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New Zn complexes based on 1,2,4-triazoles: Synthesis, structure and luminescence

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ABSTRACT

The reaction of 3-(pyridin-2-yl)-5-(2-aminophenyl)-1H-1,2,4-triazole and salicylaldehyde or benzaldehyde leads a new type of 1,2,4-triazole's derivats. Reactions of these ligands with zinc acetate in ethanol lead to the formation of two new complexes with azomethine or dihydrotriazaindolizine form of ligands. The structures of these complexes were investigated by X-ray analysis. The complexes showed strong green–blue luminescence in solid state.

1. Introduction

Our investigations on Zn^{II} triazole and tetrazole derivative coordination compounds have been encouraged due to their expected fluorescence properties. Specific spectroscopic properties of coordination complexes have made them one of the essential components in the preparation of new materials to be applied especially in organic-light-emitting-diods (OLEDs) [1–4].

1,2,4-Triazole and derivatives are on the one hand a broadly distributed class of ligands for creation a variety of interesting coordination compounds, on the other hand starting materials for necessary components of OLED devices as substances with the electron and hole conductivity [5,6]. Therefore, it is exciting to obtain fluorescent complexes containing triazole fragment. Quite a number Ir and Os complexes of 1,2,4-triazole's derivatives which exhibit intense photo- and electroluminescence are given in the literature [7,8]. However, there are relatively few reports on the photo- and electroluminescent properties of (probably much cheaper) Zn and Cd triazole coordination compounds [9]. Among them, zinc complexes have received much attention because they exhibit many advantageous electroluminescent properties, such as electron transporting ability, light emitting efficiency, high thermal stability, ease of sublimation, and great diversity of electronic properties tunable by various ligand substitution. One of the reasons for the limited exploration of Zn and Cd 1,2,4-triazole's complexes is their low solubility in low-polarity solvents, making the production of high-quality thin films difficult which would be required for the OLED production.

In this work we report new stable and readily soluble in low-polarity solvents zinc complexes on 1,2,4-triazoles bases with strong photo- and electroluminescent activity.

2. Experimental part

2.1. Materials and methods

Commercially available solvents, salicylaldehyde, benzaldehyde, 2-cyanopyridine, hydrazine hydrate, isatoic anhydride, $Zn(OAc)_2 \cdot 2H_2O$ were used without further purification. 2-Aminobenzoic acid hydrazide was obtained by hydrazinolis ofisatoic anhydride. 3-(Pyridin-2-yl)-5-(2-aminophenyl)-1H-1,2,4-triazole was prepared by reacting 2-cyanopyridine with 2-aminobenzoic acids hydrazides according to the literature [10].

IR spectra of the complexes were recorded as KBr pellets in the range of 4000–400 cm^{-1} on a Nicolet Nexus 470 FT-IR spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker VXR-400 spectrometer at 400 and 75 MHz respectively. NMR spectra were obtained from solutions in DMSO-d_6. Thermogravimetric experiments were performed on a Paulik–Paulik–Erdey Q-derivatograph under a static air atmosphere. Absorption spectra were recorded on a Perkin-Elmer Lambda-9 UV–Vis/NIR spectrophotometer. Luminescence spectra of solid samples were obtained with a LOMO SDL-1 spectrometer equipped with a FEU-79 photomultiplier. Excitation and luminescence spectra of solutions were recorded on a

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Horiba Jobin-Yvon Fluorolog-FL 3-22 spectrophotometer equipped with a 450 W Xe lamp.

2.2. Synthesis

2.2.1. Synthesis of ligands (L^1 and L^2)

A solution of 2.1 mmol of salicylaldehyde (256 mg) or benzaldehyde (222 mg) in 10 mL of ethanol was added to a solution of 2 mmol (474 mg) of the 3-(pyridin-2-yl)-5-(2-aminophenyl)-1H-1,2,4-triazole in 10 mL of ethanol (96%). The resulting reaction mixture was stirred under heating with a magnetic stirrer for 1 h until the solid complex precipitated. The precipitate was filtered off, washed with ethanol and dried in vacuum.

