ISSN 0036-0236, Russian Journal of Inorganic Chemistry, 2011, Vol. 56, No. 1, pp. 32–38. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © A.N. Gusev, V.F. Shul'gin, S.B. Meshkova, Z.M. Topilova, M.A. Kiskin, G.G. Aleksandrov, I.L. Eremenko, 2011, published in Zhurnal Neorganicheskoi Khimii, 2011, Vol. 56, No. 1, pp. 35–42.

Zinc Complexes with 3-Pyridinyl-5-(2-salicylideneiminophenyl)-1H-1,2,4-triazoles

A. N. Gusev[a], **V. F. Shul'gin**[a], **S. B. Meshkova**[b], **Z. M. Topilova**[b],
M. A. Kiskin[c], **G. G. Aleksandrov**[c], **and I. L. Eremenko**[c]

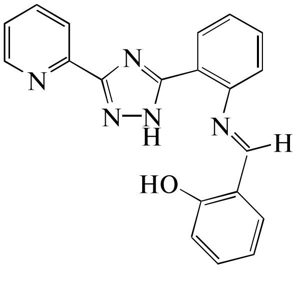
[a] *Taurida National Vernadsky University, pr. Vernadsokogo 4, Simferopol, 95007 Ukraine*
[b] *Bogatsky Physicochemical Institute of the National Academy of Sciences of Ukraine, Lustdorfskaya doroga 86, Odessa, 65080 Ukraine*
[c] *Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninskii pr. 31, Moscow, 119991 Russia*

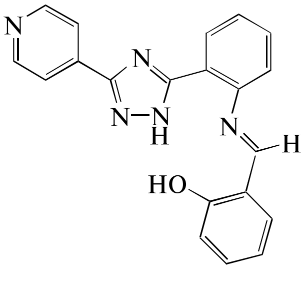
Received June 19, 2009

Abstract—New coordination compounds of zinc with 3-(pyridine-2-yl)-5-(2-salicylideneiminophenyl)-1H-1,2,4-triazole (H_2L^1) and 3-(pyridine-4-yl)-5-(2-salicylideneiminophenyl)-1H-1,2,4-triazole (H_2L^2) are obtained. According to X-ray diffraction data, binuclear zinc complexes with L^1, namely, $\left[Zn_2L^1_2\right] \cdot 0.5EtOH$ and $\left[Zn_2L^1_2\right] \cdot 2C_4H_8O_2 \cdot 2H_2O$ obtained in different solvents, are structurally related molecular complexes. The product of the reaction with H_2L^2 is the $\{[ZnL^2(Py)] \cdot CHCl_3\}_n$ coordination polymer. The 1,2,4-triazoles under study and the complexes on their basis luminesce in solutions with emission maxima ranging from 412 to 503 nm. These coordination compounds in the solid state emit in the green range of the spectrum (λ_{max} = 496 and 485 nm).

DOI: 10.1134/S0036023611010116

Coordination compounds of 1,2,4-triazoles are known to be useful as magnetic and optical materials [1–5]. The majority of the complexes with this type of ligand described in the literature are ionogenic, which considerably decreases their solubility in low-polarity solvents and restricts their utility in practice. One of the ways to solve this problem is to change an ionic structure to a molecular one by introducing additional chelate groups with mobile hydrogen atoms to the ligand. In this work, we present the results of the study of molecular zinc complexes with 3-pyridinyl-5-(2-salicylideneiminophenyl)-1H-1,2,4-triazoles.


3-(pyridine-2-yl)-5-(2-salicylidene-iminophenyl)-1H-1,2,4-triazole
(H_2L^1)


3-(pyridine-4-yl)-5-(2-salicylidene-iminophenyl)-1H-1,2,4-triazole
(H_2L^2)

EXPERIMENTAL

The starting reagents, 3-(pyridinyl)-5-(2-aminophenyl)-1H-1,2,4-triazoles, were prepared by reacting nitriles of suitable pyridinecarboxylic acids with 2-aminobenzoic acid hydrazide [6].

Synthesis of the coordination compounds under study was performed as follows. A solution of 250 mg (2.1 mmol) of salicylaldehyde in 10 mL of ethanol was added to a solution of 472 mg (2 mmol) of the appropriate 3-(pyridinyl)-5-(2-aminophenyl)-1H-1,2,4-

triazole in 10 mL of 96% ethanol. The resulting reaction mixture was stirred under heating with a magnetic stirrer for 1 h. To the suspension formed, 2 mmol of zinc acetate dihydrate was added, and the mixture was stirred for 2 h. The precipitate was kept under the mother liquor for 12 h, then filtered off, washed with ethanol, and dried in air. The product was obtained as 520–660 mg of a yellow crystalline substance; triazole yield, 65–75%.

