
**COORDINATION
COMPOUNDS**

*In memory of Academician of the Academy of Sciences of the Republic
of Uzbekistan N.A. Parpiev (1931–2021)*

Zinc(II) Complexes with Thiadiazole-1,3,4 Derivatives

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Abstract—Zn(II) complexes $[ZnL_n^mX_2]$ and $[ZnL_3^n(NO_3)_2]$, where $n = 1, 2$; $X = Cl, Br, I$; L^1 is 2-aminothiadiazole-1,3,4, and L^2 is 2-amino-5-methylthiadiazole-1,3,4, have been synthesized. The resulting complexes have been studied using elemental analysis, IR and 1H NMR spectroscopies. The structure of complex $[ZnL_2^2Br_2]$ has been determined by X-ray diffraction (CIF file CCDC no. 2251742). It has been found that the ligand molecules of 2-amino-5-R-thiadiazoles-1,3,4 ($R = -H, -CH_3$) are coordinated monodentately by the endocyclic nitrogen atom located in the α -position to the amino group. The polyhedron of the central atom of halide complexes is a slightly distorted tetrahedron, the coordination sphere of which is formed by two halide atoms and two endocyclic nitrogen atoms. According to the spectral data, during complexation in a solution of complex $[ZnL_2^2Br_2]$, coordinated ligands L^2 undergo amino-imine tautomerism to form a heterocyclic amine with a nitrogen atom in the heterocycle. The polyhedron of the central atom for nitrate complexes is a slightly distorted trigonal bipyramid, in the coordination sphere of which three nitrogen atoms of the ligands are located in the equatorial plane and two oxygen atoms of two nitrate anions are located in the axial position.

Keywords: 2-aminothiadiazole-1,3,4, 2-amino-5-methylthiadiazole-1,3,4, zinc complexes, X-ray diffraction, polyhedral

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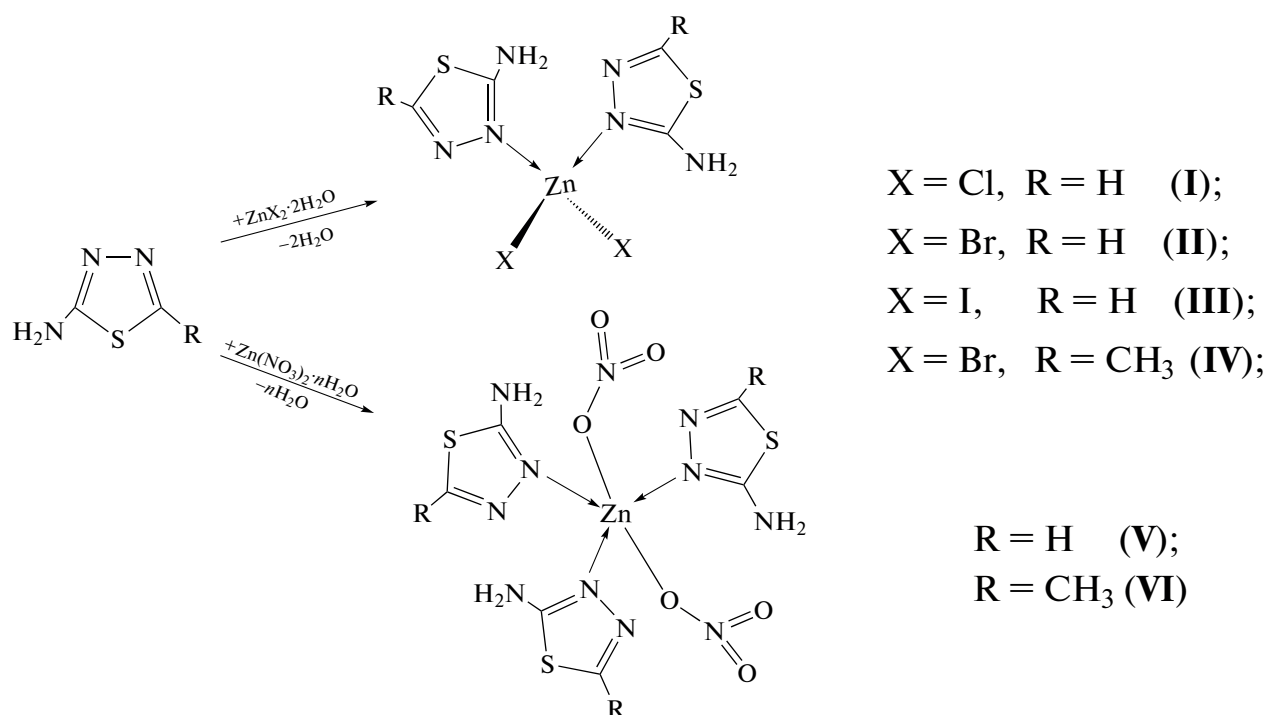
INTRODUCTION

Complexes based on heterocyclic compounds form a large class of coordination compounds that have been intensively studied for many years [1–6]. From the point of view of structural chemistry, it is distinguished by a wide variety of structural types [7–16] depending on the synthesis conditions, the nature of the metal and organic or acid ligands, the structure of which contains coordination polymers [17–19] and N-, O-, S-donor atoms forming discrete complexes of different nuclearities [20–25].

