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# Copper(II), Nickel(II), and Zinc(II) Complexes with *o*-Tozylaminobenzaldehyde 4,6-Dimethylpyrimidyl Hydrazone

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**Abstract**—*o*-Tosylaminobenzaldehyde dimethylpyrimidyl hydrazone and its copper(II), nickel(II), and zinc(II) complexesare synthesized and studied. According to the X-ray diffraction data, the zinc(II) complex has the structure of a tetragonal pyramid with the $N_3O$ donor ligand environment. According to EPR and magnetochemistry data, the copper(II) complex has a similar structure of the chelate core. In the nickel(II) complex, the solvent molecule completes the coordination core to an octahedron.

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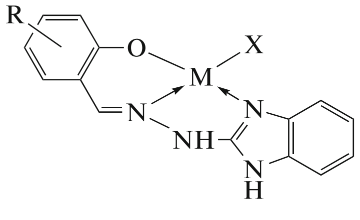
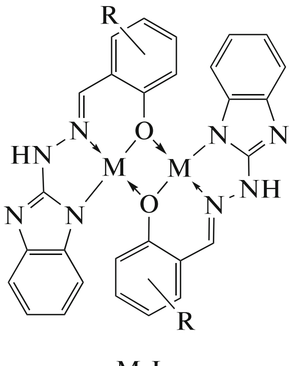
Hetarylhydrazones of aldehydes and ketones are of interest in coordination chemistry as potential polydentate ligand systems that can exhibit both mono- and dibasic nature. This fact makes it possible to obtain various complex compounds based on them, the structure of which depends on the synthesis conditions and the nature of the complexing metal [1–6]. In particular, *N*-2-benzimidazolyl hydrazones and *N*-2-benzoxo(thia)zolyl hydrazones of salicylic aldehyde served us to synthesize both mono- and binuclear complexes **I**–**III**.



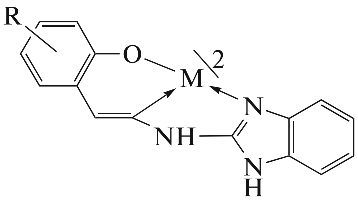
M(HL); X = Hal, $ClO_4$, $NO_3$

**I**



$M_2L_2$

**II**



$M(HL)_2$

**III**

Hetarylhydrazones based on hydrazinopyrimidine are related to the systems discussed above. The purpose of this paper is to study the effect of the nature of the pyrimidine fragment of the *o*-tosylaminobenzaldehyde hydrazone molecule on the protolytic and complexing properties and structure of the resulting coordination compounds. This ligand system was chosen primarily because pyrimidyl hydrazones and complexes based on them are poorly known [7–11]. In addition, the introduction of a tosyl group into molecules of the ligand systems often leads to significant changes in the structure and physicochemical properties of the complexes [12–18]. The potential biological activity of the compounds obtained should also be mentioned: it is known that compounds containing the sulfamide fragment have high antibacterial activity, whereas the pyrimidine ring is found in many drugs with a wide range of physiological effects [19–22].

## EXPERIMENTAL

**2-Hydrazino-4,6-dimethylpyrimidine** was synthesized according to the procedure reported in [23].

**Synthesis of hetaryl hydrazone IV.** A solution of *o*-tosylaminobenzaldehyde (1 mmol) in isopropanol (5 mL) was added to a hot solution of 2-hydrazino-4,6-dimethylpyrimidine (1 mmol) in isopropanol (5 mL). The resulting solution was refluxed for 3 h. The white precipitate which precipitated on cooling was filtered off, washed with ethanol, and recrystallized from a toluene : heptane mixture (1 : 1). Yield, 75%; white crystals; $T_m$ = 159–161°C.

For $C_{20}H_{21}N_5O_2S$ anal. calcd. (%): C, 60.74; H, 5.35; N, 17.71; S, 8.11.

Found (%): C, 60.61; H, 5.47; N, 17.86; S, 8.03.