5-(2-Hydroxyphenyl)-2-(2′-pyridiyl)-7,8-benzo-6,5-dihydro-1,3,6-triazaindolizine (L^1) – white powder. Yield was 53%. *Anal.* Calc. for $C_{20}H_{15}N_5O$: C, 70.38; H, 4.40; N, 20.53. Found: C, 70.22; H, 4.28; N, 20.61%. M.p. = 237 °C (EtOH). ^{1}H NMR (400 MHz, DMSO-d^6, ppm): δ = 10.1 (1H, s, OH); 8.65 (1H, d, CH_{arom}); 8.12 (1H, d, CH_{arom}), 7.90(1H, d-tr, CH_{arom}), 7.80(1H, d, CH_{arom}), 7.40 (2H, mult, CH_{arom}), 7.27 (1H, tr, CH_{arom}); 7.24–7.19 (2H, mult, CH_{arom}), 6.95–6.85 (3H, mult, CH_{arom}+N–H), 6.85(1H, tr, CH_{arom}), 6.80 (1H, tr, CH_{arom}). ^{13}C NMR (75 MHz, DMSO-d^6, ppm): δ = 161.65, 155.29, 151.19, 150.05, 149.95, 143.73, 137.54, 132.33, 130.65, 127.75, 126.10, 124.60, 124.46, 122.22, 119.56, 118.39, 116.34, 115.05, 110.04, 67.67. IR (KBr, cm^{-1}): ν = 3270, 1629, 1597, 1523, 1457, 1361, 1292, 1281, 1236, 1159, 742.

5-Phenyl-2-(2′-pyridiyl)-7,8-benzo-6,5-dihydro-1,3,6-triazaindolizine (L^2) – white powder. Yield was 46%. *Anal.* Calc. for $C_{20}H_{15}N_5$: C, 73.67; H, 4.65; N, 21.54. Found: C, 73.85; H, 4.62; N, 21.70%. M.p. = 216 °C (EtOH). ^{1}H NMR (400 MHz, DMSO-d^6, ppm): δ = 8.62 (1H, d, CH_{arom}); 8.07 (1H, d, CH_{arom}), 7.89 (1H, d-tr, CH_{arom}), 7.79 (1H, d, CH_{arom}), 7.69 (1H, s, CH_{arom}); 7.44–7.36 (6H, mult, CH_{arom}), 7.29 (1H, d-tr, CH_{arom}), 6.99 (1H, s, NH), 6.92 (H, d, CH_{arom}), 6.86 (1H, tr, CH_{arom}). ^{13}C NMR (75 MHz, DMSO-d^6, ppm): δ = 160.93, 154.72, 150.27, 150.01, 149.27, 142.98, 138.32, 132.38, 130.81, 126.24, 126.10, 124.49, 124.46, 122.28, 119.39, 118.57, 116.31, 114.96, 109.96, 67.65. IR (KBr, cm^{-1}): ν = 3296, 1624, 1590, 1528, 1480, 1412, 1356, 1152, 740.

2.2.2. Synthesis of $[Zn_2(L^1)_2]\cdot 0.5EtOH$ (**1**)

Zinc acetate dihydrate (2 mmol, 438 mg) was added to suspension of L^1 (2 mmol, 682 mg) in 10 mL of ethanol (96%). The mixture was stirred while heating for 2 h. The formed precipitate was kept under the mother liquor for 12 h, then filtered off, washed with alcohol, and dried in air. The procedure yielded 510 mg (61.3%) of a yellow crystalline substance. Recrystallization from mixture DMSO–EtOH gave yellow prism crystals suitable for X-ray analysis. *Anal.* Calc. for $C_{41}H_{29}N_{10}O_{2.5}Zn_2$: Zn, 15.59; C, 59.13; H, 3.48; N, 16.66. Found: Zn, 15.62; C, 58.91; H, 3.69; N, 16.36%. IR (KBr, cm^{-1}): 1610 (ν(C=N_{Schiff})), 1593, 1533, 1457, 1444, 1330, 1147, 800, 752.