The zinc content was calculated from complexometric titration data [7] after thermal decomposition of the test sample; the nitrogen content was determined by the Dumas method [8].

IR spectra of the complexes were recorded as KBr pellets in the range of 400–4000 cm^{-1} on a Nicolet Nexus 470 FTIR spectrometer.

For $\left[Zn_2L^1_2\right] \cdot 0.5EtOH$ ($C_{41}H_{29}N_{10}O_{2.5}Zn_2$) (**I**), anal. calcd. (wt %): Zn, 15.59; N, 16.66.

Found (wt %): Zn, 15.62; N, 16.36.

IR (cm^{-1}) for **I**: 1610 ($\nu(C{=}N_{Schiff})$), 1593, 1533, 1457, 1444, 1330, 1147, 800, 752.

For $[ZnL^2] \cdot EtOH$ ($C_{22}H_{21}N_5O_2Zn$) (**III**), anal. calcd. (wt %): Zn, 14.47; N, 15.48.

Found (wt %): Zn, 14.09; N, 15.71.

IR (cm^{-1}) for **III**: 1614 ($\nu(C{=}N_{Schiff})$), 1577, 1535, 1467, 1444, 1321, 1153, 754.

Thermogravimetric experiments were performed on a Paulik-Paulik-Erdey Q-derivatograph in an open ceramic crucible under a static air atmosphere with heating at a rate of 10 K/min; the standard was a calcined aluminum oxide sample.

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

X-ray crystallography measurements were performed using a Bruker Apex-II CCD diffractometer (MoK_α radiation, graphite monochromator, λ = 0.71073 Å). Single crystals of the zinc complex with 3-(pyridine-2-yl)-5-(2-salicylideneiminophenyl)-1H-1,2,4-triazole were obtained by recrystallization from a DMSO–ethanol mixture (2 : 1 vol/vol), as well as from dioxane. The compositions of single crystals grown from DMSO–ethanol and dioxane were $\left[Zn_2L^1_2\right] \cdot 0.5EtOH$ (**I**) and $\left[Zn_2L^1_2\right] \cdot 2C_4H_8O_2 \cdot 2H_2O$ (**II**), respectively. Single crystals of the zinc complex with 3-(pyridine-4-yl)-5-(2-salicylideneiminophenyl)-1H-1,2,4-triazole were obtained by slow diffusion of chloroform vapors into a pyridine solution of complex **III**. The crystal composition is formulated as $\{[ZnL^2(Py)] \cdot CHCl_3\}_n$ (**IV**). Experimental details and selected crystallographic data are shown in Table 1. Semi-empirical correction for absorption was applied (0.8646/0.7723 for **I**, 0.8982/0.8527 for **II**, and 0.8827/0.7132 for **IV**) [9]. The structures were solved by the direct method and refined by full-matrix least-squares in the anisotropic approximation (SHELX-97) [10]. Crystallographic data for compounds **I**, **II**, and **IV** have been deposited with the Cambridge Crystal Database, nos. 733658, 733659, and 7333660, respectively, and can be free downloaded from the site http://www.ccdc.cam.ac.uk/data_request/cif.

RESULTS AND DISCUSSION

Our studies show that the products of condensation of salicylaldehyde and 3-(pyridine)-5-(2-aminophenyl)-1H-1,2,4-triazoles react with zinc acetate to form molecular complexes with the metal : ligand ratio of 1 : 1. The complexes are stable up to 40–50°C, and a further increase in temperature leads to desolvation of the complexes. A crystallization ethanol molecule entering the composition of complex **I** is removed at 40–100°C without noticeable thermal features. The ethanol molecule of compound **III** is eliminated at a higher temperature (50–180°C). The process is accompanied by a small exotherm on the DTA curve with a maximum at 70°C. At 235°C, complex **III** melts. Thermal oxidative destruction of triazoles is observed (at 230 and 300°C for complexes **I** and **III**, respectively, followed by combustion of the organic residue. The process is completed at 650–700°C.

