence in contrast with previously published data [17] on the PL properties of 1-propyl-2-(2'-tosylaminophenyl)-5-aminobenzimidazole and its zinc(II) complex characterized with high value of quantum yield of fluorescence.

Conclusion

Herein we have reported three novel complexes with {ZnN4} coordination core based on 1-alkyl-2-(2'-tosylaminophenyl)-5-nitrobenzimidazoles. From single X-ray analysis it has been established that complexes **4, 5** are mononuclear species whereas molecules of **6** are bound in supramolecular chains in crystal due to weak π-π stacking interactions between benzimidazole rings. The introduction of withdrawing nitro group in the fifth position of benzimidazole moiety of ligands **1-3** causes the absence of fluorescence in the Zn(II) complexes **4-6** in contrast with the structural analogous Zn(II) compounds comprising donor amino group [17].

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X-ray diffraction studies were performed at the Centre of Shared Equipment of IGIC RAS.

IR, NMR and UV-vis spectra were obtained using facilities of the "Molecular Spectroscopy" Multi-Center of the Southern Federal University.

NMR spectra were recorded on a Bruker DPX-250 (62.9 MHz for ^{13}C) spectrometer at the Scientific and Educational Laboratory of Resonance Spectroscopy, Department of Natural and High Molecular Compounds Chemistry of Southern Federal University.

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Table 1

Experimental data for crystallographic analysis of **2**, **3**, **5** and **6**

Complex / Parameter	**2**	**3**	**5**	**6**
formula	$C_{23}H_{22}N_4O_4S$	$C_{24}H_{24}N_4O_4S$	$C_{46.5}H_{42.5}Cl_{1.5}N_8O_8S_2Zn$	$C_{48}H_{46}N_8O_8S_2Zn$
fw (g·mol^{-1})	450.51	464.53	1024.05	992.42
T (K)	150(2)	173(2)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
space group	$C2/c$	P-1	$P2_1/n$	$C2/c$
a (Å)	25.555(10)	9.740(3)	9.5399(14)	28.514(4)
b (Å)	10.423(4)	10.225(3)	26.241(4)	11.7046(18)
c (Å)	18.234(8)	11.321(3)	19.084(3)	20.003(3)
α(deg)	90	95.981(4)	90	90
β(deg)	118.692(7)	100.051(4)	93.737(2)	123.380(2)
γ (deg)	90	94.667(4)	90	90
V (Å^3)	4260(3)	1098.5(5)	4767.3(12)	5574.6(15)
Z	8	2	4	4
D_{calc} (g·cm^{-3})	1.405	1.404	1.427	1.182
μ (mm^{-1})	0.191	0.188	0.748	0.568
total no. of reflns/unique	16910 / 4652	9027 / 4461	36315/10140	20370/5727
R_{int}	0.0624	0.0239	0.0531	0.0460
$T_{\mathrm{min/max}}$	0.9943 / 0.9774	0.7464 / 0.6358	0.9635 / 0.7539	0.8480 / 0.7840
$\theta_{\max}$ (deg)	27.00	26.50	26.79	26.46
GOF	1.013	1.058	1.041	0.931
R_1 ($I > 2\sigma(I)$)	0.0497	0.0406	0.0432	0.0340
wR_2 ($I > 2\sigma(I)$)	0.1087	0.1053	0.1075	0.0831
R_1 (all data)	0.0879	0.0504	0.0670	0.0452
wR_2 (all data)	0.1214	0.1110	0.1240	0.0858