2.2.3. Synthesis of $[Zn(L^2)(OAc)_2]\cdot i\text{-}PrOH$ (**2**)

$Zn(OAc)_2\cdot 2H_2O$ (657 mg, 3 mmol) was added to a suspension of L^2 (1.05 g, 3 mmol) in *i*-PrOH (10 ml), and the mixture was stirred while heating for 2 h. The formed precipitate was left to stay overnight under the mother liquor, then filtered off, washed with alcohol, and dried in air. The yield of **2** was 1.1 g (65%). Recrystallization from *i*-PrOH gave white crystals of prismatic habitus suitable for X-ray analysis. *Anal.* Calc. for $C_{27}H_{29}N_5O_5Zn$: Zn, 11.52; C, 55.99; H, 5.10; N, 11.52. Found: Zn ,11.43; C, 55.24; H, 5.77; N, 11.37%. IR (KBr, cm^{-1}): 3236 ν(NH), 3052, 1626, 1588 ν_{as}(COO$^-$), 1452 ν_s(COO$^-$), 1154, 740.

2.3. X-ray studies

Single crystal structure determination of **1** and **2** by X-ray diffraction was performed on a Bruker Apex-II CCD diffractometer (Mo Kα radiation, graphite monochromator, λ = 0.71073 Å) at 298 K. For both complexes semiempirical absorption corrections were applied [11]. The structures were 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 [12]. The crystallographic parameters for complexes **1** and **2** are given in Table 1.

3. Results and discussion

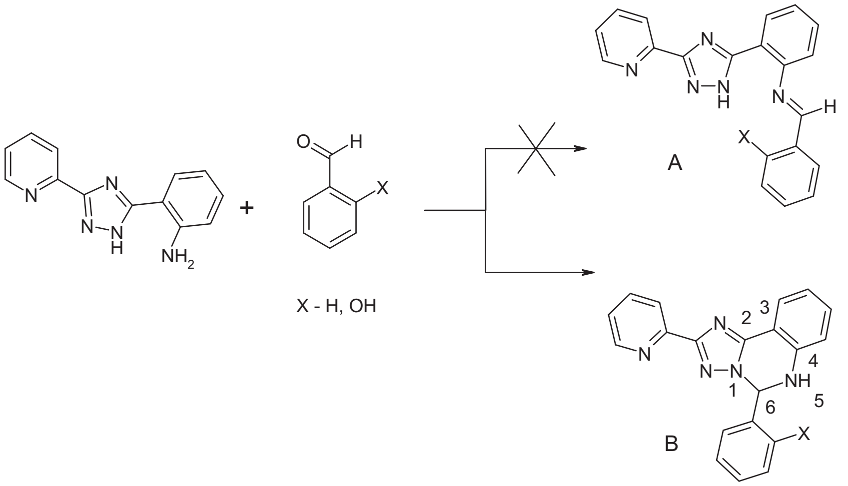
3.1. Synthesis, NMR and IR data of L^1 and L^2

The interaction of aromatic aldehyde with the 3-(pyridin-2-yl)-5-(2-aminophenyl)-1H-1,2,4-triazole can lead to two isomeric forms of ligands: azomethine – A and dihydrotriazaindolizine cyclic form – B (Scheme 1).

NMR and IR data indicate that in a free state L^1 and L^2 exist in cyclic form. For the PMR-spectra of the ligands L^1 and L^2 C^6–H proton group signals were observed in the 7.19–7.44 ppm region, while the signals of hydrogen atoms of the azomethine groups in the region 8.7–9.3 ppm (expected as a singlet peak) are missing, that is a strong argument in favor of the formation of the cyclic form. It should be noted that the same shift was registered for the C^6–H protons in the related compounds [13] There is no signal

Table 1
Crystal data and structure refinement statistics for **1** and **2**.