The IR spectra of complexes **I** and **III** do not contain bands corresponding to the stretching vibrations of N–H and O–H groups, which are observed in the IR spectra of the ligands at 3380 and 3270 cm^{-1}, respectively. 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 1290 cm^{-1} in the free triazoles to 1330–1321 cm^{-1} in the complexes. A shift of the band of the stretching vibrations of the –HC=N– bond by 15–20 cm^{-1} to the shortwave range is indicative of the coordination of the imine nitrogen atom.

According to X-ray crystallography, complex **I** is binuclear (Fig. 1). Each zinc ion is coordinated by two pentadentate bridging ligands in the doubly deprotonated form. Each central atom has a distorted tetragonal-bipyramidal environment formed 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 Zn(1) and Zn(2) atoms deviate by 0.48 Å and 0.65 Å, respectively, to the apical oxygen atoms from the plane of the four nitrogen atoms. The intramolecular Zn···Zn distance is 4.038 Å, which is characteristic of binuclear complexes of 1,2,4-triazoles [1]. The planar configuration and deprotonation of the 1,2,4-triazole moiety facilitate delocalization of C=N double bonds in the N_3C_2 five-membered ring. Because of this, the N(2)–N(3) bond

Table 1. Crystal data and experimental details for complexes **I**, **II**, and **IV**

Parameter	I	II	IV
Formula	$C_{41}H_{29}N_{10}O_{2.5}Zn_2$	$C_{48}H_{46}N_{10}O_8Zn_2$	$C_{26}H_{19}Cl_3N_6OZn$
Crystal dimension, mm	0.20 × 0.14 × 0.11	0.15 × 0.13 × 0.10	0.34 × 0.23 × 0.12
T, K	298(2)	298(2)	296(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$	$P2_1/n$
Unit cell parameters			
a, Å	25.405(18)	23.074(12)	8.839(14)
b, Å	14.938(11)	13.869(7)	30.31(4)
c, Å	19.430(14)	16.675(9)	11.760(11)
β, deg	96.006(10)	119.664(8)	95.782(2)
V, Å^3	7333.9(9)	4637(4)	3134.9(7)
Z	8	4	4
ρ_{calcd}, g/cm^{-3}	1.508	1.464	1.278
μ_{Mo}, mm^{-1}	1.362	1.098	1.066
F(000)	3400	2072	1224
θ_{max}, deg	30.07	31.39	25.03
Index ranges	$-29 \le h \le 35$	$-32 \le h \le 32$	$-10 \le h \le 10$
	$-21 \le k \le 20$	$-20 \le k \le 16$	$-36 \le k \le 36$
	$-27 \le l \le 25$	$-21 \le l \le 24$	$-13 \le l \le 13$
Reflections measured/reflections independent	28343/10636	18414/7217	20422/5360
R_{int}	0.0328	0.0294	
GOOF	1.048	1.044	1.001
R (all data)	$R_1 = 0.0842$	$R_1 = 0.1148$	$R_1 = 0.1582$
	$wR_2 = 0.1278$	$wR_2 = 0.2548$	$wR_2 = 0.1964$
R ($I > 2\sigma(I)$)	$R_1 = 0.0424$,	$R_1 = 0.0682$,	$R_1 = 0.0648$,
	$wR_2 = 0.1095$	$wR_2 = 0.2146$	$wR_2 = 0.1580$
Residual electron density (max/min), e/Å^3	0.654/–0.254	1.482/–0.653	0.907/–0.403

is considerably shorter (1.353(3) Å) than a standard nitrogen–nitrogen single bond (1.451 Å [11]). 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. The O(2) and H atoms of the solvated ethanol molecule are bound by a strong hydrogen bond (O(2)···O(1S) 2.82 Å).

Crystallization of **I** from dioxane leaves the molecular structure of the complex unchanged, but changes the packing of complex molecules in a crystal of **II** (Fig. 2). As in **I**, the coordination polyhedron of the central atom in **II**, too, is a distorted square pyramid, and the central metal ring has the boat conformation. The intramolecular Zn···Zn distance is 4.030 Å. The crystal structure has an extensive net of short intermolecular contacts. An interesting structural feature of compound **II** is bonding due to stacking interaction between 2-aminobenzene rings of the ligands of adjacent molecules, whose planes are at a distance of 3.56 Å from each other (Fig. 3). The solvation water molecule is disordered and occupies two positions, in one of which it forms hydrogen bonds with the oxygen atoms of the coordinated ligands (O(1w)···O(1) 2.76 Å; O(1)O(1w)O(1a), 114.5°) (Fig. 2).