IR (Nujol mull), ν, $cm^{-1}$: 3330 s, 1589 s, 1552 s, 1524 s, 1497 s, 1376 s, 1335 s, 1280 m, 1216 w, 1159 s, 1093 m, 935 m, 822 w, 753 m, 711 w, 664 w.

$^1$H NMR (DMSO-$d_6$), δ, ppm: 2.2 (s, 6H, $2CH_3$), 2.3 (s, 3H, $CH_3$), 6.7–7.8 (m, $9H_{ap}$), 8.10 (s, 1H, CH=N), 11.4 (s, 1H, NH), 11.98 (s, 1H, NH).

**Synthesis of complex compounds V (the general procedure).** A hot solution of 1 mmol of the corresponding metal salt in methanol (10 mL) was added to a hot suspension of 1 mmol of hetarylhydrazone in methanol (10 mL). The mixture was refluxed for 4 h. The precipitate was filtered off, washed with hot methanol, and dried in vacuum.

Complex **Va** (M = Cu, X = Cl) was isolated as violet crystals. Yield, 56%; $T_m$ > 260°C.

For $C_{20}H_{20}ClCuN_5O_2S$ anal. calcd. (%): C, 48.68; H, 4.09; Cu, 12.88; N, 14.19; S, 6.50.

Found (%): C, 49.51; H, 4.23; Cu, 12.72; N, 14.38; S, 6.57.

IR (Nujol mull), ν, $cm^{-1}$: 3181 w, 1614 s, 1548 s, 1271 m, 1157 w, 1129 m, 1078 w, 949 w, 883 w.

Complex **Va'** (M = Cu, X = $ClO_4$) was isolated as dark green crystals. Yield, 59%; $T_m$ > 260°C.

For $C_{20}H_{20}ClCuN_5O_6S$ anal. calcd. (%): C, 43.09; H, 3.62; Cu, 11.40; N, 12.56; S, 5.75.

Found (%): C, 43.32; H, 3.87; Cu, 10.95; N, 12.88; S, 5.52.

IR (Nujol mull), ν, $cm^{-1}$: 3196 w, 1619 s, 1548 s, 1284 m, 1238 s, 1161 m, 1108 s, 1036 m, 973 w, 877 w, 840 m, 753 w.

Complex **Va"** (M = Zn, X = Cl) was isolated as yellow crystals. Yield, 48%; $T_m$ > 260°C.

For $C_{20}H_{20}ClZnN_5O_2S$ anal. calcd. (%): C, 48.50; H, 4.07; Zn, 13.20; N, 14.14; S, 6.47.

Found (%): C, 48.74; H, 4.16; Zn, 12.95; N, 14.36; S, 6.55.

IR (Nujol mull), ν, $cm^{-1}$: 3191 w, 1612 s, 1553 s, 1287 m, 1149 w, 1127 m, 1078 w, 959 w, 876 w.

Complex **Vb** (M = Ni) was isolated as brown amorphous precipitate. Yield, 65%; $T_m$ > 260°C.

For $C_{21}H_{24}ClNiN_5O_3S$ anal. calcd. (%): C, 48.44; H, 4.78; Ni, 11.27; N, 13.45; S, 6.16.

Found (%): C, 48.28; H, 4.75; Ni, 11.43; N, 13.57; S, 6.25.

IR (Nujol mull), ν, $cm^{-1}$: 3379 w, 3168 w, 1603 s, 1546 s, 1287 m, 1233 w, 1152 w, 1112 m, 1057 w, 968 w, 873 w.

**Elemental analysis** was performed on a Perkin-Elmer 240C spectrophotometer in the microanalysis laboratory at the Southern Federal University.

