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2-(N-Tosylamino)benzaldehyde Thiobenzoylhydrazone and Its Complexes with Copper(II) and Zinc(II): Synthesis and Structures

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Abstract—2-(N-Tosylamino)benzaldehyde thiobenzoylhydrazone and its copper(II) and zinc(II) complexes with dimethylformamide (DMF) and methanol, [CuL(DMF)] and [ZnL(CH_3OH)], respectively, were synthesized. The structures of the copper(II) complex and the cyclic product of hydrazone oxidation (1,3,4-thiadiazole derivative) were determined by X-ray diffraction analysis.

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INTRODUCTION

Thio-containing hydrazine derivatives have long ago attracted researchers' attention as carriers of pronounced biological activity [1–5] and complexation ability [6–10]. Transition metal complexes with thiohydrazones are also characterized by the high biological activity [3, 5, 11]. Compounds of this class are interesting in the theoretical aspect due to the possibility of the formation of various tautomeric forms in the metal complexes. Many thiosemicarbazones of diverse carbonyl compounds are described, whereas data on thioacylhydrazones are few [12–18].

Here we report the results of the synthesis and structural study of thiobenzoylhydrazone 2-(N-tosylamino)benzaldehyde (H_2L), the product of its oxidation (HL'), and the H_2L-based Cu(II) and Zn(II) complexes, [Cu(L)(DMF)] (**I**) and [ZnL(CH_3OH)] (**II**), as well as the X-ray diffraction analysis results of compounds HL' and **I**.

EXPERIMENTAL

Commercially available thiobenzhydrazide was used for the synthesis of H_2L. N-Tosylaminobenzaldehyde was synthesized by a described procedure [19]. Solvents were purified and dried using standard procedures [20].

IR spectra were recorded on a Varian Scimitar 1000 FT-IR instrument in the range from 400 to 4000 cm^{-1} (suspensions in Nujol). ^1H NMR spectra were detected in deuterated dimethyl sulfoxide (DMSO-d_6) on a Varian Unity 300 spectrometer (300 MHz) in the Fourier impulse mode using hexamethyldisilane as an internal standard. Elemental analysis was carried out on a PerkinElmer 240C instrument at the Laboratory of Microanalysis of the Southern Federal University. The specific magnetic susceptibility of complex **I** was determined by the relative Faraday method in the temperature range from 77.4 to 300 K using $Hg[Co(CNS)_4]$ as a standard for calibration.

Synthesis of H_2L. A hot solution of 2-(N-tosylamino)benzaldehyde (5 mmol) in ethanol (10 mL) was poured to a hot solution of thiobenzhydrazide (5 mmol) in ethanol (10 mL). Glacial acetic acid (3 drops) was added to the obtained solution, and the mixture was refluxed for 3 h. A precipitate that formed was filtered off, washed with ethanol and water, dried in vacuo at ambient temperature, and recrystallized from butanol. The yield of H_2L was 1.13 g (55%), mp = 191°C.

For $C_{21}H_{19}N_3O_2S_2$

anal. calcd., %:	C, 61.59;	H, 4.68;	N, 10.26.
Found, %:	C, 61.85;	H, 4.62;	N, 10.39.

IR (ν, cm^{-1}): 3393, 3273 ν(NH), 1606 ν(C=N), 1276 $\nu_{as}(SO_2)$, 1157 $\nu_s(SO_2)$, 1355, 840 ν(C=S).

Synthesis of compound HL' was carried out by the slow crystallization of thiobenzoylhydrazone H_2L from a DMF solution in the presence of air oxygen.

For $C_{21}H_{17}N_3O_2S_2$

anal. calcd., %:	C, 61.90;	H, 4.20;	N, 10.31.
Found, %:	C, 62.07;	H, 4.12;	N, 10.44.

IR (ν, cm^{-1}): 3317 ν(NH), 1600 ν(C=N), 1278 $\nu_{as}(SO_2)$, 1155 $\nu_s(SO_2)$. ^1H NMR (DMSO-d_6), δ, ppm: 12.84 s (1H, NH), 7.98 d (2H, *J* = 7.8 Hz, CH_{arom}), 7.70 d (2H, *J* = 7.6 Hz, CH_{arom}), 7.5 m (6H, CH_{arom}), 7.23 d (1H, *J* = 7.5 Hz, CH_{arom}), 6.8 m (2H, CH_{arom}), 2.45 s (3H, CH_3).