Interest in the chemistry of derivatives of cyclic thiadiazole compounds is explained primarily by the fact that they are convenient objects for studying the mutual influence of atoms and groups of various tau-

tomeric transformations. In addition, heterocycles, especially five-membered ones, occupy one of the leading places in their importance among already known biologically active substances [26–28]. Among polydentate organic ligands for the chemistry of complex compounds, 2-amino-1,3,4-thiadiazole is of particular interest. This is due to the presence of several potential donor atoms in its composition and its widespread use in medicine, agriculture, and industry [28–30].

In this work, complexes of zinc(II) halides (**I–IV**) and zinc(II) nitrate (**V–VI**) with ligands L^1 (2-aminothiadiazole-1,3,4) and L^2 (2-amino-5-methylthiadiazole-1,3,4) were synthesized and their structures were determined. The indicated complexes were obtained by the reaction present in Scheme 1.



Scheme 1.

The purpose of this work is to develop a method for the synthesis of mononuclear zinc(II) halide and nitrate complexes with new ligands and study their composition and structure using elemental analysis, IR and ^1H NMR spectroscopy, as well as X-ray diffraction.

EXPERIMENTAL

All experiments related to the synthesis of complexes I–VI were carried out at a temperature of 70–75°C using commercially available chemical reagents without additional purification, namely, $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{ZnBr}_2 \cdot 2\text{H}_2\text{O}$, $\text{ZnI}_2 \cdot 2\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$ (pure for analysis, Russian State Standard), 2-aminothiadiazole-1,3,4 ($\geq 99.0\%$), 2-amino-5-methylthiadiazole-1,3,4 ($\geq 98.0\%$) (Alibaba.com), as well as EtOH solvent (chemically pure grade, Russian State Standard, distilled).

Synthesis of complex $[\text{ZnL}_2^1\text{Br}_2]$ (II). A hot solution of $\text{ZnBr}_2 \cdot 2\text{H}_2\text{O}$ (0.78 g, 0.003 mol) in ethanol (35 mL) was added to a hot solution of ligand L_1 (0.606 g, 0.006 mol) in ethanol (50 mL) with gradual stirring. The resulting mixture was heated under reflux for 1 h to form beige polycrystals. After 2 days, the precipitated polycrystals were filtered off and dried in air.

Complexes $[\text{ZnL}_2^1\text{Cl}_2]$ (I) [31], $[\text{ZnL}_2^1\text{I}_2]$ (III) [32], and $[\text{ZnL}_2^2\text{Br}_2]$ (IV) were synthesized similarly.

Synthesis of complex $[\text{ZnL}_3^2(\text{NO}_3)_2]$ (VI). A hot solution of zinc(II) nitrate (0.57 g, 0.003 mol) in ethanol (50 mL) was added to a hot solution of ligand L^2

(1.036 g, 0.009 mol) in ethanol (50 mL) with gradual stirring. The resulting mixture was heated under reflux for 1 h, filtered off, and left for crystallization. A day later, the beige crystals precipitated were filtered and dried in air.

Complex $[\text{ZnL}_3^1(\text{NO}_3)_2]$ (V) was synthesized similarly [33]. Elemental analysis of compounds for C, H, N was performed on an EA 1108 Carlo Erba instrument; Zn was determined on a Perkin Elmer 3030B instrument. By recrystallization of $[\text{ZnL}_2^2\text{Br}_2]$ from ethanol, single crystals $\text{C}_6\text{H}_{10}\text{N}_6\text{S}_2\text{Br}_2\text{Zn}$ suitable for X-ray diffraction were obtained.

IR absorption spectra were recorded on a Spectrum 3 FT-IR Spectrometer by PerkinElmer Inc. in the range of 400–4000 cm^{-1} . The melting point was determined in sealed evacuated capillaries.

L^1 : pale yellow crystals, $T_m = 191\text{--}192^\circ\text{C}$.

For $\text{C}_2\text{H}_3\text{N}_3\text{S}$ anal. calcd. (%): C, 23.75; H, 3.00; N, 41.50.

Found (%): C, 23.36; H, 3.13; N, 41.51.

IR (ν , cm^{-1}): 1615 $\nu(\text{CH}=\text{N})$, 1020 $\nu(=\text{N}-\text{N}=\text{N})$, 3279, 3090, 3017 $\nu_{\text{as}}(\text{N}-\text{H})$ and $\nu_{\text{s}}(\text{N}-\text{H})$, 1506 $\delta(\text{N}-\text{H})$, 890 $\nu(\text{C}-\text{S})$.

L^2 : pale yellow crystals, $T_m = 225^\circ\text{C}$.

For $\text{C}_3\text{H}_5\text{N}_3\text{S}$ anal. calcd. (%): C, 31.28; H, 4.38; N, 36.49.

Found (%): C, 32.00; H, 4.49; N, 37.02.

IR (ν , cm^{-1}): 1640 $\nu(\text{CH}=\text{N})$, 1072 $\nu(=\text{N}-\text{N}=\text{N})$, 3216, 3065, 2966 $\nu_{\text{as}}(\text{N}-\text{H})$ and $\nu_{\text{s}}(\text{N}-\text{H})$, 1505 $\delta(\text{N}-\text{H})$, 977 $\nu(\text{C}-\text{S})$.

I: pale yellow crystals, $T_{\text{m}} = 236^{\circ}\text{C}$; yield, 0.972 g (86.0% with respect to $[\text{ZnL}_2\text{Cl}_2]$).