Complex **IV**, which crystallizes as a solvate with chloroform, has a polymeric structure. The chloroform molecule is disordered over two positions with the site occupancies of 0.35 and 0.65. A fragment of the polymeric chain of complex **IV** is shown in Fig. 4. The coordination sphere of the zinc atom is a distorted trigonal bipyramid with nitrogen atoms of the azomethine moiety and the pyridine ring of the adjacent molecule in the axial positions. The equatorial plane is formed by the oxygen and nitrogen atoms of the doubly deprotonated chelatophore group of the triazole and the nitrogen atom of the coordinated pyridine

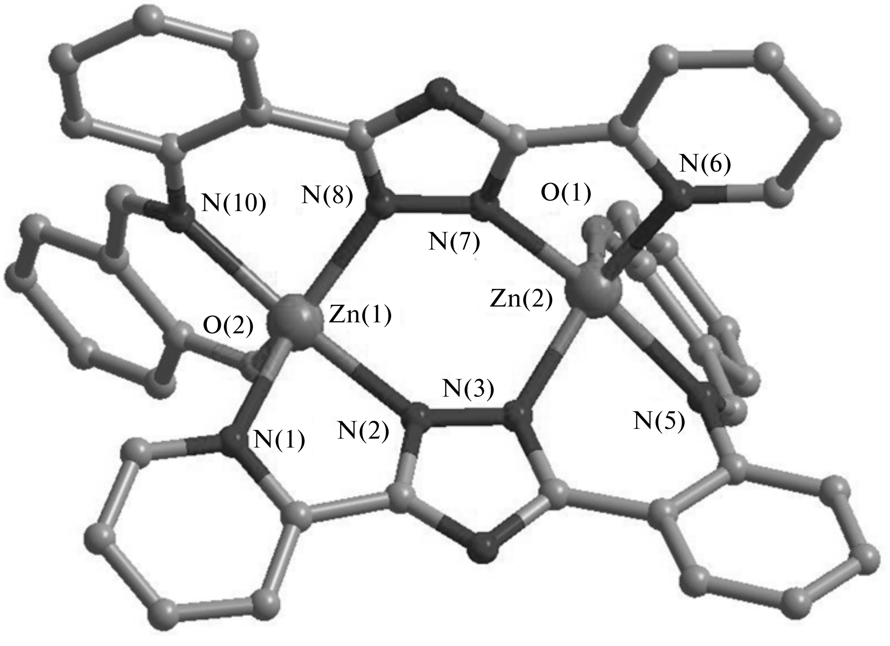


Fig. 1. Structure of complex **I** (hydrogen atoms are omitted). Selected bond lengths (Å) and bond angles (deg) are Zn(1)–N(1) 2.166(2), Zn(1)–N(2) 2.097(2), Zn(1)–N(8) 2.043(2), Zn(1)–N(10) 2.102(2), Zn(1)–O(2) 1.9270(19), O(2)Zn(1)N(8) 129.76(9), O(2)Zn(1)N(2) 100.17(9), N(8)Zn(1)N(2) 89.49(8), O(2)Zn(1)N(10) 93.75(8), N(8)Zn(1)N(10) 82.87(8), N(2)Zn(1)N(10) 165.98(9), O(2)Zn(1)N(1) 100.56(9), N(8)Zn(1)N(1) 129.51(9), N(2)Zn(1)N(1) 76.17(8), N(10)Zn(1)N(1) 99.69(8).

molecule. The N(3) atom of the triazole ring is not coordinated, which is not characteristic of 1,2,4-triazoles [1]. This may be due to additional coordination of the N(1) atom of the salicylidene chelatophore group, which stabilizes the monodentate coordination of the triazole. The polymeric chain of complex **IV** has a zigzag structure; the ZnZnZn angle is 87.17°. A characteristic structural feature of compound **IV** is the formation of channels in which disordered solvation chloroform molecules are placed.

The absorption spectra of DMSO solutions of the compounds under study (Fig. 5) show that the maximum absorption occurs in the range of 350–400 nm. This implies that the luminescence can be excited by the intense mercury line at 365 nm. A broad emission bands at 413 (H_2L^1) and 479 nm (H_2L^2) in the photoluminescence spectra of solutions of the Schiff bases studied (Table 2) are due to energy transfers between the highest occupied and the lowest unoccupied molecular orbitals. Deprotonation of organic ligands on formation of d^{10} metal complexes is known to considerably decrease the energy gap between these orbitals and to result in a bathochromic shift of maxima in photoluminescence spectra [12]. The data we obtained show that this tendency is intrinsic to complexes **I** and **III**: the complexes emit in the green range (maxima at 503 and 493 nm, respectively) (Table 2).