**$^1$H NMR spectra** were obtained on a Varian Unity (300 MHz) spectrometer at 20°C.

**IR spectra** were recorded on a Varian Scimitar 1000 FT-IR instrument in Nujol mulls in the 400–4000 $cm^{-1}$ region.

**Electronic absorption spectra** were recorded on a Varian Cary 5000 spectrophotometer in the range of 200–800 nm.

**Experimental determination of p$K_a$.** For the potentiometric determination of p$K_a$, the ligand (0.1 mmol) was dissolved in a mixture of ethanol + water (95% ethanol solution), 0.1 M hydrochloric acid (2 mL) was added, and the resulting solution was titrated with a 0.1 M NaOH solution. All measurements were carried out at a constant ionic strength (0.1 M NaCl) with continuous stirring. The titrant was introduced from the microburette in portions of 0.02 mL. The calculation was carried out according to the formula [24]:

$$\mathrm{p}K_\mathrm{a} = \mathrm{pH} + \log\frac{(1-a)C_\mathrm{R} - [\mathrm{H}^+] + [\mathrm{OH}^-]}{aC_\mathrm{R} + [\mathrm{H}^+] - [\mathrm{OH}^-]},$$

where $a$ is the degree of neutralization; $C_R$ is the molar concentration of the ligand. When pH > 5, $[H^+]$ can be neglected both in the numerator and in the denominator, and when pH < 9, $[OH^-]$ can be neglected.

**Electron paramagnetic resonance (EPR) spectra** of the copper (II) complex were recorded on a Bruker E-680X Elexsys radiospectrometer in the X-band range at room temperature and liquid nitrogen temperature. The compound was studied both in a polycrystalline form and in a DMF solution. The parameters of the spin

Hamiltonian of the complex were determining finding the best fit between the experimental and theoretical spectra by the error functional minimization procedure:

$$F = \sum_i \left(Y_i^T - Y_i^E\right)^2 \Big/ N,$$

where $Y_i^E$ is the experimental EPR intensity array measured in constant intervals of magnetic field $H$; $Y_i^T$ are the theoretical values at the same $H$ values; and $N$ is the number of points.

The theoretical spectra were constructed by a procedure described in [25]. A sum of Lorentzian and Gaussian functions [26] was used as the line shape function. According to the relaxation theory, the line width was described by the relationship

$$\Delta H = \alpha + \beta m_I + \gamma m_I^2,$$

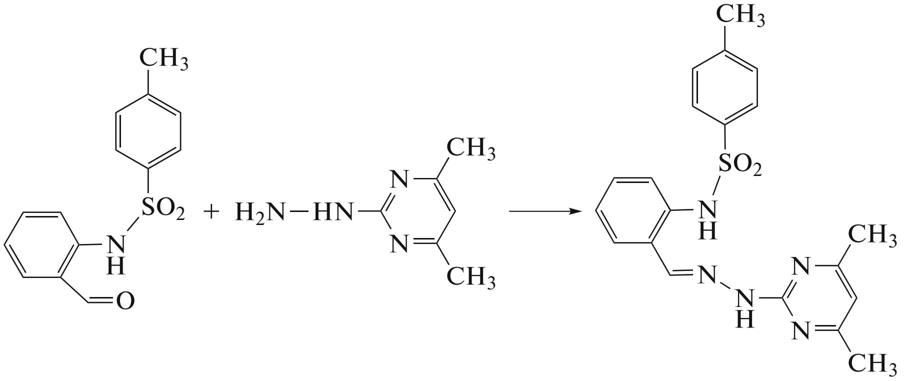
where $m_I$ is the nuclear spin projection onto the magnetic field direction; and α, β, and γ are parameters. In the course of minimization, $g$ values, hyperfine structure constants, and line widths and shapes were varied.

**Magnetic susceptibility** of polycrystalline samples was determined by the relative method of Faraday in the temperature range of 77.4–300 K. The measurements were carried out at a magnetic field strength of $7.16 \times 10^5$ A/m. $Hg[Co(CNS)_4]$ was used as the calibration standard.