Synthesis of I. A solution of copper(II) acetate (1 mmol) in hot methanol (20 mL) was added to a hot solution of H_2L (1 mmol) in methanol (10 mL). The reaction mixture was refluxed for 5 h. A brown precipitate was filtered off, washed with methanol, and recrystallized from DMF. The yield of **I** was 0.32 g (59%).

For $C_{24}H_{24}N_4O_3S_2Cu$

anal. calcd., %:	C, 52.98;	H, 4.45;	N, 10.30;	Cu, 11.68.
Found, %:	C, 53.06;	H, 4.32;	N, 10.47;	Cu, 11.59.

IR (ν, cm^{-1}): 1602 ν(C=N), 1264 $\nu_{as}(SO_2)$, 1136 $\nu_s(SO_2)$.

Synthesis of II. A solution of zinc(II) acetate (1 mmol) in methanol (10 mL) was added to a hot solution of H_2L (1 mmol) in methanol (10 mL). The reaction mixture was refluxed for 1 h. A yellow precipitate was filtered off, washed with methanol, and dried in vacuo at ambient temperature. The yield of **II** was 0.35 g (70%).

For $C_{22}H_{21}N_3O_3S_2Zn$

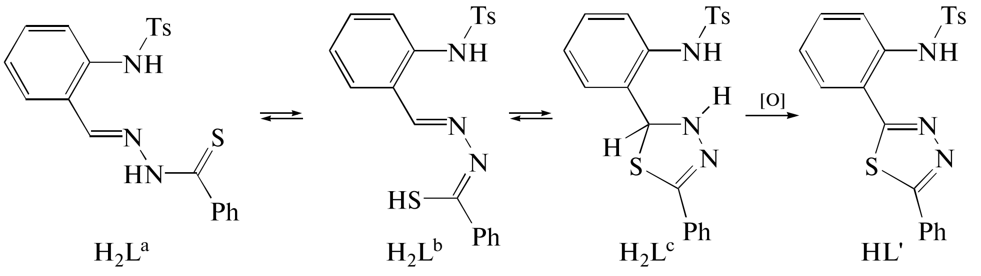
anal. calcd., %:	C, 52.33;	H, 4.19;	N, 8.32.
Found, %:	C, 52.6;	H, 4.05;	N, 8.49.

IR (ν, cm^{-1}): 3350 ν(OH), 1600 ν(C=N), 1267 $\nu_{as}(SO_2)$, 1140 $\nu_s(SO_2)$. ^1H NMR (DMSO-d_6), δ, ppm: 8.74 s (1H, CHN), 8.15 m (2H, CH_{arom}), 7.67 d (2H, *J* = 8.4 Hz, CH_{arom}), 7.48 m (4H, CH_{arom}), 7.33 d (1H, *J* = 7.8 Hz, CH_{arom}), 7.26 m (3H, CH_{arom}), 6.95 t (2H, *J* = 8.1 Hz, CH_{arom}), 4.09 m (1H, *J* = 5.4 Hz, $OH_{methanol}$), 3.16 d (3H, *J* = 5.4 Hz, CH_3), 2.28 s (3H, CH_3).

X-ray diffraction analyses of compounds HL' and **I** were carried out on Bruker SMART 1000 CCD and Bruker APEX II diffractometers (MoK_α, λ = 0.71073 Å, graphite monochromator) at 120 and 100 K, respectively. The initial array of the measured intensities was processed using the SAINT [21] and SADABS [22] programs. The structures of HL' and **I** were solved by a direct method and refined by full-matrix least squares in the anisotropic approximation for non-hydrogen atoms for F^2. All calculations were performed using the SHELXTL program package [23]. The experimental characteristics and crystallographic data for HL' and **I** are given in Table 1. Selected interatomic distances and bond angles are listed in Table 2. The coordinates of atoms and temperature factors were deposited with the Cambridge Crystallographic Data Centre (nos. 794877 (HL') and 794882 (**I**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