3-(Pyridine-2-yl)-5-(2-salicylideneiminophenyl)-1H-1,2,4-triazole does not display any visible luminescence in the solid state (Fig. 6), whereas complex **I**

Table 2. Spectral-luminescent characteristics of the H_2L^1, H_2L^2 ligands and complexes **I**, **III** (recorded at equal conditions)

Compound	Absorption		Excitation		Emission			
					solution		solid sample	
	λ, nm	*A*	λ, nm	*I*, quantum/s	λ, nm	I_{lum}, quantum/s	$λ_{max}$, nm	I_{lum}, rel. units
H_2L^1	348	0.242	390	682568	412.7	853420	–	–
I	399	0.531	359.1	10612	503.5	10534	496	930
H_2L^2	354	0.348	406	67500	479	65300	540	76
III	395	0.272	437	31000	490	32000	485	82

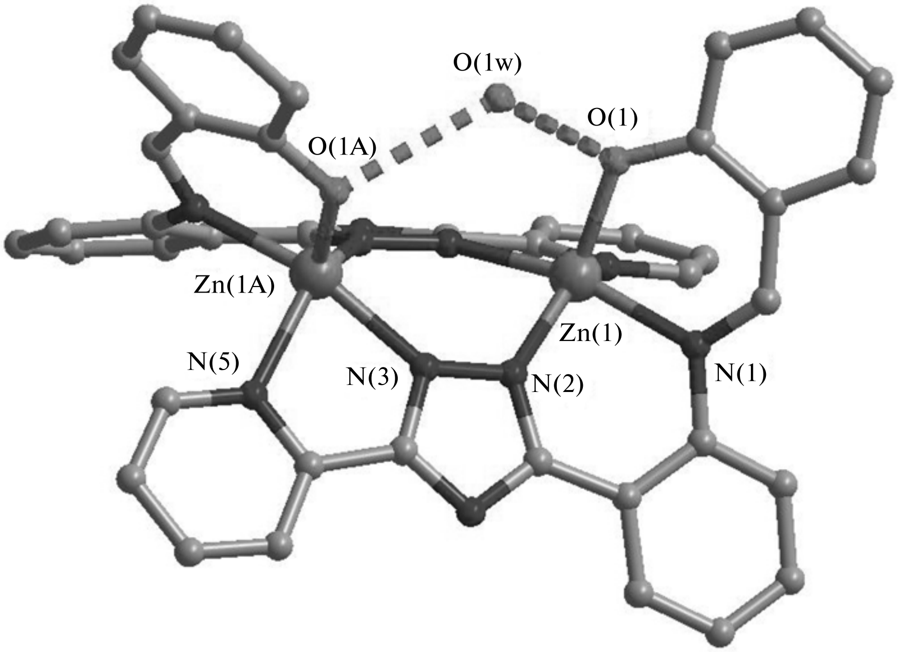


Fig. 2. Structure of complex **II** (hydrogen atoms are omitted). Selected bond lengths (Å) and bond angles (deg) are Zn(1)–N(1) 2.096(3), Zn(1)–N(2) 2.033(3), Zn(1)–N(3A) 2.106(3), Zn(1)–N(5A) 2.161(3), Zn(1)–O(1) 1.932(3), O(1)Zn(1)N(2) 122.00(13), O(1)Zn(1)N(1) 93.54(13), N(2)Zn(1)N(1) 83.93(13), O(1)Zn(1)N(3A) 103.52(12), N(2)Zn(1)N(3A) 89.42(13), N(1)Zn(1)N(3A) 162.69(13), O(1)Zn(1)N(5A) 105.55(13), N(2)Zn(1)N(5A) 132.34(13), N(1)Zn(1)N(5A) 96.98(12), N(3A)Zn(1)N(5A) 75.81(12).