For $\text{C}_4\text{H}_6\text{N}_6\text{S}_2\text{Cl}_2\text{Zn}$ anal. calcd. (%): C, 14.19; H, 1.79; N, 24.83; Zn, 19.31.

Found (%): C, 14.46; H, 1.45; N, 24.52; Zn, 19.10.

IR (ν , cm^{-1}): 1640, 1590 $\nu(\text{CH}=\text{N})$, 1030, 1020 $\nu(=\text{N}-\text{N}=\text{N})$, 3384, 3336, 3287 $\nu_{\text{as}}(\text{N}-\text{H})$ and $\nu_{\text{s}}(\text{N}-\text{H})$, 1512 $\delta(\text{N}-\text{H})$, 899 $\nu(\text{C}-\text{S})$, 467 $\nu(\text{Zn}-\text{N})$.

II: pale yellow crystals, $T_{\text{m}} = 228-230^{\circ}\text{C}$; yield, 1.17 g (84.0% with respect to $[\text{ZnL}_2\text{Br}_2]$).

For $\text{C}_4\text{H}_6\text{N}_6\text{S}_2\text{Br}_2\text{Zn}$ anal. calcd. (%): C, 11.24; H, 1.41; N, 19.66; Zn, 15.29.

Found (%): C, 11.04; H, 1.40; N, 19.29; Zn, 15.43.

IR (ν , cm^{-1}): 1639, 1598 $\nu(\text{CH}=\text{N})$, 1100, 1042 $\nu(=\text{N}-\text{N}=\text{N})$, 3385, 3339, 3291, 3106 $\nu_{\text{as}}(\text{N}-\text{H})$ and $\nu_{\text{s}}(\text{N}-\text{H})$, 1523 $\delta(\text{N}-\text{H})$, 894 $\nu(\text{C}-\text{S})$, 452 $\nu(\text{Zn}-\text{N})$.

III: yellow crystals, $T_{\text{m}} = 224^{\circ}\text{C}$; yield, 1.32 g (79.0% with respect to $[\text{ZnL}_2\text{I}_2]$).

For $\text{C}_4\text{H}_6\text{N}_6\text{S}_2\text{I}_2\text{Zn}$ anal. calcd. (%): C, 9.21; H, 1.16; N, 16.12; Zn, 12.54.

Found (%): C, 9.43; H, 2.34; N, 16.51; Zn, 13.19.

IR (ν , cm^{-1}): 1638, 1588 $\nu(\text{CH}=\text{N})$, 1038, 1025 $\nu(=\text{N}-\text{N}=\text{N})$, 3376, 3324, 3265, 3111 $\nu_{\text{as}}(\text{N}-\text{H})$ and $\nu_{\text{s}}(\text{N}-\text{H})$, 1539 $\delta(\text{N}-\text{H})$, 897 $\nu(\text{C}-\text{S})$, 449 $\nu(\text{Zn}-\text{N})$.

IV: pale yellow crystals, $T_{\text{m}} = 242^{\circ}\text{C}$; yield, 1.224 g (83.0% with respect to $[\text{ZnL}_2\text{Br}_2]$).

For $\text{C}_6\text{H}_{10}\text{N}_6\text{S}_2\text{Br}_2\text{Zn}$ anal. calcd. (%): C, 15.82; H, 2.22; N, 18.45; Zn, 14.35.

Found (%): C, 15.74; H, 2.16; N, 18.58; Zn, 14.42.

IR (ν , cm^{-1}): 1598, 1550 $\nu(\text{CH}=\text{N})$, 1080, 1046 $\nu(=\text{N}-\text{N}=\text{N})$, 3364, 3250, 3188, 3167 $\nu_{\text{as}}(\text{N}-\text{H})$ and $\nu_{\text{s}}(\text{N}-\text{H})$, 1550 $\delta(\text{N}-\text{H})$, 972 $\nu(\text{C}-\text{S})$, 455 $\nu(\text{Zn}-\text{N})$.

V: pale yellow crystals, $T_{\text{m}} = 183-185^{\circ}\text{C}$; yield, 1.24 g (84.0% with respect to $[\text{ZnL}_3(\text{NO}_3)_2]$).

For $\text{C}_6\text{H}_9\text{N}_{11}\text{S}_3\text{O}_6\text{Zn}$ anal. calcd. (%): C, 14.62; H, 1.84; N, 31.27; Zn, 13.27.

Found (%): C, 14.48; H, 2.13; N, 31.21; Zn, 13.09.

IR (ν , cm^{-1}): 1622, 1588 $\nu(\text{CH}=\text{N})$, 1050, 1015 $\nu(=\text{N}-\text{N}=\text{N})$, 3281, 3139 $\nu_{\text{as}}(\text{N}-\text{H})$ and $\nu_{\text{s}}(\text{N}-\text{H})$, 1543 $\delta(\text{N}-\text{H})$, 930 $\nu(\text{C}-\text{S})$, 439 $\nu(\text{Zn}-\text{N})$.

VI: pale yellow crystals, $T_{\text{m}} = 195^{\circ}\text{C}$; yield, 1.36 g (85.0% with respect to $[\text{ZnL}_3(\text{NO}_3)_2]$).

For $\text{C}_9\text{H}_{15}\text{N}_{11}\text{S}_3\text{O}_6\text{Zn}$ anal. calcd. (%): C, 20.21; H, 2.83; N, 28.81; Zn, 12.22.