Parameter	1	2
Formula	$C_{41}H_{29}N_{10}O_{2.5}Zn_2$	$C_{27}H_{29}N_5O_5Zn$
Formula weight (g mol^{-1})	832.48	568.92
Crystal dimensions (mm)	0.20 × 0.14 × 0.11	0.35 × 0.18 × 0.14
T (K)	296	296
Crystal system	monoclinic	triclinic
Space group	$C2/c$	$P\bar{1}$
Unit cell parameters		
a (Å)	25.405(18)	9.593(3)
b (Å)	14.938(11)	11.080(4)
c (Å)	19.430(14)	13.106(4)
α (°)		76.641(6)
β (°)	96.006(10)	84.847(7)
γ (°)		80.300(7)
V (Å^3)	7333.9(9)	1334.1(8)
Z	8	2
$\rho_{calc.}$ (g cm^{-3})	1.508	1.416
μ (mm^{-1})	1.362	0.97
F(0 0 0)	3400	592
θ_{max} (°)	30.07	27.75
Index ranges	$-29 \leqslant h \leqslant 35$ $-21 \leqslant k \leqslant 20$ $-27 \leqslant l \leqslant 25$	$-12 \leqslant h \leqslant 10$ $-14 \leqslant k \leqslant 14$ $-13 \leqslant l \leqslant 16$
Reflections measured/reflections independent	28343/10636	9264/6194
R_{int}	0.0328	0.0149
Goodness-of-fit (GOF) on F^2	1.048	1.010
R (all data)	R_1 = 0.0842 wR_2 = 0.1278	R_1 = 0.1015 wR_2 = 0.1503
R [$I > 2\sigma(I)$]	R_1 = 0.0424 wR_2 = 0.1095	R_1 = 0.0516 wR_2 = 0.1221
T_{min}/T_{max}	0.8646/0.7723	0.8765/0.7284
Residual electron density (max/min) (e Å^{-3})	0.664/−0.254	0.508/−0.531



Scheme 1. Preparative scheme of ligands and numbering of the atoms of cyclic form.

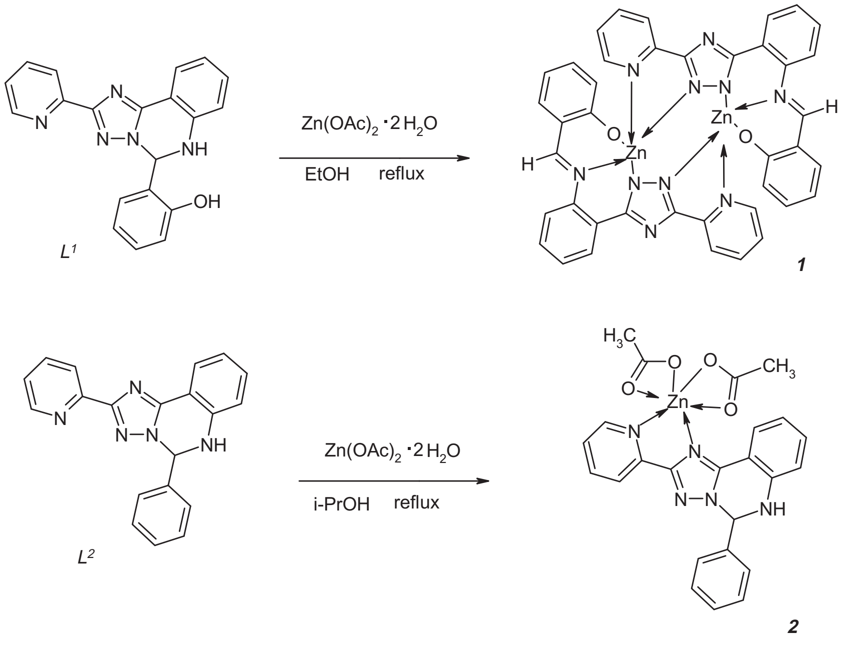
in the PMR spectra of a hydrogen atom associated with triazole's ring, usually manifested in the region 13–14 ppm, but the typical signal of the hydrogen atom of a secondary amine is recorded at 6.95–6.99 ppm. All other signals in the NMR spectra are typical for related functional groups: OH-group at 10.1 ppm and aromatic proton at 8.65–6.80 ppm. Cyclic form is also evidenced by the ^{13}C NMR spectroscopy data. The most revealing in terms of evidence of cyclic structure of the ligand is characteristic signal of the carbon atom C^6–H which is observed at 67 ppm. This agrees with the shift data described for related heterocycles [13]. The possible signals of the carbon atom of CH=N usually lies in the 57–164 ppm region [14]. The values of chemical shifts for the other signals are typical of aromatic carbon atoms.