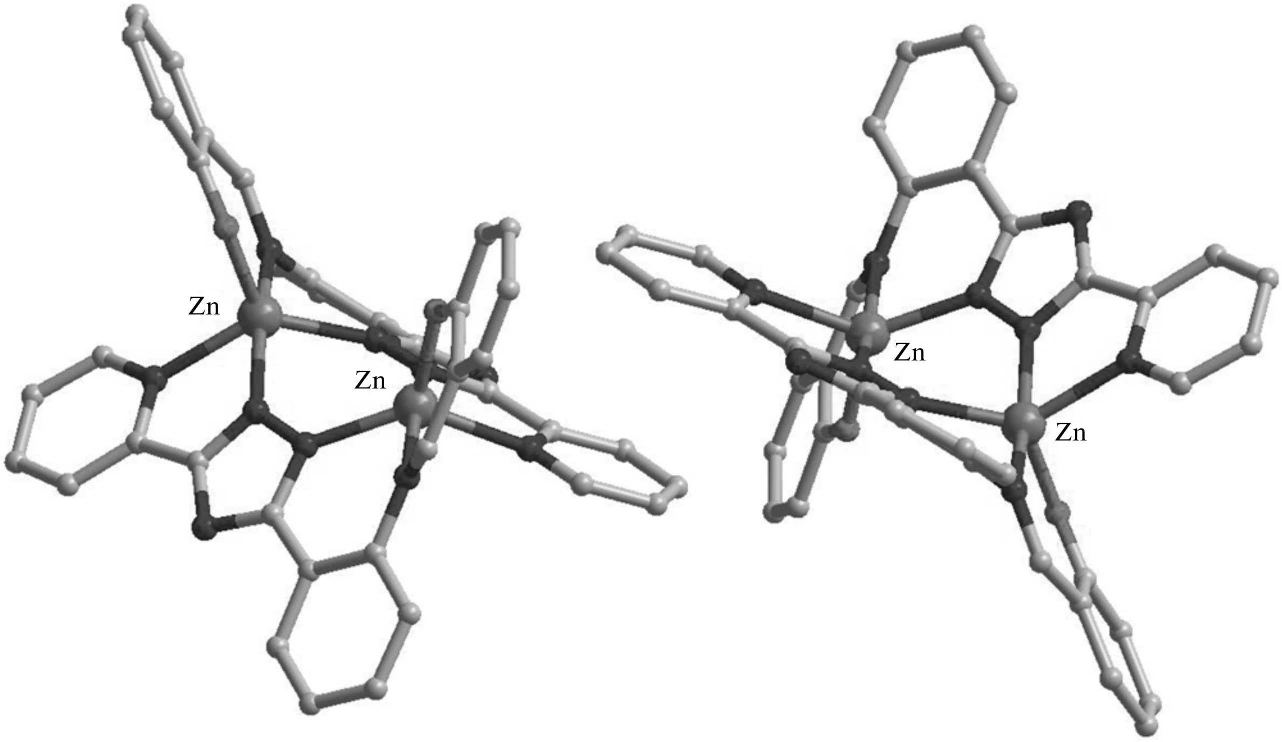


Fig. 3. Fragment of crystal packing of compound **II**.