**X-ray diffraction studies of complex Va" · $CH_3OH$ (M = Zn, X = Cl).** The crystal was obtained from the mother liquor. The set of diffraction reflection intensities for crystal **Va"** · $CH_3OH$ was obtained at 150 K on an Xcalibur Eos X-ray diffractometer ($MoK_\alpha$ radiation, graphite monochromator). The yellow single crystals of $C_{21}H_{24}ClZnN_5O_3S$ are monoclinic: $a$ = 13.2846(4) Å, $b$ = 11.0072(4) Å, $c$ = 15.7870(6) Å, β = 94.110(3)°, $V$ = 2302.5(1) Å$^3$, FW = 527.33, $Z$ = 4, $\rho_{calcd}$ = 1.521 g/cm$^3$, $\mu(MoK_\alpha)$ = 1.307 mm$^{-1}$, space group $P2_1/c$. The intensities of 11 567 reflections were measured in the range of $2\theta \le 58.14°$ on the ω-scan mode using a single crystal with the size of 0.30 × 0.25 × 0.20 mm. The data were corrected for absorption empirically according to the Multiscan procedure. After elimination of systematically extinguished reflections and averaging of the intensities of equivalent reflections, the working array of the measured $F^2(hkl)$ and $\sigma(F^2)$ included 6100 independent reflections, from which 4907 with $F^2 > 2\sigma(F^2)$. The structure was solved by a direct method and refined by the full-matrix least-squares method using the SHELXTL program in the anisotropic approximation for non-hydrogen atoms. Most of the hydrogen atoms were located in the difference Fourier synthesis. The coordinates and isotropic thermal parameters of all the hydrogen atoms were calculated by the least-squares method using the "rider" model [27]. In the last cycle of the full-matrix refinement, the absolute shifts of all 284 varying parameters of the structure were less than 0.001σ. The final refinement parameters were $R_1$ = 0.0382; GOOF = 1.015. After the refinement was completed, the maximum and minimum values of the difference electron density were 0.703 and –0.396 e/Å$^3$, respectively. The CIF file containing the complete information on the structure studied was deposited with the Cambridge Structural Database (CCDC no. 1487820); these data can be obtained free of charge via www.ccdc. cam.ac.uk/data_request/cif.

## RESULST AND DISCUSSION

The synthesis of ligand system **IV**, the condensation product of 2-hydrazino-4,6-dimethylpyrimidine with *o*-tosylaminobenzaldehyde, was carried out according to Scheme 1:



**IV**

**Scheme 1.**

The structure of compound **IV** was determined by elemental analysis as well as IR, $^1H$ NMR, and electronic absorption spectroscopies.

In the $^1H$ NMR spectrum of hetaryl hydrazone **IV** in DMSO-$d_6$, the following signals were recorded: two singlets from the methyl groups of the tosyl and pyrimidine fragments in the region of 2.2 and 2.3 ppm with an integrated intensity of 9H; signals from nine aromatic protons in the region of 6.7–7.8 ppm, a singlet with an intensity of 1H from the azomethine (=CH–N) proton at 8.10 ppm, and two singlets at 11.4

and 11.98 ppm from the protons of the NH groups of the hydrazine and tosylamine fragments. When $D_2O$ was added, the signals from the NH-group protons disappeared, indicating their "acidic" nature.

In the IR spectrum of compound **IV** in Nujol mull, there is an intense absorption band with a maximum at 3330 $cm^{-1}$ corresponding to the stretching vibrations of the NH groups of the sulfamide and hydrazine fragments. In the region of 1589–1497 $cm^{-1}$, a series of high-intensity signals corresponding to the stretching vibrations of the $\nu(C{=}N)$ absorption bands of the azomethine and heterocyclic fragments was recorded. Absorption bands corresponding to the symmetric and antisymmetric stretching vibrations of the $SO_2$ group are observed with the maxima at 1159 and 1280 $cm^{-1}$, respectively.