Found (%): C, 20.65; H, 2.94; N, 28.42; Zn, 12.12.

IR (ν , cm^{-1}): 1644, 1560 $\nu(\text{CH}=\text{N})$, 1085, 1035 $\nu(=\text{N}-\text{N}=\text{N})$, 3440, 3290, 3190, 3112 $\nu_{\text{as}}(\text{N}-\text{H})$ and $\nu_{\text{s}}(\text{N}-\text{H})$, 1510 $\delta(\text{N}-\text{H})$, 975 $\nu(\text{C}-\text{S})$, 427 $\nu(\text{Zn}-\text{N})$.

^1H NMR spectra were recorded on a JNM-ECZ400R spectrometer and a JNM-ECZ600R spectrometer (Jeol, Japan) at 400 MHz. TMS (0 ppm) was used as an internal standard in the ^1H NMR spectra. NMR spectra were processed using the MestReNova 14.2.0 software (Mestrelab Research S.L., Santiago de Compostela, Spain).

The X-ray diffraction experiment was carried out on an NRS XtaLAB Synergy diffractometer (Rigaku, Japan) [34] using $\text{CuK}\alpha$ radiation (double-mirror monochromator, ω -scanning).

The structures were solved by the direct method using the SHELXS-97 software package [35]. The structure was refined using the SHELXL-2014/7 program [36]. All non-hydrogen atoms were refined by the least squares method (using F^2) in the full-matrix anisotropic approximation. The positions of hydrogen atoms at the carbon atom were identified geometrically and refined with fixed isotropic displacement parameters $U_{\text{iso}} = nU_{\text{eq}}$, where $n = 1, 2$, and U_{eq} is the equivalent isotropic displacement parameter of the corresponding carbon atoms.

Atomic coordinates and other structural parameters of $[\text{ZnL}_2\text{Br}_2]$ have been deposited in the Cambridge Crystallographic Data Center (CCDC) (no. 2251742); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif.

RESULTS AND DISCUSSION

The $\nu(\text{Zn}-\text{N})$ absorption bands in the IR spectra of the complexes, in comparison with the spectra of the ligands, appear in the region of 427–467 cm^{-1} . The spectra of zinc complexes (**I–VI**) also differ from the spectra of the corresponding ligands; the intense absorption bands of stretching vibrations of the $>\text{C}=\text{N}-$ bond at 1615 cm^{-1} (L^1) and 1640 cm^{-1} (L^2) are split into two intense bands: 1640, 1590 (**I**), 1639, 1598 (**II**), 1638, 1588 (**III**), 1598, 1550 (**IV**), 1622, 1588 (**V**), and 1644, 1560 cm^{-1} (**VI**), respectively). This fact can be explained by the inequality of the $>\text{C}=\text{N}-$ bonds in the ligand molecule coordinated through one nitrogen atom of the thiadiazole ring. The vibration band $\nu(>\text{N}-\text{N}<)$ (in the spectra of ligands, 1020 for L^1 and 1072 cm^{-1} for L^2) in the spectra of the complexes also splits into two intense bands at 1030–1100 and 1015–1042 cm^{-1} in the case of L^1 , at 1080–1085 and 1035–1046 cm^{-1} in the case of L^2 . The stretching vibrations of amino groups remain unchanged, being located in the region of 3440–3017 cm^{-1} , and the bending vibration frequencies are observed in the range of 1550–1505 cm^{-1} [31, 37, 38]. This spectral