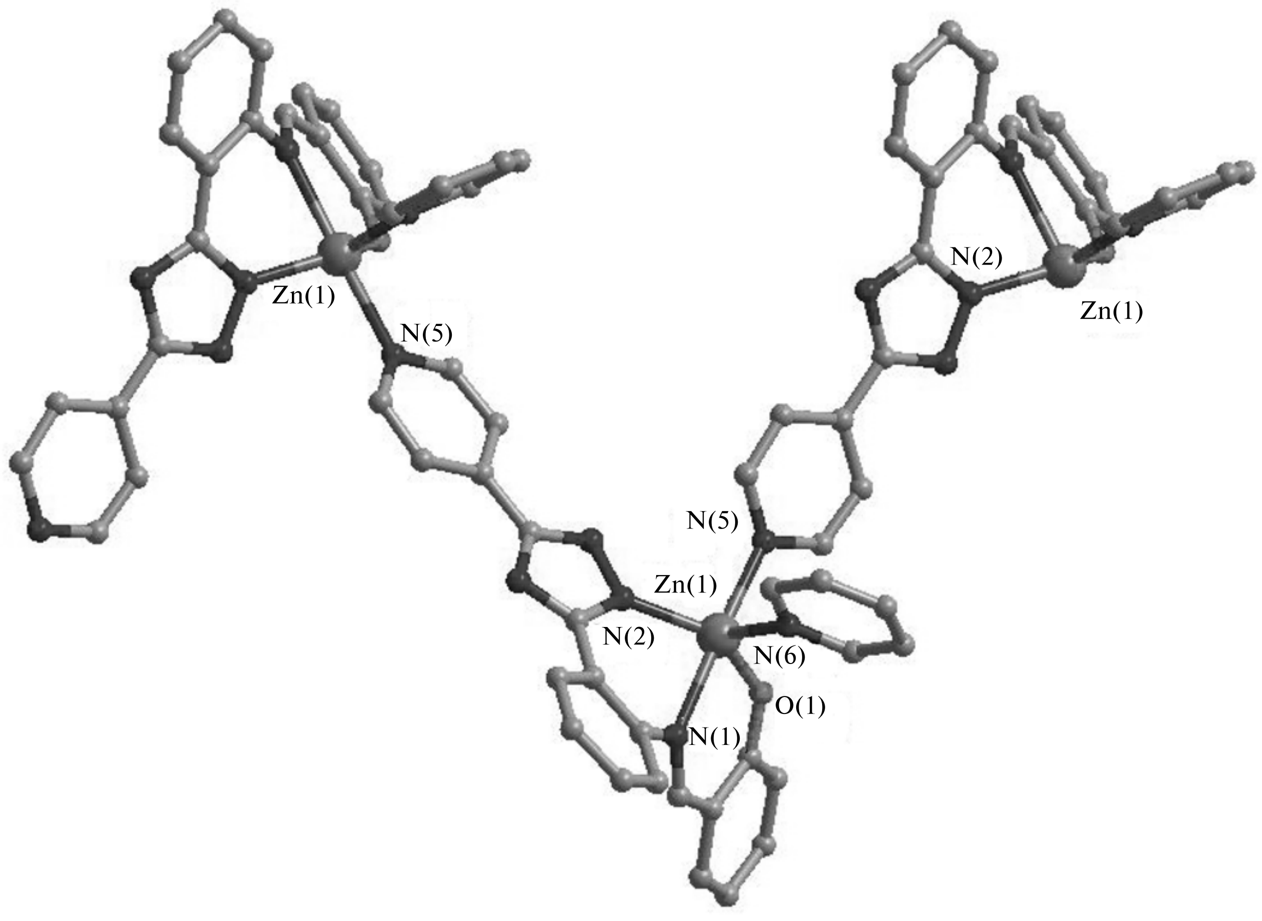


Fig. 4. Fragment of crystalline polymeric chain of compound **IV** (hydrogen atoms are omitted). Selected bond lengths (Å) and bond angles (deg) are Zn(1)–O(1) 1.937(6), Zn(1)–N(2) 2.001(6), Zn(1)–N(6) 2.091(7), Zn(1)–N(5) 2.159(6), Zn(1)–N(1) 2.208(6), O(1)Zn(1)N(2) 136.1(3), O(1)Zn(1)N(6) 111.1(3), N(2)Zn(1)N(6) 111.8(3), O(1)Zn(1)N(5) 89.8(2), N(2)Zn(1)N(5) 99.2(2).

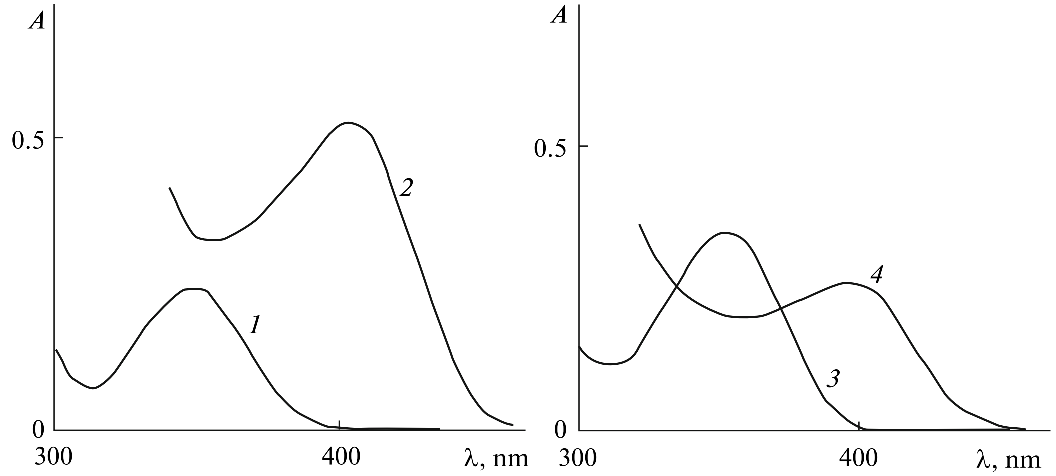


Fig. 5. Absorption spectra of solutions of (*1*) H_2L^1, (*2*) complex **I**, (*3*) H_2L^2, and (*4*) complex **III**.