3.2. Synthesis and X-ray studies of the zinc complexes

Interaction of L^1 and L^2 with zinc acetates leads to two types of complexes with both the azomethine form (complexes **1**) and the cyclic form (complex **2**) (Scheme 2).

According to X-ray crystallography, the complex **1** has binuclear molecular structure present in a double deprotonated azomethine form of L^1 (Fig. 1). The local coordination environment of the zinc(II) ion can be described as a distorted tetragonal-pyramid completed by four nitrogen atoms in the base of the pyramid and an oxygen atom in the axial position. The Zn_2N_4 central six-membered metal ring has a boat conformation. The intramolecular Zn···Zn distance is 4.038 Å, which is typical for binuclear complexes of 1,2,4-triazoles [5]. In both L^1 ligands triazole and phenyl moieties are nearly coplanar with the pyridyl plane, and the planar 2-imino(methylphenol) moiety is turned around the benzene ring plane by 37.9° in the first ligand and by 52.4° in the second. Hydrogen bonding is present between the oxygen atoms of the solvate molecule of ethanol and oxygen of L^1 (O2···O1S(EtOH) 2.82 Å).

The dihydrotriazaindolizine form of the ligand was found for the crystal structure for complex **2** (Fig. 2). The complex **2** is mononuclear and crystallizes as a solvate with one molecule of propanol-2. The zinc ion coordinates four oxygen atoms of two acetate anions and two nitrogen atoms of triazole ligand arranged at the vertices of a strongly distorted octahedron. Both acetate anions are bidentate, but if the bond length of Zn1–O1 and Zn1–O2 are almost equal (2.117(3) and 2.205(3) Å respectively) then Zn1–O3



Scheme 2. Preparative scheme of complexes.

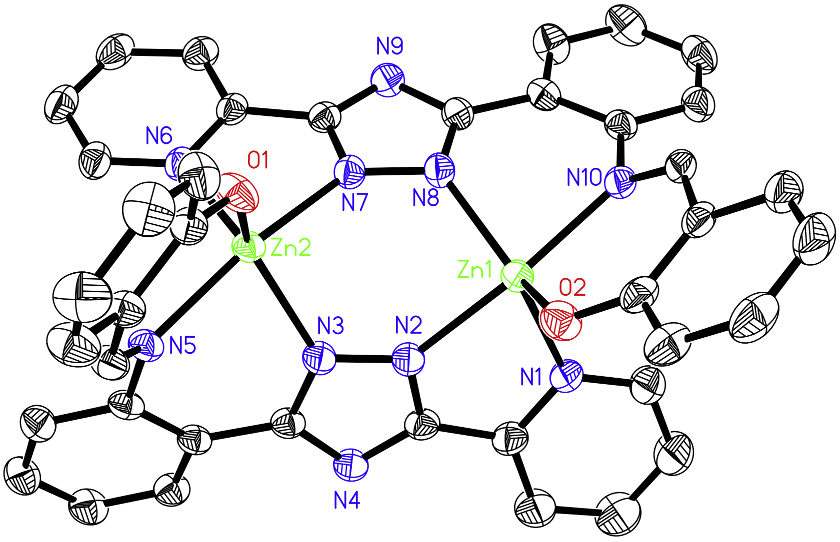


Fig. 1. Structure of complex **1** (hydrogen atoms and EtOH are not shown for clarity; thermal ellipsoids are drawn at the 30% probability level). Selected bond lengths (A) and bond angles (°): Zn1–N1 2.166(2), Zn1–N2 2.097(2), Zn1–N8 2.043(2), Zn1–N10 2.102(2), Zn2–N3 2.053(2), Zn2–N5 2.114(2), Zn2–N6 2.145(2), Zn2–N7 2.072(2), Zn1–O2 1.9270(19), Zn2–O1 1.9229(17), O2Zn1N8 129.74(8), O2Zn1N2 100.15(8), N8–Zn1–N2 89.53(8), O2–Zn1–N10 93.69(7), N8–Zn1–N10 82.96(7), N2–Zn1–N10 166.04(8), O2–Zn1–N1 100.64(8), N8–Zn1–N1 129.45(8), N2–Zn1–N1 76.09(8), N10–Zn1–N1 99.67(7).