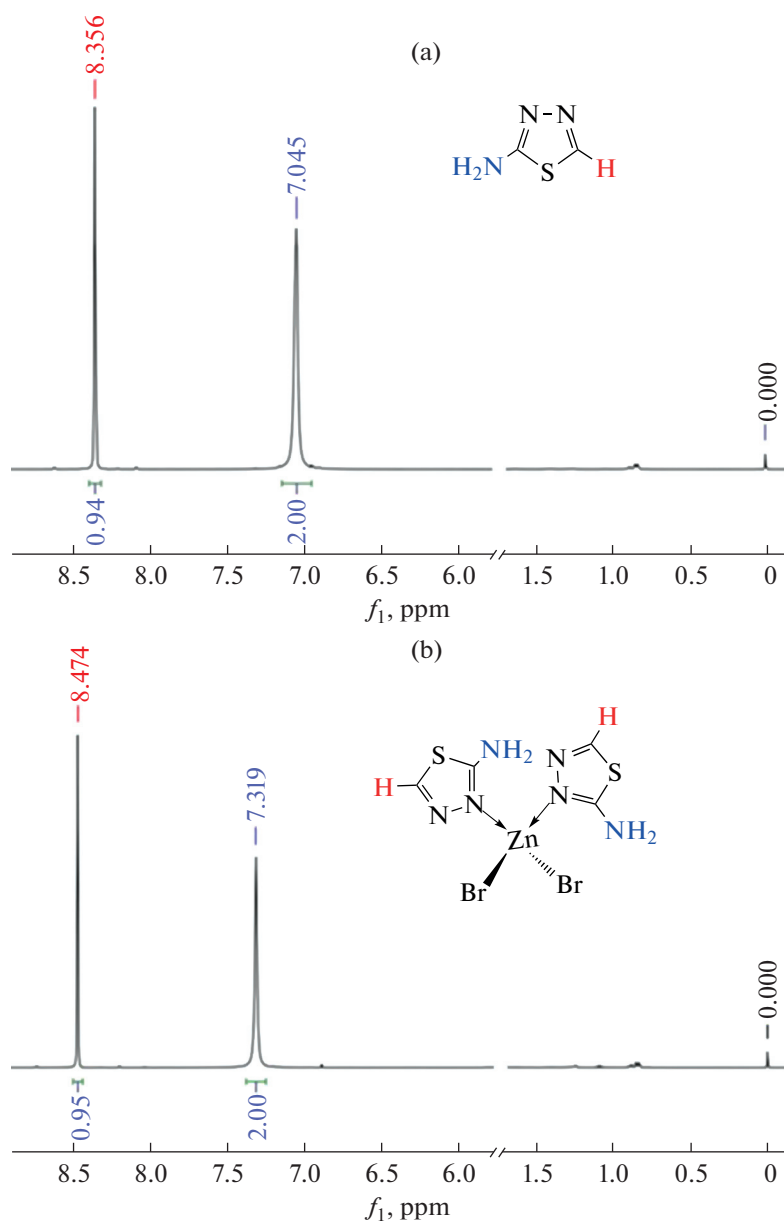


Fig. 1. (a) ^1H NMR spectra of ligand L^1 and (b) complex II ; 400 MHz, solvent is $\text{DMSO}-d_6 + \text{CCl}_4$, 298 K.

behavior of the complexes indicates the formation of a monodentate coordination structure of the ligands.

Interesting results were obtained when studying ligands and new complex compounds synthesized based on them using ^1H NMR spectroscopy in a solution of $\text{DMSO}-d_6 + \text{CCl}_4$ (400 MHz); the values of chemical shifts (δ , ppm) are shown in Figs. 1, 2. In the ^1H NMR spectrum of L^2 , a singlet signal in the field of $\delta = 2.46$ ppm refers to three protons of the CH_3 group, and the singlet signal in the field of $\delta = 6.798$ ppm belongs to two protons of the NH_2 group. Singlet signals at $\delta = 2.48$ ppm refer to the protons of the methyl

group in complex VI , and the signals at $\delta = 6.946$ ppm correspond to two protons of the amino group.

In the tetrahedral complex IV , a singlet signal from three hydrogen atoms of the methyl group was recorded at $\delta = 2.501$ ppm, and doublet signals from the hydrogen atom of the imine group and the azomethine hydrogen atom in the ring were recorded at $\delta = 7.196$ and 7.249 ppm [39, 40]. It can be concluded that ligand L^2 in solution undergoes amino-imine tautomerism when complexed with a zinc bromide salt, with one of the hydrogen atoms in the amino group shifting to the endocyclic nitrogen atom in the α -position from the amino group (Scheme 2).

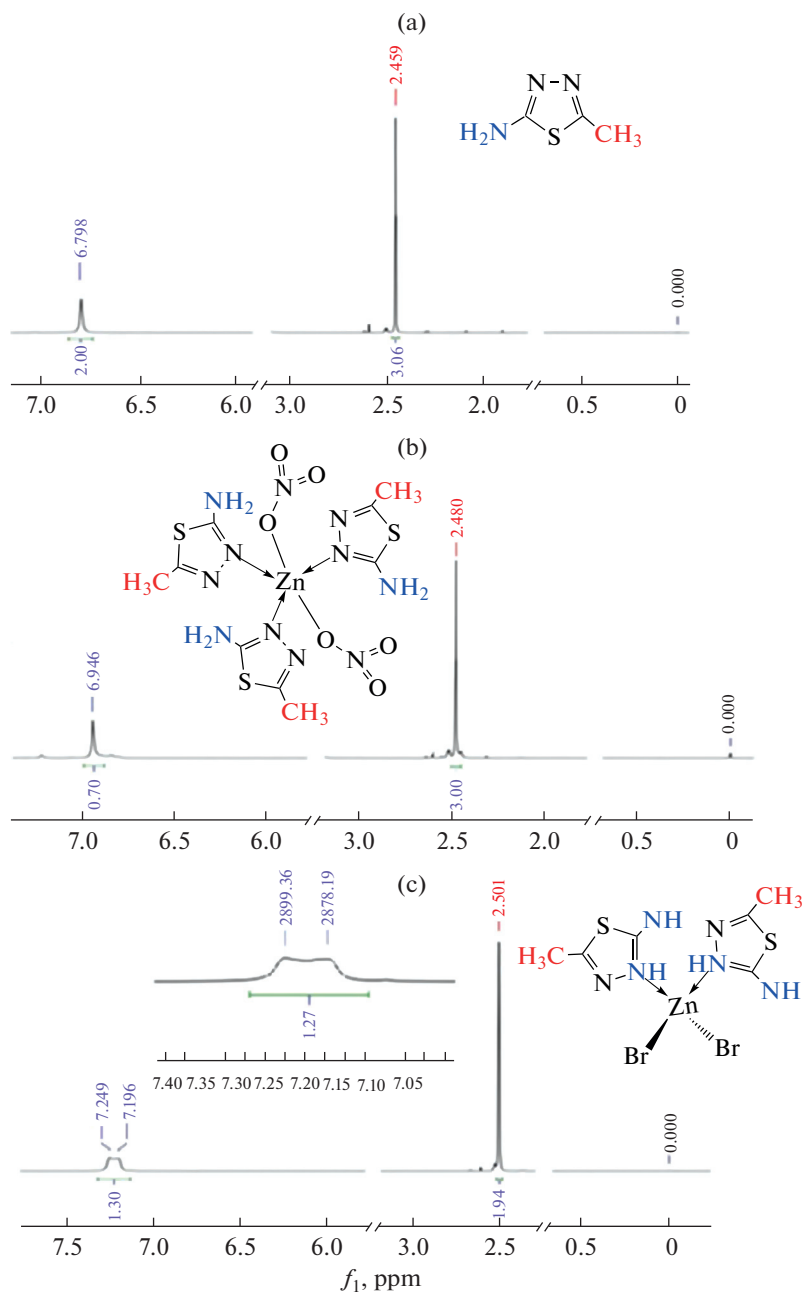
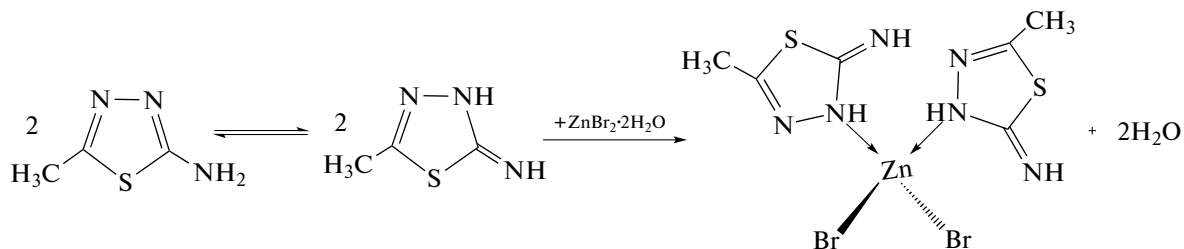