Table 2

Selected bond lengths (Å) and angles (deg.) for **2**, **3**, **5**, and **6**

2			
S(1)–N(1)	1.639(2)	O(1)–S(1)–O(2)	1.222(2)
N(1)–C(8)	1.427(3)	N(1)–S(1)–C(1)	119.87(10)
S(1)–O(1)	1.4279(17)	C(8)–N(1)–S(1)	106.19(10)
S(1)–O(2)	1.4314(16)	C(17)–N(2)–C(13)	119.19(15)
N(2)–C(17)	1.376(3)	C(22)–N(3)–C(13)	106.37(17)
N(3)–C(13)	1.322(3)	O(3)–N(4)–O(4)	105.35(18)
N(3)–C(22)	1.396(3)		
O(3)–N(4)	1.222(2)		
3			
S(1)–N(1)	1.6409(15)	O(1)S(1)O(2)	120.74(10)
N(1)–C(8)	1.427(2)	C(1)S(1)N(1)	106.10(7)
S(1)–O(1)	1.4237(15)	S(1)N(1)C(8)	119.58(12)
S(1)–O(2)	1.4303(16)	C(14)N(2)C(15)	105.19(13)
N(2)–C(15)	1.3828(19)	C(14)N(3)C(20)	106.17(12)
N(3)–C(14)	1.380(2)	O(3)N(4)O(4)	123.18(15)
N(3)–C(20)	1.373(2)		
O(3)–N(4)	1.2272(19)		
5			
Zn(1)–N(1)	2.022(2)	N(2)Zn(1)N(1)	94.31(9)
Zn(1)–N(2)	1.965(2)	N(2)Zn(1)N(5)	125.49(9)
Zn(1)–N(5)	1.970(2)	N(2)Zn(1)N(6)	119.71(9)
Zn(1)–N(6)	2.036(2)	N(5)Zn(1)N(6)	92.44(9)
		N(5)Zn(1) N(1)	122.19(9)
		N(1)Zn(1)N(6)	102.43(8)
6			
Zn(1)–N(1)	2.0060(15)	N(1)Zn(1)N(1A)	142.55(9)

Zn(1)–N(2)	2.0459(15)	N(1)Zn(1)N(2)	91.35(6)
Zn(1)–N(1A)	2.0060(16)	N(2)Zn(1)N(2A)	123.59(9)
Zn(1)–N(2A)	2.0460(15)	N(1)Zn(1)N(2A)	106.25(6)

Table 3.

Absorption spectral data for compounds **1-6** in DMSO at 293 K

Ligands			Complexes ZnL_2	
Compound	R	Absorption λ_{max} (нм)/ ε ($10^3\ M^{-1}\cdot cm^{-1}$)	Compound	Absorption λ_{max} (нм)/ε ($10^3\ M^{-1}\cdot cm^{-1}$)
1	Et	326 (13.85)	**4**	324 (27.60)
2	Pr	326 (14.48)	**5**	324 (28.50)
3	Bu	327 (13.45)	**6**	324 (27.98)