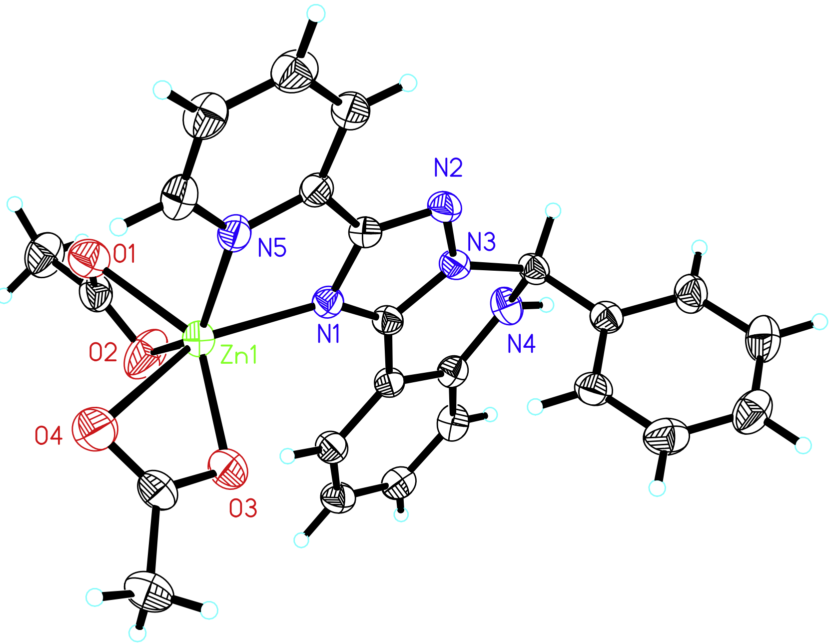


Fig. 2. Structure of complex **2** (molecule of *i*-PrOH is not shown; thermal ellipsoids are drawn at the 30% probability level). Selected bond lengths (A) and bond angles (°): Zn1–O3 2.013(3), Zn1–N1 2.106(3), Zn1–O1 2.117(3), Zn1–N5 2.137(3), Zn1–O2 2.205(3), Zn1–O4 2.449(3), O3–Zn1–N1 98.17(12), O3–Zn1–O1 140.92(12), N1–Zn1–O1 117.61(12), O3–Zn1–N5 113.44(13), N1–Zn1–N5 78.93(12), O1–Zn1–N5 89.73(12), O3–Zn1–O2 104.53(14), N1–Zn1–O2 95.06(14), O1–Zn1–O2 59.65(12), N5–Zn1–O2 142.01(13), O3–Zn1–O4 57.22(12), N1–Zn1–O4 149.65(12), O1–Zn1–O4 91.63(12), N5–Zn1–O4 94.20(12), O2–Zn1–O4 107.56(14).

and Zn1–O4 are markedly asymmetrical (2.013(3) and 2.449(3) Å). The heterocyclic ligand L^2 exists in cyclic form and is coordinated via a bidentate mode bound to the zinc atom through the N5 atom of the pyridine ring and the N1 atom of the triazole ring. The bond Zn1–N5 (2.137(3) Å) is slightly longer than Zn1–N1 (2.106(3) Å). The triazole, iminophenyl, and pyridyl cycles lie almost in the same plane, and the phenyl fragment is turned by 88.22°. Two molecules in crystal lattice unit exist both in their R and S isomer forms, creating a racemate. The crystalline lattice is stabilized by the system of intermolecular hydrogen bonds (N4···O4(x, $y + 1$, z) 2.90 Å, O3···O1S(*i*-PrOH) 2.92 Å) and nonvalent interactions between the conjugated nitrogen-containing heterocycles of the adjacent molecules of the complex, whose planes are almost parallel and lie at a distance of $\sim$3.5 Å (π-stacking interactions).