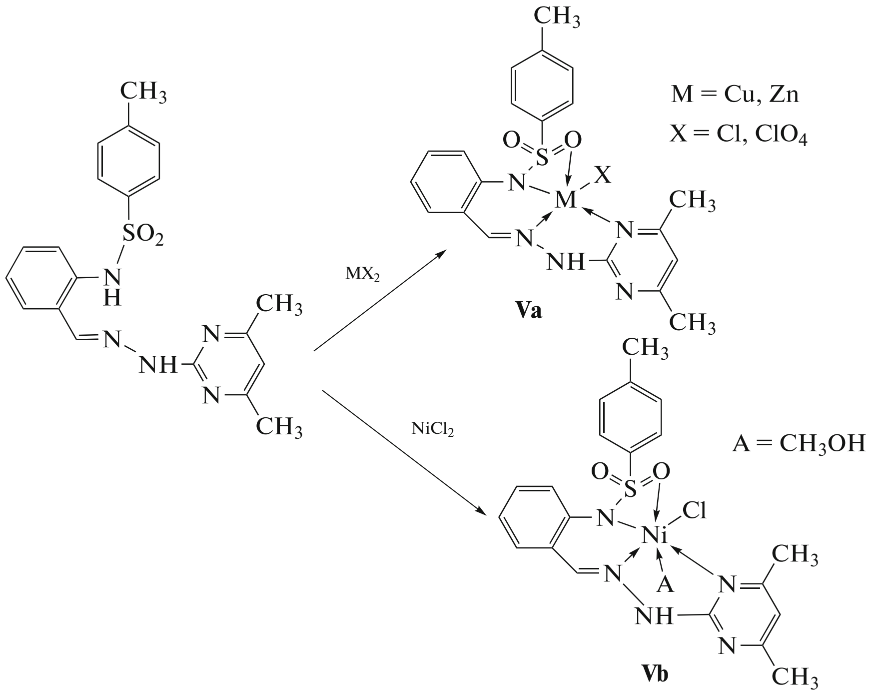
An important factor determining the complexing capacity of compound **IV** is its protolytic properties. Based on its structure, it is possible to assume the establishing of equilibrium between protonated, molecular, and ionized species depending on pH. The presence of two mobile protons from the NH groups is confirmed by NMR spectra. At the same time, due to the presence of nitrogen atoms of the azomethine group, heterocyclic, and hydrazine fragments, the protonation of the ligand can also take place to form cations in acidic media. To determine the possible protolytic equilibria and calculate their constants, a potentiometric titration of the compound in a water-ethanol solution was carried out. According to the potentiometric measurement data, two sudden changes in the titration curve are observed in the pH range from 2.5 to 10.5. The analysis of the titration curve indicates that, depending on the acidity of the medium, the hydrazone molecule can exist in the molecular, monoprotonated, and monodeprotonated forms, which corresponds to the realization of two equilibrium states:

$$H_3L^+ \rightleftarrows H^+ + H_2L,\ pK_{a1} = 2.08, \tag{1}$$

$$H_2L \rightleftarrows H^+ + HL^-,\ pK_{a2} = 9.26. \tag{2}$$

Acid-base properties in the water-ethanol solution of hydrazone were studied spectrophotometrically. This required the recording of the electronic absorption spectra in neutral, acidic, and alkaline media. In neutral and alkaline media, the long-wavelength bands in the absorption spectra of solutions practically coincide. At the same time, the absorption band in the short-wavelength region disappears in the alkaline medium, and only a small shoulder is observed in the region of 250 nm, which indicates ionization of the ligand. The shape of the spectrum of compound **IV** in an acidic medium changes significantly; two absorption bands are observed in its long-wavelength region, near 355 and 288 nm. The intensity of the short-wavelength absorption band decreases slightly as compared with the intensity of a similar band in a neutral medium. The observed spectral changes in the acidic medium indicate the protonation of compound **IV** with the formation of a cation.

When hetarylhydrazone **IV** was allowed to react with copper(II), nickel(II) or zinc(II) salts, complex compounds of the types **Va** and **Vb** were formed; their composition corresponds to the general formula [M(HL)X], where $HL^-$ is a monodeprotonated form of the ligand and X = Cl or $ClO_4$. Metal chelates were synthesized according to Scheme 2:



**Scheme 2.**

The composition and structure of the complexes obtained were determined by elemental analysis; IR, EPR, and electronic absorption spectroscopies; magnetochemistry; and X-ray diffraction analysis.