The structure of thiobenzoylhydrazone H_2L was determined by IR and ^1H NMR spectroscopy. Compound H_2L can exist as three tautomeric forms H_2L^{a-c} [24–26] (see the scheme). The character of the ^1H NMR spectrum of compound H_2L in DMSO-d_6 indicates that the solution contains two tautomeric forms: the open thiobenzoylhydrazone form H_2L^a and the cyclic 4-methyl-N-(2-(5-phenyl-2,3-dihydro-1,3,4-thiadiazolyl-2)phenyl)benzoic form H_2L^c in a molar ratio of ~2 : 1. The singlets from the NH protons of the tosylamine and hydrazide fragments at 11.4 and 9.8 ppm, respectively, and the singlet from the azomethine proton at 8.7 ppm were assigned to the open form of H_2L^a. Upon cyclization the signals from the NH protons of the tosylamine and thiadiazole fragments are shifted to 13.12 and 8.4 ppm, respectively. The signal at 6.8 ppm was attributed to the CH proton of the thiadiazole ring. The positions of signals from the protons of the methyl groups for the open and cyclic forms also differ, being at 2.34 and 2.41 ppm, respectively. The signals from the protons of the NH groups disappear upon the addition of D_2O, which indicates the acidic character of these protons.



Scheme.

Cyclic form H_2L^c undergoes irreversible oxidation by air oxygen to form the 1,3,4-thiadiazole derivative. Single crystals of the oxidation product (HL'), the structure of which was determined by X-ray diffraction

Table 1. Crystallographic data and experimental and refinement details for compounds HL' and **I**

Parameter	Value	
	HL'	**I**
Formula weight	407.50	544.13
Crystal size, mm	0.40 × 0.20 × 0.15	0.50 × 0.35 × 0.25
Temperature, K	120(2)	100(2)
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$
a, Å	9.287(2)	25.052(2)
b, Å	9.798(2)	7.5146(7)
c, Å	10.779(3)	26.017(2)
α, deg	88.693(5)	90
β, deg	77.669(5)	99.630(2)
γ, deg	78.257(5)	90
V, Å^3	937.9(4)	4828.7(8)
Z	2	8
ρ_{calcd}, g/cm^3	1.443	1.497
μ, mm^{-1}	0.307	1.112
F(000)	424	2248
$2\theta_{max}$, deg	56	56
Number of measured reflections	9564	25750
Number of independent reflections	4483	5794
Number of reflections with $I > 2\sigma(I)$	2569	4223
Ranges of reflection indices	$-12 < h < 12$, $-12 < k < 12$, $-14 < l < 14$	$-32 < h < 32$, $-9 < k < 9$, $-34 < l < 34$
Number of refined parameters	258	310
R_1 ($I > 2\sigma(I)$)	0.0520	0.0388
wR_2 (all reflections)	0.1046	0.0900
Goodness-of-fit (all reflections)	1.005	1.008
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.446/–0.502	0.506/–0.489

analysis (Fig. 1), were obtained by the slow crystallization of hydrazone H_2L from DMSO.

The thiadiazole cycle in an HL' molecule is nearly coplanar to the benzene ring of the benzaldehyde fragment, and the rotation angle with respect to the C(2)–C(3) bond is 3.60(13)°. The second benzene ring is turned with respect to the thiadiazole cycle around the C(1)–C(9) bond by 26.10(13)°. The N(2) atom is joined by an intramolecular hydrogen bond with the tosylamine group (N(1)–H(1N1) 0.81(2), N(1)···N(2) 1.99(2), and N(1)···N(2) 2.652(3) Å, N(1)H(1N1)N(2) 139(2)°). The tosyl group is turned out with respect to the S(1)–N(1) bond in such a way that the S(1)=O(1) and N(1)–H(1N1) bonds are coplanar and the S(1)–O(1) bond (1.436 Å) is somewhat longer than S(1)–O(2) (1.428 Å).

The reaction of thiobenzoylhydrazone H_2L with copper(II) acetate afforded complex **I**. The absence in its IR spectrum of absorption bands of the NH groups of the tosylamine and hydrazone fragments and ν(C=S) and the shift of the absorption band ν(C=N) to the low-frequency region indicate the coordination of the L^{2-} ligand in the doubly deprotonated thiol form. The low-frequency shift of absorption bands of stretching vibrations of the SO_2 group indicates a possible participation of the oxygen atom of the tosyl fragment in coordination.