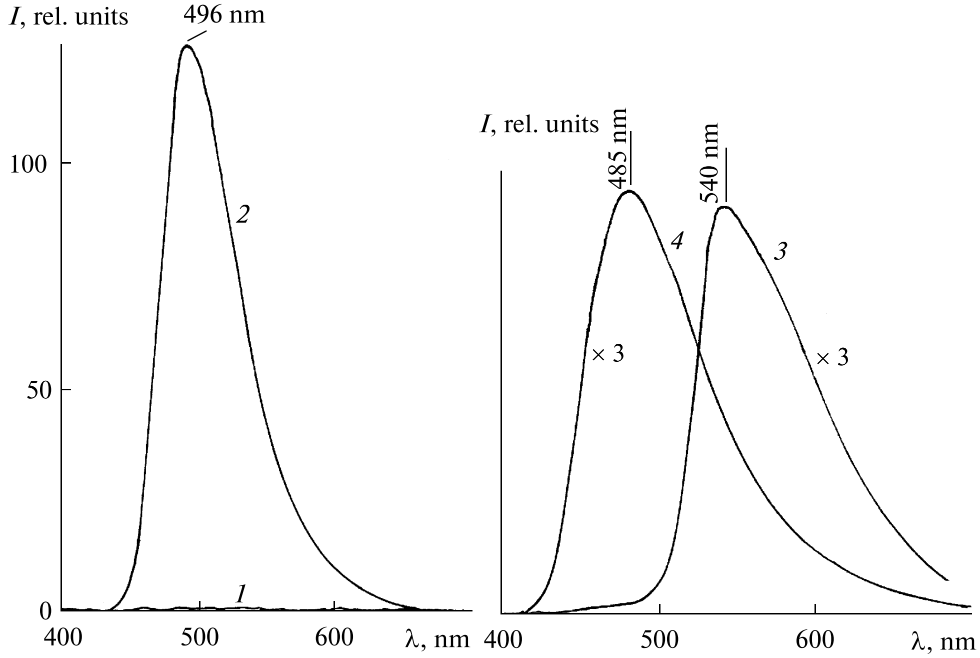


Fig. 6. Luminescence spectra of solid samples of (*1*) H_2L^1, (*2*) complex **I**, (*3*) H_2L^2, and (*4*) complex **III**.

emits an intense green light with a maximum at 495 nm. 3-(Pyridine-4-yl)-5-(2-salicylideneiminophenyl)-1H-1,2,4-triazole and complex **III** emit in the visible range with maxima at 540 and 485 nm, respectively. No considerable change in emission intensity was detected when passing from the ligand to the complex. A possible reason for this is the presence of the coordinated ethanol molecule. The stretching vibrations of the ethanol OH group lead to energy losses without emission. Intense luminescence of complexes **I** and **III** is interesting in the view of use of these compounds to obtain thin films of electroluminescent materials.

REFERENCES

1. J. G. Haasnoot, Coord. Chem. Rev. **200–202**, 131 (2000).
2. D. Mulhern, S. Brooker, H. Georls, et al., J. Chem. Soc. Dalton Trans. 51 (2006).
3. S. Ferrer, J. G. Haasnoot, J. Reedijk, et al. Inorg. Chem. **39**, 1859 (2000).
4. K. Sung and A. Lee, J. Heterocycl. Chem. **29**, 1101 (1992).
5. L. G. Lavrenova, N. G. Yudina, V. N. Ikorskii, et al., Polyhedron **14**, 1333 (1995).
6. US Pat. 4,198,513 USA, Published April 15, 1980.
7. R. Pribil, *Analytical Application of EDTA and Related Compounds* (Pergamon, Oxford (U.K.), 1972; Mir, Moscow, 1975).
8. V. A. Klimova, in *Basic Methods of Organic Microanalaysis* (Khimiya, Moscow, 1975), p. 224 [in Russian].
9. G. M. Sheldrick, *SADABS.* Program for Scanning and Correction of Area Detector Data (Göttingen Univ., Gottingen, 1997).
10. G. M. Sheldrick, *SHELX97.* Program for the Solution of Crystal Structures (Göttingen Univ., Gottingen, 1997).
11. A. J. Gordon and R. A. Ford, *The Chemist's Companion: A Handbook of Practical Data, Techniques and References* (Wiley, New York, 1972; Mir, Moscow, 1976).
12. O. V. Kotova, Extended Abstract of Candidate's Dissertation in Chemistry (Mosk. Gos. Univ., Moscow, 2008).