Thus the studied triazole ligands show diverse coordination behavior. The formation of the azomethine form of ligand for complex **1** stabilizes the coordination of phenolic oxygen atom of the L^1. In the absence of stabilizing factors the investigated triazoles are coordinated in a cyclic form (complex **2**).

3.3. NMR and IR data of zinc complexes

The results of the study of complex **1** by NMR and IR spectroscopy confirm the azomethine form structure of the ligands. The signals of azomethine protons as singlet peak were found at 8.80 ppm. In addition, the characteristic hydrogen signal of secondary amines registered for the free triazole disappeared after complex formation. There are no signals of hydrogen atoms originating from acidic groups either, confirming the deprotonation of the ligands upon coordination. In contrast the ^{1}H NMR-spectra of complex **2** contain several sets of signals, one of which coincides with the spectrum of the free L^2. This suggests equilibrium of partial dissociation of the complex **2** in solution when recording the spectrum.

The IR spectrum of complex **1** does not contain bands corresponding to stretching vibrations of N—H and O—H groups. The coordination of the phenoxyl oxygen atom is accompanied by a shift of the band of the stretching vibrations of the C_{phen}—O bond from 1292 cm^{-1} in the free triazole to 1330 cm^{-1} in the complex. A shift of the band of the stretching vibrations of the —HC=N— bond by 20 cm^{-1} to the shortwave range from the tabulated values is indicative of the coordination of the imine nitrogen atom. For the IR spectrum of complex **2**, most bands do not undergo significant variations compared with free L2. However, two new intense bands at 1588 and 1452 cm^{-1} are registered, related to asymmetric and symmetric stretching vibrations of the carboxyl group of acetate anion, respectively.

3.4. Thermogravimetric analysis of zinc complexes

For creating thin-film devices by vacuum deposition the thermal stability of the complexes plays a significant role to allow the transport of the stable species in the gas phase [15]. The thermal stability has been studied by thermogravimetric analysis. The complex **1** is stable up to a temperature of 100 °C. A further increase of temperature leads to desolvation. Removal of ethanol molecules occurs in the temperature range 100–350 °C and is not accompanied by noticeable thermal effects. At a temperature of 410 °C starts the oxidative decomposition of the complex which passes to the process of burning out the organic ligand. Burnout is accompanied with a series of powerful exothermic effects at 600–670 °C. The process of decomposition is completed at a temperature of 900 °C.

Desolvation of complex **2** occurs in one stage: in the temperature range 100–160 °C molecule of propanol-2 is removed. Desolvation processes are accompanied by minor endothermic effect with minimum at 140 °C. Further heating leads to thermal oxidative degradation, transforming into a burnout of the organic part of the complex. The last stage is accompanied by a series of powerful exothermic effects with maxima at 480 °C.

Obviously, zinc complex **1** exhibited high thermal stability that can be used to create thin films by thermal evaporation in vacuum. Unfortunately, this method is not suitable for the complex **2**, due to its destruction, even at 160 °C.

3.5. Photo and electroluminescent properties

From the literature data it is known that the luminescent properties for thin films and solid samples are close to each other [16]. Since the complexes of zinc are considered as candidates for thin-film electroluminescent materials, optophysical characteristics of solid samples of complexes **1** and **2** have been studied. The luminescence of the ligands L^1 and L^2 was not high and therefore was not studied in detail. In contrast zinc complexes in the solid state showed a strong luminescence in the visible region. The photoluminescence spectra of the complex **1** represents a broad band with emission maximum at 495 nm (Fig. 3i) and at 450 nm for complex **2** (Table 2) when excited with 350 nm radiation, due to energy transfer between the highest occupied and lowest unoccupied molecular orbitals.