The effective magnetic moment of complex **I**, being 1.88 μ_B at 293 K, remains almost unchanged

Table 2. Selected interatomic distances and bond angles in the structures of compounds HL' and **I**

Bond	d, Å	Angle	ω, deg
		HL'	
S(1)–O(2)	1.4278(19)	O(2)S(1)C(15)	107.41(12)
S(1)–O(1)	1.4359(18)	O(1)S(1)C(15)	109.46(11)
S(1)–N(1)	1.626(2)	N(1)S(1)C(15)	105.71(12)
S(1)–C(15)	1.758(3)	C(1)S(2)C(2)	87.42(13)
S(2)–C(1)	1.729(3)	C(4)N(1)S(1)	127.8(2)
S(2)–C(2)	1.729(3)	N(2)C(2)C(3)	124.3(2)
N(1)–C(4)	1.398(3)	N(2)C(2)S(2)	112.5(2)
N(2)–C(2)	1.305(3)	C(3)C(2)S(2)	123.23(19)
N(2)–N(3)	1.360(3)	N(1)C(4)C(5)	121.8(2)
N(3)–C(1)	1.303(3)	N(1)C(4)C(3)	119.0(2)
C(1)–C(9)	1.472(4)	N(3)C(1)C(9)	123.2(2)
C(2)–C(3)	1.473(4)	N(3)C(1)S(2)	113.6(2)
		I	
Cu(1)–S(1)	2.2116(7)	N(1)Cu(1)N(2)	92.54(8)
Cu(1)–N(1)	1.9419(19)	N(1)Cu(1)O(3)	96.64(8)
Cu(1)–N(2)	1.9421(19)	N(2)Cu(1)O(3)	139.78(8)
Cu(1)–O(3)	1.9891(17)	N(1)Cu(1)S(1)	158.14(6)
Cu(1)–O(2)	2.677(3)	N(2)Cu(1)S(1)	86.85(6)
		O(3)Cu(1)S(1)	97.88(5)
		N(1)Cu(1)O(2)	60.56(8)
		N(2)Cu(1)O(2)	135.76(7)
		O(3)Cu(1)O(2)	81.43(6)
		S(1)Cu(1)O(2)	105.70(4)

(1.82 μ_B) on cooling to the boiling point of liquid nitrogen, which indicates the absence of an intermolecular exchange interaction between the copper(II) ions [27].

The structure of complex **I** with the composition [Cu(L)(DMF)] was determined by X-ray diffraction analysis (Fig. 2). Hydrazone H_2L is coordinated in the doubly deprotonated thiol form, which is confirmed by the pronounced conjugation of ordinary and double bonds in the chain of atoms C(8)=N(3)–N(2)=C(7)–C(6) and the correspondence of the C(8)–S(1) interatomic distance (1.748(2) Å) to the carbon–sulfur ordinary bond.

The coordination polyhedron of the copper atom can be described as a strongly distorted trigonal bipyramid, whose axial positions are occupied by the S(1) and N(1) atoms of the L ligand (the S(1)Cu(1)N(1) angle is 158.13(7)°), while the equatorial positions are occupied by the atoms N(2) of the hydrazone fragment, O(2) of the tosyl group of the ligand L, and O(3) of the coordinated DMF molecule. The Cu(1)–O(2) bond is weak (2.6775(18) Å, which is by 0.24 Å shorter than the sum of the van der Waals radii of Cu and O) [28]. The coordination of the O(2) atom to the copper atom is confirmed by a significant distortion of the coordination polyhedron and an almost planar structure of the four-membered chelate cycle Cu(1)N(1)S(2)O(2) (the maximum deviation of the atoms from the root-mean-square plane of the cycle is ≤0.027 Å).

The five- and six-membered chelates in a molecule of complex **I** are nonplanar. The former has an envelope conformation, and the Cu(1) atom serving as a "flap" deviates from the mean plane of other four atoms by 0.2219(3) Å. The six-membered chelate has an asymmetrical sofa conformation: the N(1), C(1), C(6), and C(7) atoms lie in one plane, whereas the N(2) and Cu(1) atoms are shifted with respect to this plane by 0.144(2) and 0.5322(3) Å, respectively. The hydrogen atoms of the methyl group of the tosyl fragment are disordered over two equally populated positions, each of which corresponds to the turn of the methyl group by 60° around the C(18)–C(21) bond.