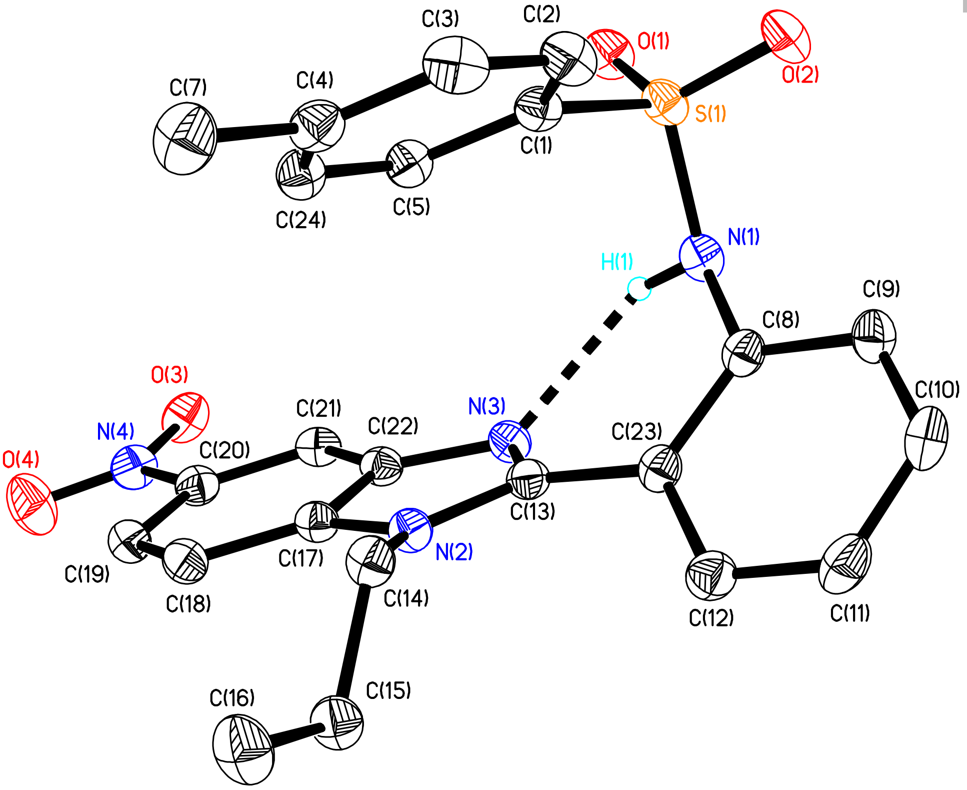

Fig. 1. Molecular structure of **2** (the hydrogen atoms are not shown; thermal ellipsoids are drawn at the 30% probability level).

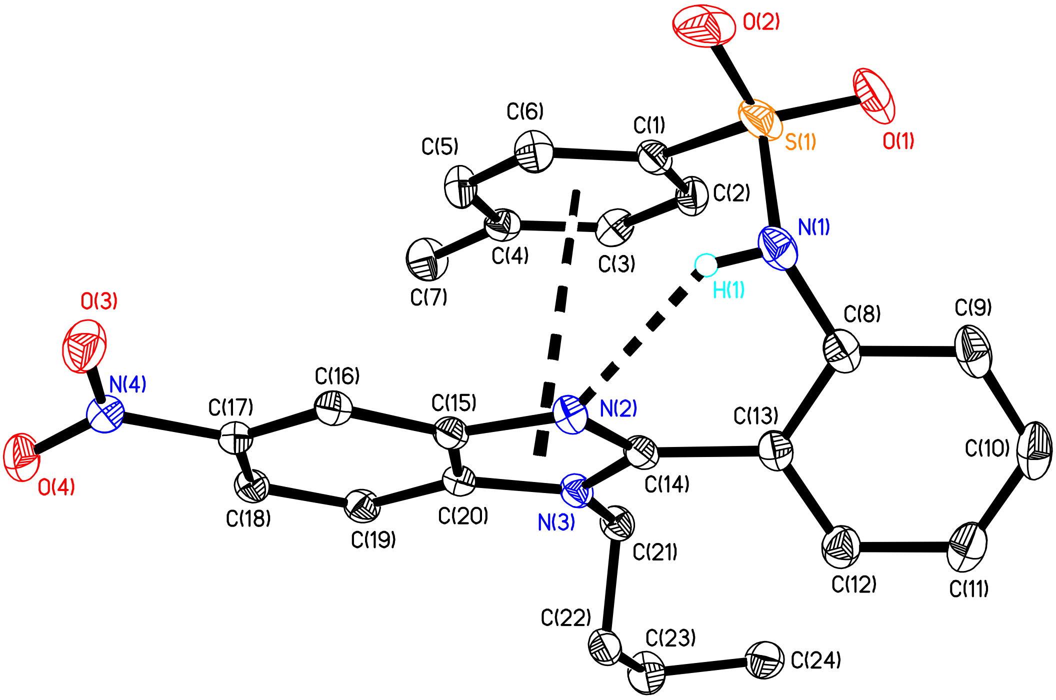

Fig. 2. Molecular structure of **3** (the hydrogen atoms are not shown; thermal ellipsoids are drawn at the 30% probability level).

