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Metal Chelates of Benzeneazo-*N*-Tosyl-2-Naphthylamine

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Abstract—New Cu(II), Co(II), and Pd(II) complexes with benzeneazo-*N*-tosyl-2-naphthylamine are synthesized by chemical and electrochemical methods and characterized by IR, ^{1}H NMR, and XRD. XRD was used to determine that two six-membered metal rings are formed in transplanar Ni(II) and Pd(II) complexes.

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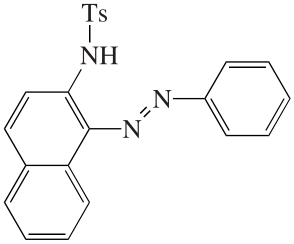
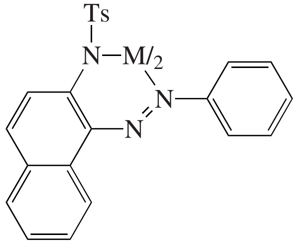
The persistent interest in the complexes of azo ligands is due to the fact that they served as the base for formulation and development of the views on chelate isomerism, i.e., the possibility of formation of metal rings with different size in one chelate molecule [1–11]. As shown by X-ray diffraction [12], the replacement of phenylamino or hydroxy groups in the ortho-position to the azo group by a tosylamino group gives rise to a structure with different (five- and six-membered) metal rings. It was of interest to consider how the replacement of the benzene ring in azo compounds by a naphthalene ring would influence the structure.

This communication presents the results of chemical and electrochemical syntheses and X-ray diffraction analysis of benzeneazo-*N*-tosyl-2-naphthylamine (LH) and metal chelates (ML_2, **I**) based on it:



LH



ML_2: M^{2+} = Cu (Ia), Ni (Ib), Co (In), Pd (Id).

EXPERIMENTAL

LH was synthesized by a reported procedure [13].

^{1}H NMR (300 MHz, $CDCl_3$) δ, ppm: 2.30 (3 H, s, CH_3), 7.14–8.01 (14 H, m, C_{Ar}–H), 8.86 (1 H, d, C_{Ar}–H_8, ^3J = 8.5 Hz), 13.38 (1 H, s, NH).

The chemical synthesis (CS) of complexes I was carried out as reported previously [6, 7] by direct reaction between the components. A solution of the hydrate of the corresponding metal acetate (Cu, Ni, Co) (1 mmol) in methanol (20 ml) was added to a solution of LH (2 mmol) in methanol (50 ml). Palladium acetate was dissolved in acetone (10 ml). The mixture was refluxed on a water bath for 1 h. The complexes that precipitated on cooling of the solutions were filtered off, washed with methanol (2 × 5 ml), and dried in a drying oven at 100°C. The crystals for X-ray diffraction were grown from a chloroform–methanol mixture (1 : 2). Yield 60–65%.

The electrochemical synthesis (ES) of complexes I was carried out, taking into account published data [14, 15], by the reaction of LH with cations formed from a sacrificial anode made of the required metal (Cu, Ni, Co). The electrochemical cell may be represented as follows:

$$\mathrm{Pt}(-)/\mathrm{MeCN}//\mathrm{LH\ (I)}/\mathrm{M}(+).$$

A solution of LH (1 mmol) in acetonitrile (25 ml) contained $(Et_4N)ClO_4$ (0.01 g) as a conducting additive. Electrosynthesis was carried out at a constant current (40 mA) and a voltage of 15 V for 2 h. The precipitates were filtered off, washed with hot methanol (3 × 10 ml), and recrystallized from a methanol–chloroform mixture (2 : 1). Yield 65–70%.

The results of elemental analysis and characteristics of compounds *I* are given in Table 1.

Id: ^{1}H NMR (300 MHz, $CDCl_3$), δ, ppm: 1.09 (6H, s, $2CH_3$), 6.61–8.06 (28 H m, C_{Ar}–H), 8.46 (2 H, d, ^3J = 8.0, C_{Ar}–H_8).

The ^{1}H NMR spectra were recorded on a Varian Unity 300 (300 MHz) instrument in the internal stabilization mode of ^{2}H resonance line in $CDCl_3$. The IR spectra were recorded on a Nicolet Impact 400 instrument (mineral oil mulls). The magnetochemical mea-

Table 1. Elemental analysis data and physical properties of LH and **Ia**–**Id**

Compound	T_{mp}, °C	Color	Molecular formula	Contents (found/calculated), %			
				C	H	N	M
LH	186–187	Red	$C_{23}H_{19}N_3O_2S$	68.70/68.81	4.52/4.77	10.42/10.47	
Ia	200–201	Brown	$C_{46}H_{36}N_6O_4S_2Cu$	CS 63.56/63.91 ES 63.62/63.91	4.37/4.20 4.28/4.20	9.32/9.72 9.82/9.72	7.01/7.35 7.45/7.35
Ib	277–278	Dark green	$C_{46}H_{36}N_6O_4S_2Ni$	CS 64.01/64.27 ES 64.25/64.27	4.40/4.22 4.31/4.22	9.85/9.78 9.84/9.78	6.92/6.83 6.75/6.83
Ic	271–272	Dark violet	$C_{46}H_{36}N_6O_4S_2Co$	CS 64.99/64.25 ES 64.12/64.257	4.55/4.22 4.35/4.22	9.77/9.26 9.32/9.26	7.01/6.85 6.76/6.85
Id	263–264	Green	$C_{46}H_{36}N_6O_4S_2Pd$	CS 60.56/60.89	4.22/4.37	9.32/9.26	11.71/11.73

surements were carried out by the Faraday method on a setup constructed at the Department of Chemistry of Rostov State University [16].