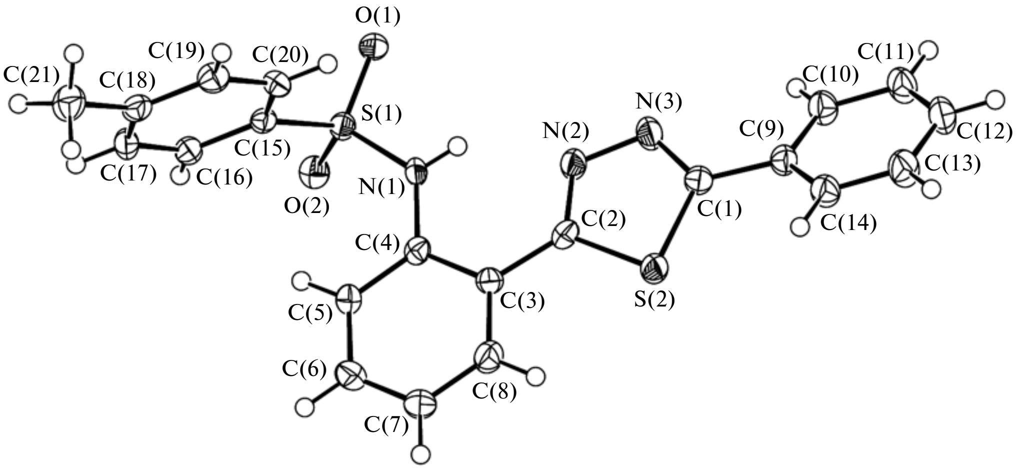


Fig. 1. Structure of compound HL' in the representation of atoms by thermal displacement ellipsoids with the 50% probability.

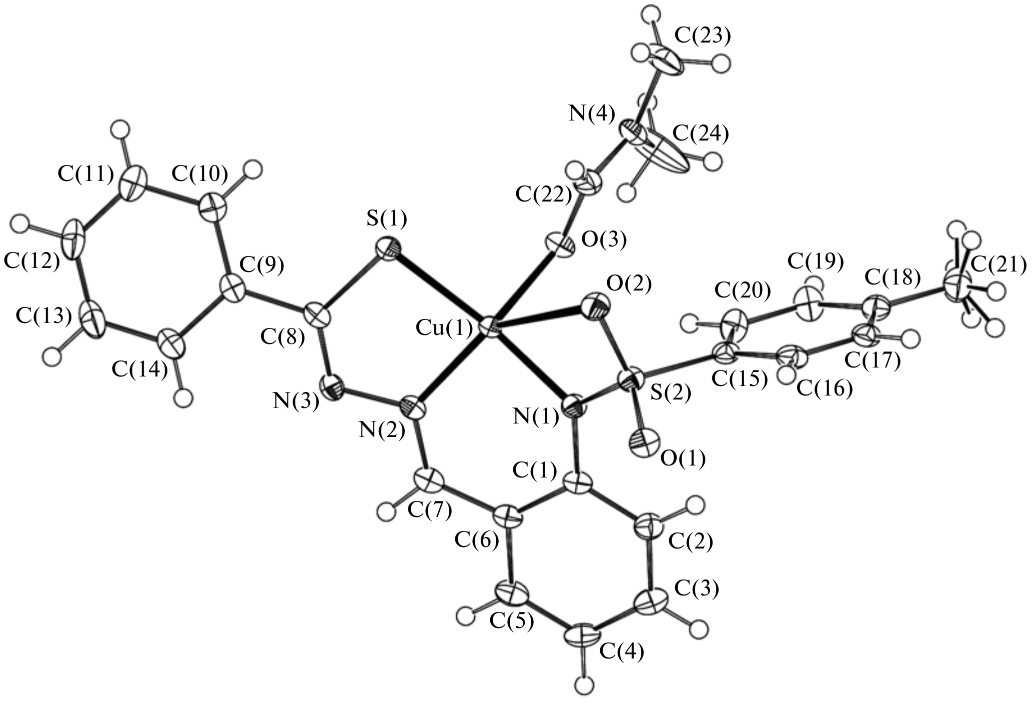


Fig. 2. Structure of complex **I** in the representation of atoms by thermal displacement ellipsoids with the 50% probability.

Complex **II** with the composition [ZnL(CH_3OH)] was obtained by the reaction of thiobenzoylhydrazone H_2L with zinc(II) acetate. Its IR spectrum is similar to that for complex **I** and indicates the coordination of the ligand in the doubly deprotonated thiol form and the possible participation in the coordination of the oxygen atom of the tosyl fragment. The broad band at 3350 cm^{-1} was assigned to vibrations of the OH group of the coordinated methanol molecule. The ^1H NMR spectrum of the complex in DMSO-d_6 contains signals from the protons of CH_3OH, whose intensities exactly correspond to one methanol molecule per L^{2-} anion [29]. These data suggest that the zinc(II) complex has a structure similar to that of the copper(I) complex, and the distinction is the coordination to the metal of the methanol molecule instead of the DMF molecule.

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