In the IR spectra of complexes **V**, the intensity of the absorption band of stretching vibrations ν(NH) decreases sharply and it is observed in the region of 3168–3329 $cm^{-1}$. We assume that this is the ν(NH) absorption band of the hydrazine fragment, while the ν(NH) absorption band of the sulfamide fragment disappears. The ν(C=N) absorption bands of the azomethine group and heterocyclic fragment are shifted slightly to the long-wavelength region and are observed at 1524–1619 $cm^{-1}$. These data confirm the coordination of the ligand with the metal ions in the monodeprotonated form through the nitrogen atoms of the azomethine group and tosylamine and pyrimidine fragments. The low-frequency shift by 10–20 $cm^{-1}$ of the absorption bands $\nu(SO_2)$ indicates the participation of the oxygen atom of the sulfo group in coordination to the metal ion.

The effective magnetic moments of the complexes with copper(II) chloride (complex **Va**) and copper(II) perchlorate (complex **Va'**) at room temperature are 1.88 and 1.92 μB, respectively; there are no changes when the temperature falls to the bp of liquid nitrogen, which indicates the absence of notable exchange interactions and the potential mononuclear structure of the complexes. To determine the structure of the chelate core, we studied EPR spectra of the copper(II) complexes.

The EPR spectra of polycrystalline samples of complex **Va** (X = Cl) at room and low temperatures are similar (Fig. 1) and are characteristic for square monomeric copper(II) complexes with oxygen-nitrogen coordination; they are described by an axially symmetric spin Hamiltonian (SH). Since the EPR spectra do not have a pronounced hyperfine structure (HFS), the hyperfine interaction constants were conditionally determined. The spin Hamiltonian can be written as follows:

$$\hat{H} = g_z\beta H_z\hat{S}_z + g_x\beta H_x\hat{S}_x + g_y\beta H_y\hat{S}_y + A\hat{I}_z\hat{S}_z + B\hat{I}_x\hat{S}_x + C\hat{I}_y\hat{S}_y,$$

where $g_z$, $g_x$, and $g_y$ are $z$, $x$, and $y$ components of the monomer $g$ tensor; $A$, $B$, and $C$ are the $z$, $x$, and $y$ components of the HFS tensor; $S_z$, $S_x$, and $S_y$ are the projections of the monomer spin operator onto the coordinate axes, $S = 1/2$; $I_z$, $I_x$, and $I_y$ are the projections of the nuclear spin operator of the monomer central atom onto the coordinate axes, $I = 3/2$. The spin Hamiltonian parameters were as follows: $g_z = 2.239$, $g_x = 2.067$, $g_y = 2.044$, $A = 7.99 \times 10^{-3}$ $cm^{-1}$, $B = 1.29 \times 10^{-3}$ $cm^{-1}$, $C = 1.29 \times 10^{-3}$ $cm^{-1}$.

The EPR spectrum of the copper(II) complex in DMF at room temperature (Fig. 2) consists of a poorly resolved HFS from the magnetic interaction of an unpaired electron with the copper atom nucleus $I_{Cu} = 3/2$.

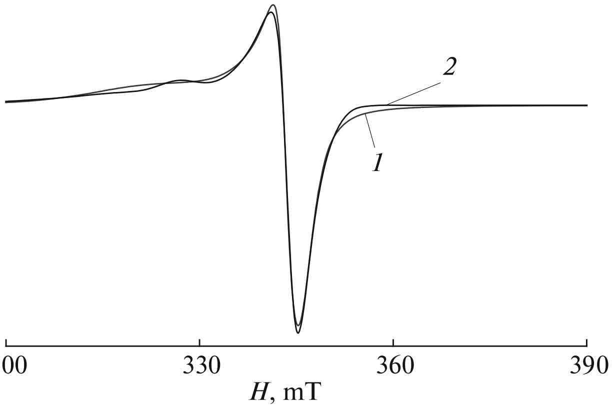


**Fig. 1.** (*1*) Experimental and (*2*) theoretical EPR spectra of polycrystalline copper(II) complex **Va** at $T = 298$ K.