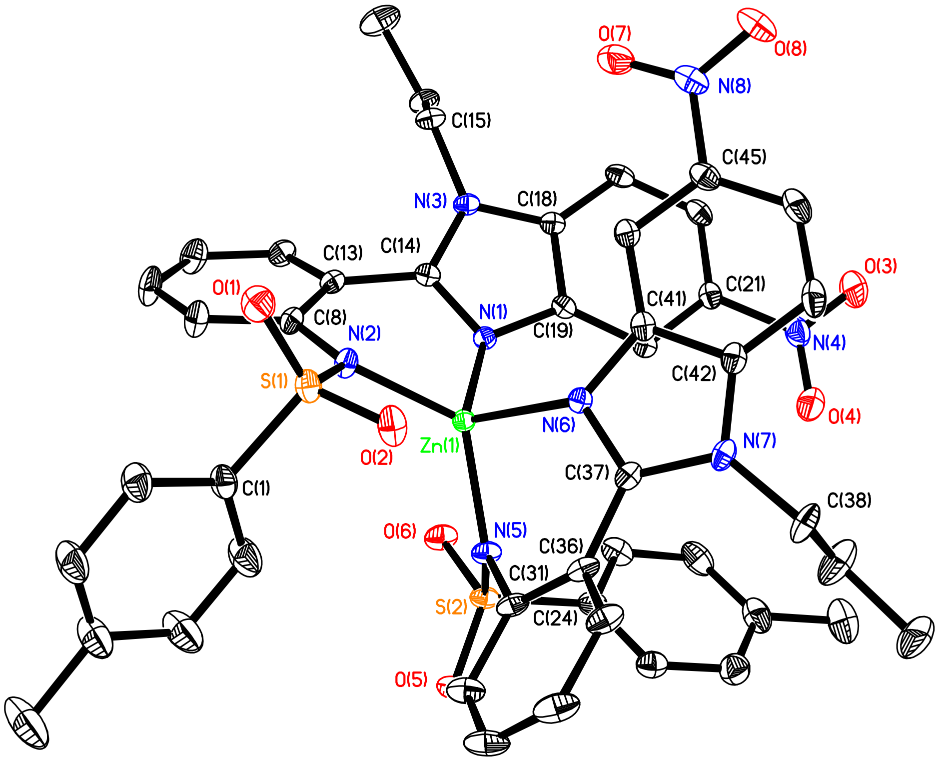

Fig. 3. Molecular structure of **5** (the hydrogen atoms are not shown; thermal ellipsoids are drawn at the 30% probability level).

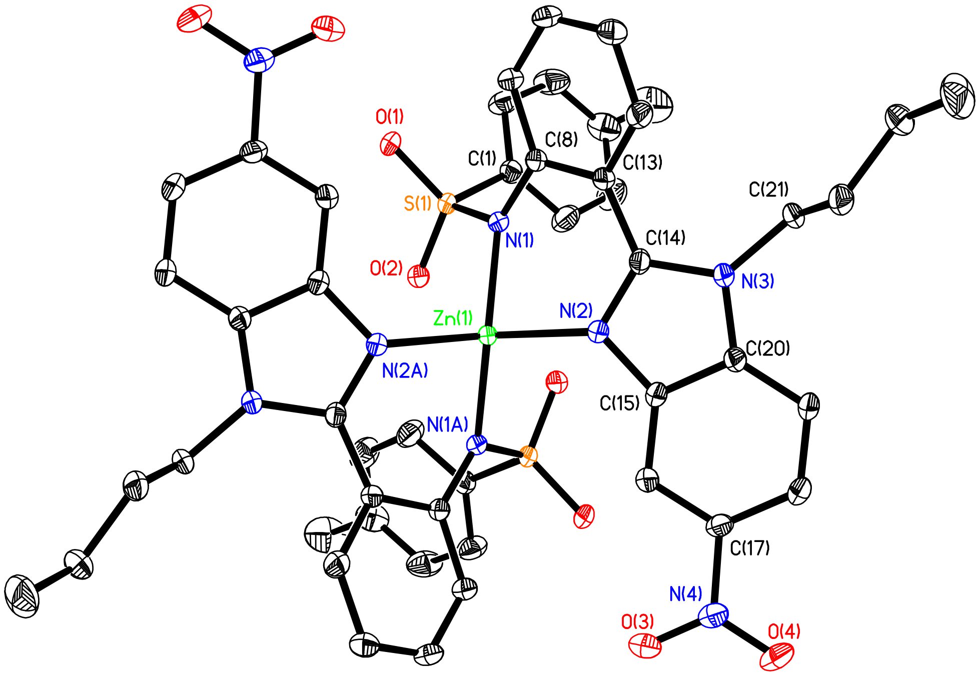

Fig. 4. Molecular structure of **6** (the hydrogen atoms are not shown; thermal ellipsoids are drawn at the 30% probability level).