Exciting spectra of complex **1** contains two peaks at 362 and 447 nm (Fig. 3ii). The spectrum clearly shows that excitation by UV radiation is more effective than visible light excitation. Photoluminescent spectra of complex **1** undergo a bathochromic shift (36 nm) compared with the spectra of free ligand. Such a shift is associated with the transition of the ligand in the azomethine deprotonated form in the coordination and, consequently, increasing the length of conjugated double bonds.

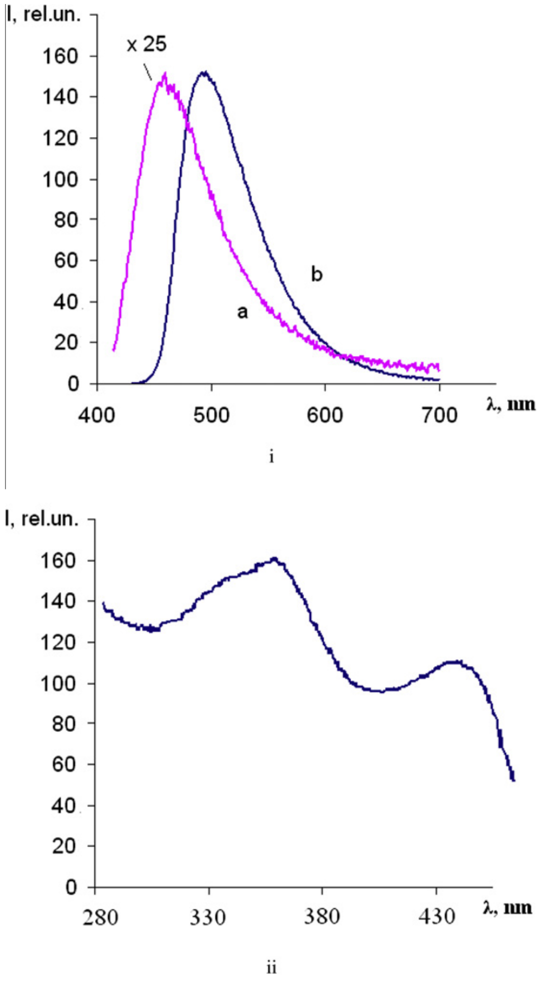


Fig. 3. (i) The emission spectrum of L^1 (*a*) and **1** (*b*) in solid state at room temperature, (ii) exciting spectra of complex **1**.

Table 2
The photoluminescence properties of L^1, L^2, **1** and **2**.

Compound	λ_{max} (nm)	I_{lumi}, rel. un.
L^1	459	5
L^2	450	5
1	496	152
2	450	82

The blue fluorescence of complexes **2** can be observed with the maximum emission wavelength at 450 nm. There is no considerable shift compared to free ligand emission was observed. This is consistent with the conservation cyclic form of the L^2 in complex **2**. So, the formation of metal chelates with Zn ions promotes fluorescence by increasing rigidity and minimizing internal vibrations.

The high luminescence efficiency in the green and blue light region, as well as the high thermally stability, indicates that the two complexes may be excellent candidates for highly thermally stable fluorescent materials.

Electroluminescent properties were studied for the complex **1**. The current–voltage and current-brightness characteristics of the sandwich device ITO/PEDOT/PVC:$Zn_2(L1)_2$/LiF/CaMg/Ag (ITO is indium tin oxide; PEDOT is poly(3,4-ethylenedioxythiophene)) was described in [17]. At 6 V the device generates light with a peak at 493 nm. It should be noted that the electroluminescence of zinc complexes with 1,2,4-triazole derivatives have not been described previously.

4. Conclusion and perspectives

In summary, we have successfully synthesized two novel zinc complexes. The X-ray analysis show that ligand can exist in two forms: azomethine and dihydrotriazaindolizine. With a highly thermal stability and high luminescence the synthesized zinc complexes are expected as candidate for fabrication of organic light emitting diodes (OLEDs).

Acknowledgements

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Appendix A. Supplementary material

CCDC 733658 and 817001 contain the supplementary crystallographic data for compounds **1** and **2** respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.07.009.

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