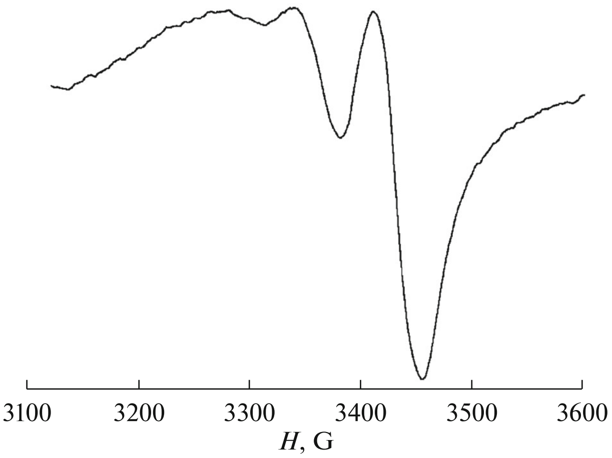


**Fig. 2.** EPR spectrum of copper(II) complex **Va** in DMF at $T = 298$ K.

The spectrum of the copper(II) complex in the solution is described by an isotropic Hamiltonian with hyperfine interaction:

$$\hat{H} = g\beta HS + A^0 IS,$$

where $g$ is the averaged component of the monomer $g$ tensor; $A^0$ is the averaged component of the HFS tensor. The spin Hamiltonian parameters were as follows: $g = 2.140$, $A_{Cu} = 70.231$ G. No additional hyperfine structure from the coordinated nitrogen atoms of the ligand is observed. A strongly distorted isotropic EPR signal indicates that the rotation of the molecule is spatially hindered.

Thus, based on the results of physicochemical studies we can assume that the coordination polyhedron around the copper(II) atom in complex **Va** is a tetragonal pyramid whose square base is formed by the

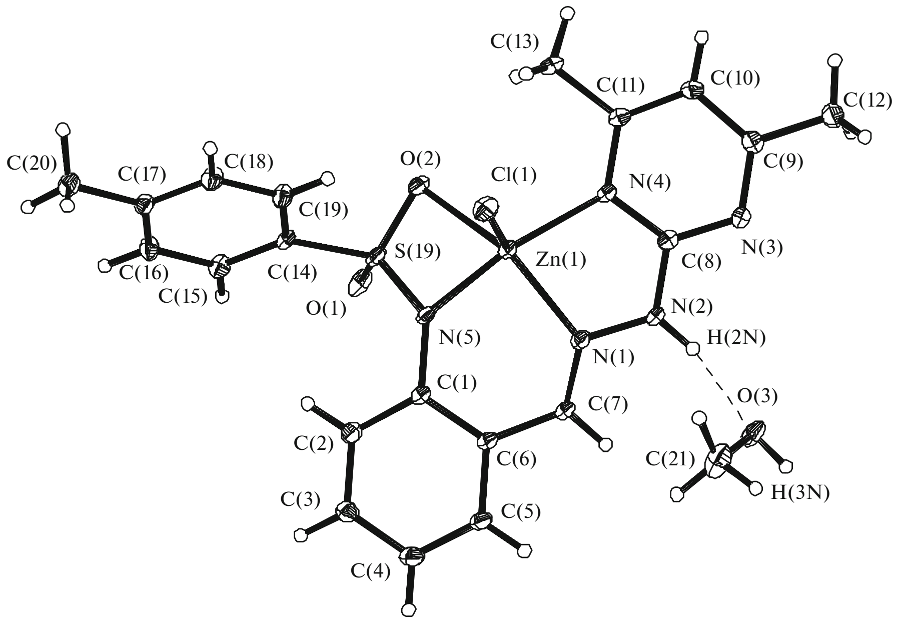


**Fig. 3.** Molecular structure of zinc(II) complex **Va"**.

$N_3O$ ligand environment, and the chlorine atom is in the axial vertex.