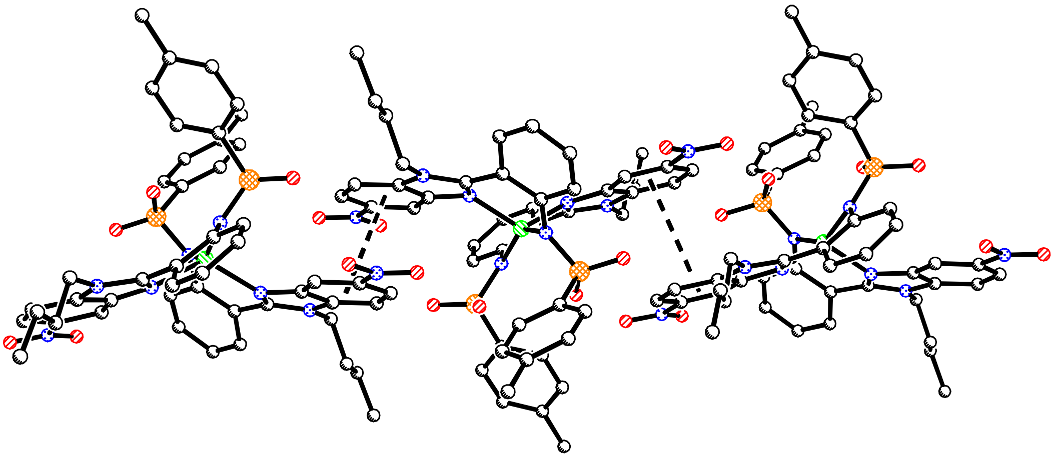

Fig. 5. Packing fragment for compound **6** (the hydrogen atoms are not shown).

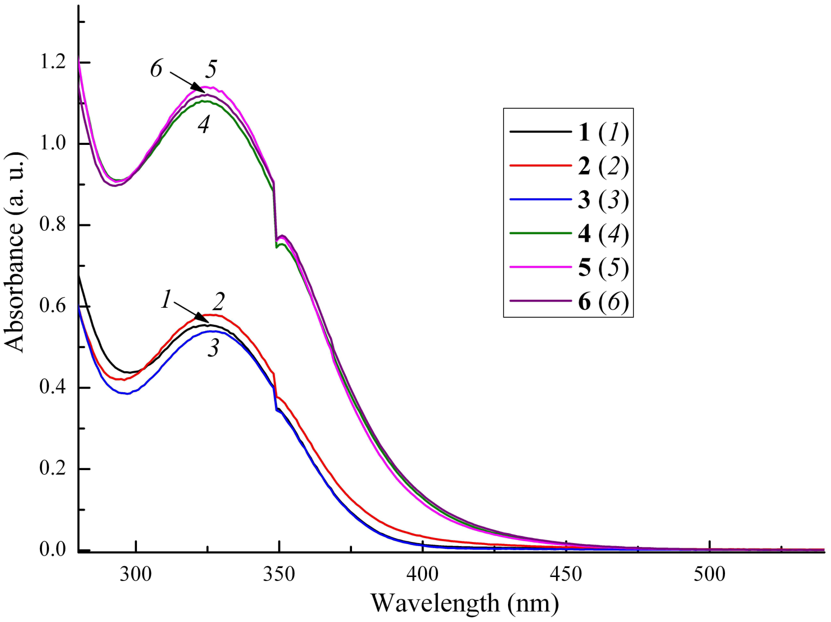

Fig. 6. UV-vis absorption spectra (*1*-*6*) of compounds **1-6** in DMSO solutions ($C = 4 \cdot 10^{-5}$ mol L^{-1}, l = 1 cm, T = 293 K).

HIGHLIGHTS

- N, N bidentate Benzimidazole containing ligands and their Zn(II) complexes.
- X-ray crystallographic analysis of ligands and Zn(II) complexes.
- Optical behavior of mononuclear Zn(II) compounds.