Fig. 2. (a) ^1H NMR spectra of ligand L^2 and complexes (b) VI and (c) IV; 400 MHz, solvent is $\text{DMSO}-d_6 + \text{CCl}_4$, 298 K.



Scheme 2.

Table 1. Crystallographic parameters and refinement details for $[\text{ZnL}_2\text{Br}_2]$

Parameter	Value
Formula	$\text{ZnC}_6\text{H}_{10}\text{N}_6\text{S}_2\text{Br}_2$
FW	455.51
T , K	293
Crystal system	Monoclinic
Space group	$P2_1/c$
a , Å	9.27376(13)
b , Å	20.3510(2)
c , Å	7.48449(11)
α , deg	90
β , deg	98.2811(14)
γ , deg	90
V , Å ³	1397.82(3)
Z	4
ρ_{calcd} , g/cm ³	2.164
μ , mm ⁻¹	11.85
θ range, deg	4.3–71.4
h, k, l indexes	$-11 \leq h \leq 11$, $-24 \leq k \leq 22$, $-9 \leq l \leq 9$
Number of reflections collected	13854
unique (R_{int})	2702 (0.043)
with $I > 2\sigma(I)$	2442
Number of parameters to be refined	172
GOOF (F^2)	1.04
R_1, wR_2 ($I > 2\sigma(I)$)	0.026, 0.067
R_1, wR_2 (all data)	0.029, 0.069
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$, e Å ⁻³	0.38, -0.45

To unambiguously confirm the conclusions drawn about the structure of Zn(II) complexes (based on the results of IR and ¹H NMR spectroscopies), single crystals $[\text{ZnL}_2\text{Br}_2]$ were grown, which were obtained by recrystallizing from EtOH. The main crystallographic data and the results of refinement of the structure of $[\text{ZnL}_2\text{Br}_2]$ are given in Table 1.

Table 2. Selected bond lengths and bond angles in the coordination polyhedron of complex **IV**

Bond	d , Å
Zn(1)–Br(1)	2.3751(5)
Zn(1)–Br(2)	2.3938(5)
Zn(1)–N(1A)	2.032(2)
Zn(1)–N(1B)	2.021(2)
Angle	ω , deg
Br(1)Zn(1)Br(2)	112.33(2)
N(1A)Zn(1)N(1B)	104.46(8)
N(1A)Zn(1)Br(2)	107.88(6)
N(1B)Zn(1)Br(2)	112.98(7)
N(1A)Zn(1)Br(1)	108.90(6)
N(1B)Zn(1)Br(1)	109.92(7)

It is known that coordination compounds of zinc(II) dihalides and other divalent metal ions of transition series I with monodentate ligands are mainly crystals of a tetrahedral structure, the distortions in which result from (in the absence of the influence of the nature of the central atom, the spherically symmetric d^{10} shell) the nature of the acido-ligands and monodentate ligands, as well as the packing features of monomer polyhedra in the crystal structure [31, 32, 41].

In the complexes of zinc(II) halides with L¹ (**I**–**III**), a distorted tetrahedral configuration is also realized, at the vertices of which there are two halogen atoms and two donor nitrogen atoms of the thiadiazole rings [31, 32, 42].

The crystal structure of **IV** consists of discrete mononuclear molecules bonded by hydrogen bonds (Figs. 3, 4). The zinc atom coordinates two bromine ions and two endo-nitrogen atoms in a distorted tetrahedral geometry. The Zn–Br bond lengths (2.3751(5) and 2.3938(5) Å) differ significantly (Table 2), and only the largest value is close to the sum of the covalent radii of Zn and Br (1.31 + 1.11 = 2.42 Å, Pauling covalent radii of atoms). The two Zn–N bond lengths in **IV** (2.032(2) and 2.021(2) Å) are significantly close to the sum of the covalent radii of 2.05 Å [43].