According to the X-ray diffraction studies of complex **Va"** · $CH_3OH$, the structure of the Zn(II) complex is similar to the structure of the Cu(II) complex **Va** discussed above. The structure of the Zn(II) complex is shown in Fig. 3. The coordinating polyhedron of the zinc atom is a tetragonal pyramid, the base of which is formed by donor nitrogen atoms of the tosyl, hydrazine, and pyrimidine moieties, and the oxygen atom of the sulfonic group of the organic ligand. These atoms are coplanar with an accuracy of 0.11 Å, the zinc atom leaves their plane by 0.82 Å. The axial position is occupied by the chlorine atom. The distance S=O to the oxygen atom involved in coordination with the zinc atom is 1.457(2) Å, while for the second oxygen atom it is significantly shorter (1.433(2) Å). The Cambridge Structural Database contains structure information on (*N*-(2-(1*H*-benzimidazol-2-yl)phenyl)-4-methylbenzenesulfonamidato)copper chloride [28], in which the nitrogen atom and one of the oxygen atoms of the $SO_2$ group similarly participate in coordination with the complexing copper atom; the distances S=N and S=O are 1.467 and 1.442 Å, respectively.

The described structure contains a methanol molecule, and the O(3)···H(2N)–N(2) hydrogen bond is realized between the oxygen atom of the solvate molecule and the hydrogen atom at the nitrogen atom (O(3)···H(2N) 1.95(2), N(2)–H(2N) 0.86(2), O(3)···N(2) 2.772(2) Å, the O(3)H(2N)N(2) angle is 159(1)°). The pairs of molecules of the complex and the solvent connected by a hydrogen bond are oriented relative to one another so that the H(3N) hydrogen atoms at the oxygen atom of the solvent of one pair are at a distance of 2.04(2) Å from the N(3) nitrogen atom of the other, forming blocks of two solvent molecules and two complexes.

The nickel(II) complex **Vb** probably has a similar coordination of donor atoms. However, three low intensity bands are unambiguously detected in the diffuse reflection electronic absorption spectra of the complex corresponding in energy to transitions $^3A_{2g} \to {}^3T_{2g}$ ($^3F$) ($\lambda_{\max}$ = 979 nm), $^3A_{2g} \to {}^3T_{1g}$ ($^3F$) ($\lambda_{\max}$ = 767 nm), and $^3A_{2g} \to {}^3T_{1g}$ ($^3P$) ($\lambda_{\max}$ = 494 nm), which indicate the octahedral coordination of the $Ni^{2+}$ ion. Thus, it can be assumed that the C.N. of the nickel ion is completed to CN = 6 due to the coordination of methanol molecule. This assumption is confirmed by the appearance of a broad absorption band in the IR spectrum of the Ni(II) complex in the 3380 $cm^{-1}$ region. In copper(II) and zinc(II) metal chelates this band is absent. The value of the effective magnetic moment of the nickel(II) complex which is 3.04 μB at room temperature correlates with the assumed octahedral coordination of the central ion in the structure of **Vb**. It is known that, for octahedrally coordinated nickel(II) complexes, the orbital contribution to the resulting magnetic moment is negligible. Therefore, the experimental values of the effective magnetic moments of these complexes have insignificant difference from the merely spin value (2.83 μB) and constitute an average of 2.9–3.2 μB. [29].

Thus, we have shown that the reaction of *o*-tosylaminobenzaldehyde dimethylpyrimidyl hydrazone acting as a monobasic $N_3O$ donor ligand with copper(II), nickel(II), and zinc(II) salts affords mononuclear complex compounds. The structure of complex compounds is also determined by the nature of the metal complex-former. It has been shown that the copper(II) and zinc(II) complexes have the structure of a tetragonal pyramid with an axial coordination of the chlorine atom, while the nickel(II) complex has the octahedral structure of the chelate core due to an additional coordination of a solvent molecule.

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