The bond angles of NZnBr in the structure of complex $[\text{ZnL}_2\text{Br}_2]$ (107.88(6)°–112.98(7)°) are close to the values in other tetrahedral zinc complexes. The NZnN and BrZnBr angles are increased to 104.46(8)° and 112.33(2)°, respectively [31, 32, 42].

In both coordination polyhedra, the potential tridentate ligand aminothiadiazole is coordinated by the zinc atom via an endocyclic nitrogen atom located in

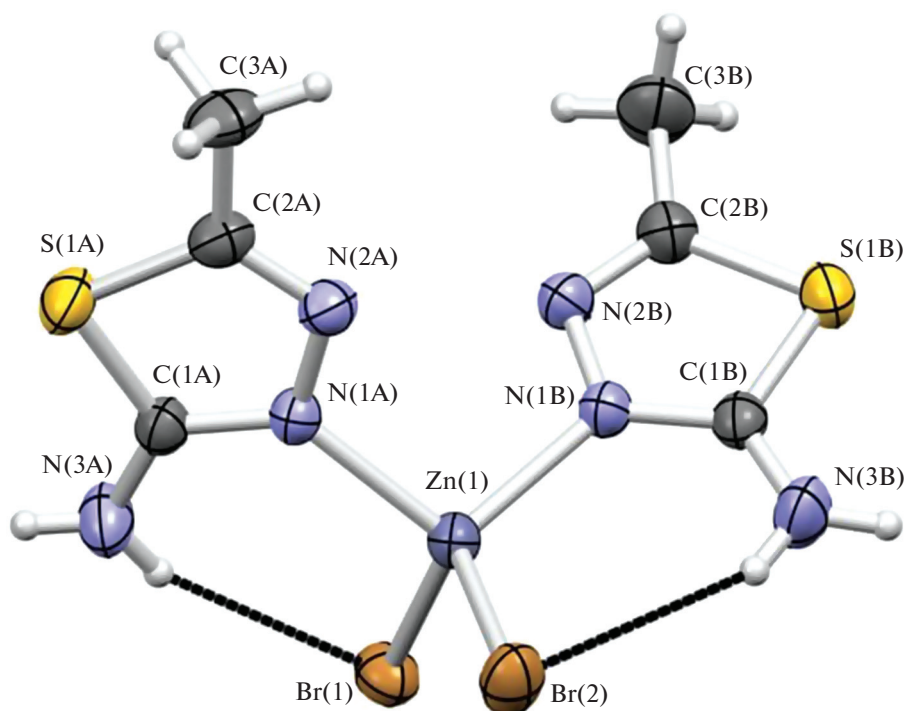


Fig. 3. Crystal structure of complex $[\text{ZnL}^2_2\text{Br}_2]$. Intramolecular hydrogen bonds are shown. Thermal ellipsoids are shown with a probability of 50%.

the α -position to the exocyclic nitrogen atom of the amino group. It should be noted that the “soft” donor center in the form of a sulfur atom in the aminothiadiazole ring does not participate in coordination with the “soft” acid—zinc(II) ion.

From the point of view of the hydrogen bond potential, ligands L^1 and L^2 have two acceptor elements, namely, two hydrogen atoms of the NH_2 group, and two donors, namely, the N(1) and N(2) atoms of the thiadiazole ring [31, 44, 45], as well as Br^- ions.

The NH_2 groups in the structure of complex **IV** participate in the formation of weak intramolecular hydrogen bonds $\text{N}-\text{H}\cdots\text{Br}$ ($\text{N}(3\text{A})-\text{H}(2)\cdots\text{Br}(1)$ 3.410(3) Å and $\text{N}(3\text{B})-\text{H}(4)\cdots\text{Br}(2)$ 3.611(3) Å), closing six-membered M, H-cycles (M is metal), with hal-

ogen ions (Br^-) acting as a donor. The crystal structure also contains asymmetrical intermolecular hydrogen bonds (Table 3).

A comparison of the remaining structural data of the thiadiazole rings of compound **IV** shows that the deviation of the atoms from the “average” plane is somewhat smaller (Table 4) [45].

Zinc(II) nitrate forms a five-coordinate complex compound with ligands L^1 and L^2 . The increase in the coordination number in this case is obviously explained by the greater repulsion of bulky nitrate ions from each other, as a result of which it becomes possible for coordination to the central atom of the third molecule of the heterocycle. The resulting complex of zinc(II) nitrate with aminothiadiazole is a trigonal bipyramid, in the equatorial plane of which there are

Table 3. Characteristics of hydrogen bonds in the structure of **IV** (D is donor, A is acceptor)

D–H⋯A	Symmetry codes	Distance, Å			DHA angle, deg
		D–H	H⋯A	D⋯A	
Intramolecular hydrogen bonds					
$\text{N}(3\text{A})-\text{H}(2)\cdots\text{Br}(1)$	x, y, z	0.86(4)	2.60(4)	3.410(3)	158(3)
$\text{N}(3\text{B})-\text{H}(4)\cdots\text{Br}(2)$	x, y, z	0.85(4)	2.82(4)	3.611(3)	156(4)
Intermolecular hydrogen bonds					
$\text{N}(3\text{A})-\text{H}(1)\cdots\text{Br}(2)$	$-x, 1-y, 1-z$	0.79(4)	2.73(7)	3.531(8)	144(6)
$\text{N}(3\text{B})-\text{H}(3)\cdots\text{N}2(\text{A})$	$x, 1/2-y, 1/2+z$	0.83(4)	2.30(4)	3.114(4)	165(3)

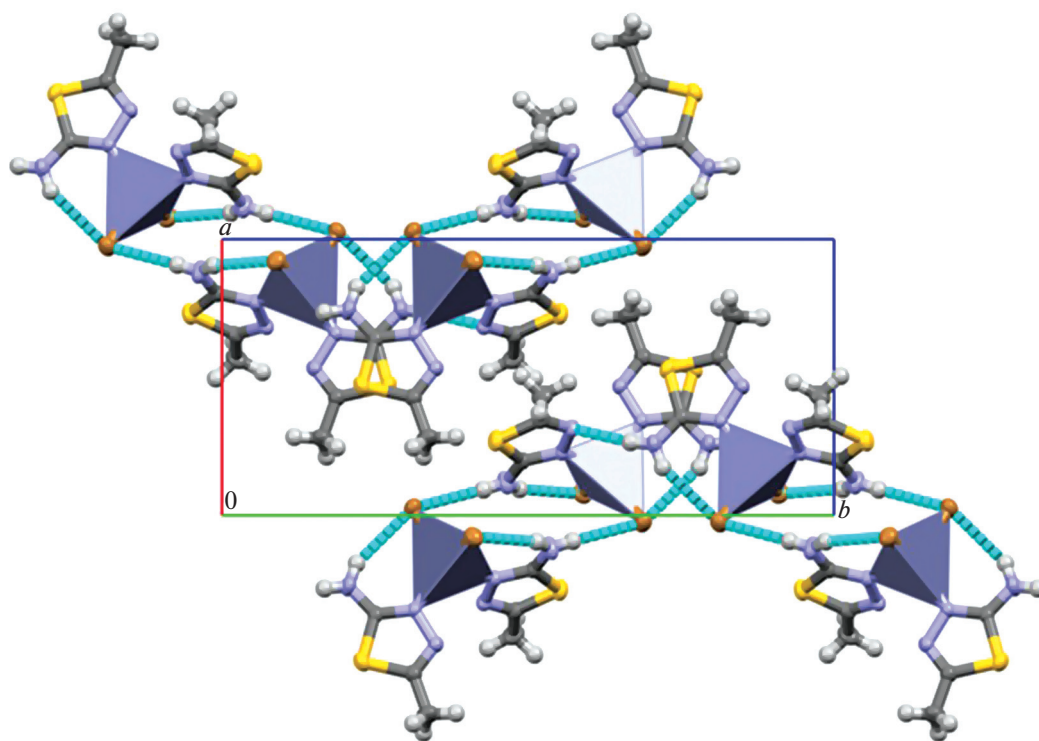


Fig. 4. Projection of the crystal packing of molecules $[\text{ZnL}_2\text{Br}_2]$ along axis c . Coordination polyhedra ZnN_2Br_2 are shown.

three nitrogen atoms of three heterocycle molecules; the axial positions of the polyhedron are occupied by the oxygen atoms of two nitrate ions [33].

CONCLUSIONS

In this work, the synthesized complexes, the structure of which is described by the formulas $[\text{ZnL}_2\text{X}_2]$, where $\text{X} = \text{Cl}, \text{Br}, \text{I}$ (**I–III**, respectively), $[\text{ZnL}_2\text{Br}_2]$ (**IV**), $[\text{ZnL}_3(\text{NO}_3)_2]$ (**V**), and $[\text{ZnL}_3(\text{NO}_3)_2]$ (**VI**) were

studied by IR and ^1H NMR spectroscopies and X-ray diffraction. It was found that during complexation, ligands are coordinated through endocyclic nitrogen atoms, which are in the α -position relative to the amino group in the solid state. The parameters of the ^1H NMR spectra of complex $[\text{ZnL}_2\text{Br}_2]$ (**IV**) (coordinated L^2 ligands in solution) undergo amino-imine tautomerism during complexation.

In the case of halide complexes, the polyhedron of the central atom is a slightly distorted tetrahedron, the coordination sphere of which is built by two halide atoms and two endocyclic nitrogen atoms. When a nitrate anion is present in the complex as an acidoligand, the polyhedron of the central atom is a trigonal bipyramid, in the coordination sphere of which there are three nitrogen atoms of three molecules of ligand L^2 in the equatorial plane and two oxygen atoms of nitrate anions located in the axial position.

Table 4. Deviation of atoms from the “average” planes in the structure of **IV**

Atom	Deviation, Å	Atom	Deviation, Å
N(1A)	0.0005	N(1B)	0.002
N(2A)	−0.004	N(2B)	0.003
C(1A)	0.002	C(1B)	−0.004
C(2A)	0.004	C(2B)	−0.005
S(1A)	−0.003	S(1B)	0.004
N(3A)*	0.03	N(3B)*	−0.045
Zn(1)*	−0.1396	Zn(1)*	0.296
Br(1)*	0.503	Br(1)*	2.558
Br(2)*	−2.395	Br(2)*	−0.395

* Atoms are not included in the calculation of this plane.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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