X-Ray diffraction study of LH, *Ib*, and *Id* was carried out on a SMART APEX II CCD diffractometer (MoK_α radiation, graphite monochromator, ω scan mode, $T = 100$ K). The experimental data were processed and averaged using the SAINT-*Plus* program package [17]; absorption correction was applied semiempirically using equivalent reflections [18].

The structures were solved by the direct method and refined by least squares in the anisotropic full-matrix approximation on F^2_{hkl}. The positions of hydrogen atoms (except for H(1N) in the ligand) were calculated geometrically and refined in the isotropic approximation. The main crystal data and refinement parameters are summarized in Table 2. All calculations were carried out by the SHELXTL-Plus program package [19].

RESULTS AND DISCUSSION

Metal chelates were prepared by direct reaction of components (chemical synthesis) and by electrochemical synthesis according to the following scheme

$$\mathrm{I} + \mathrm{MAc_2} \cdot n\mathrm{H_2O} \xrightarrow[\text{chemical synthesis}]{\text{MeOH}} \mathrm{II} \xleftarrow[\text{electrochemical synthesis}]{\mathrm{CH_3CN}} \mathrm{I} + \mathrm{M}^0.$$

According to elemental analysis data, complexes **I** have the composition ML_2.

Table 3 presents the stretching frequencies for LH and for complexes ML_2 (**Ia**–**Id**) and their effective magnetic moments (μ_{ef}). On going from azo compounds to complexes **Ia**, **Id**, ν(NH) bands disappear from the IR spectra, which is indicative of replacement of the proton in the ligand amino group by a metal ion. This is confirmed by ^1H NMR data. The ^1H NMR spectrum of LH exhibits a singlet from the NH group proton at 13.88 ppm, which disappears for complex **Id**, while the signals of the aromatic protons shift upfield. These spectral characteristics of complexes attest to their chelate structure.

Copper (**Ia**) and cobalt (**Ic**) complexes are paramagnetic (Table 3). The μ_{ef} value (4.21 μ_B) of the cobalt complex attests to a tetrahedral structure of the coordination unit. The nickel complex (**Ic**) is diamagnetic, which may imply its planar structure. The value $\mu_{ef} = 2.0$ μ_B for **Ia** corresponds to the effective magnetic moment of one unpaired electron including the orbital contribution.

The complexes obtained by electrosynthesis have similar magnetic and spectral characteristics.

The X-ray diffraction data of nickel (**Ib**) and palladium (**Id**) complexes (Figs. 1, 2) confirmed the conclusions based on spectroscopic data.

According to X-ray diffraction, complexes **Ib** and **Id** have similar structures with *trans*-planar N_4 coordination with *trans*-arrangement of donor nitrogen atoms. Two benzeneazo-*N*-tosyl-2-naphthylamine molecules function as monodeprotonated bidentate N,N-ligands forming two identical six-membered metal rings with Ni^{2+} and Pd^{2+} ions. In the crystal both

Table 2. Selected crystal data and X-ray experiment details for LH, **Ib**, and **Id**

Parameter	Value		
	LH	Ib	Id
Molecular formula	$C_{23}H_{19}N_3O_2S$	$C_{46}H_{36}N_6NiO_4S_2$	$C_{48}H_{38}Cl_6N_6O_4PdS_2$
M	401.47	859.64	1146.06
System	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/n$	$\hat{e}\bar{1}$
Z(Z')	4(1)	2(0.5)	1(0.5)
a, Å	7.8815(4)	11.2230(8)	9.9859(4)
b, Å	20.8055(11)	16.3089(12)	11.5365(5)
c, Å	12.1553(7)	11.7940(8)	12.1976(5)
α, deg	90.00	90.00	98.4210(10)
β, deg	100.769(5)	106.343(2)	104.0800(10)
γ, deg	90.00	90.00	111.2540(10)
V, $Å^3$	1958.1(4)	2071.5(3)	1226.73(9)
ρ(calcd), g cm^{-3}	1.362	1.378	1.551
μ, cm^{-1}	1.9	6.21	8.41
F(000)	840	892	580
$2\theta_{max}$, deg	58	59.2	60
The number of measured reflections	23714	25943	32252
The number of independent reflections	5213	5819	7157
The number of reflections with $I > 2\sigma(I)$	4091	3958	6794
The number of refined parameters	267	268	308
R_1	0.0423	0.0461	0.0236
wR_2	0.1162	0.1173	0.0651
GOOF	0.979	0.989	1.052
$\Delta\rho_{max}/\Delta\rho_{min}$, *e* $Å^{-3}$	0.514/–0.429	0.533/–0.528	0.890/–0.745

Table 3. Stretching frequencies (ν, cm^{-1}) and effective magnetic moment (μ_{ef}) of benzeneazo-*N*-tosyl-2-naphthylamine and its complexes **Ia–Id**

Compound	M	ν, cm^{-1}				μ_{ef}, μB
		ν(N–H)	$\nu_{as}(SO_2)$	$\nu_s(SO_2)$	ν(N=N)	
LH	H	3100–3240	1308 w	1130 m	1421 w	
Ia	Cu		1290 s	1090 s	1410 w	2.00
Ia*	Cu		1291 s	1090 s	1410 w	2.00
Ib	Ni		1290 s	1092 s	1421 w	Diamagnetic
Ib*	Ni		1291 s	1092 s	1421 w	″
Ic	Co		1306 w 1283 m	1090 s	1400 w	4.21
Ic*	Co		1306 w 1283 m	1090 s	1400 w	4.21
Id	Pd		1290 m	1092 s	1420 w	Diamagnetic ″

* Obtained by electrochemical method.

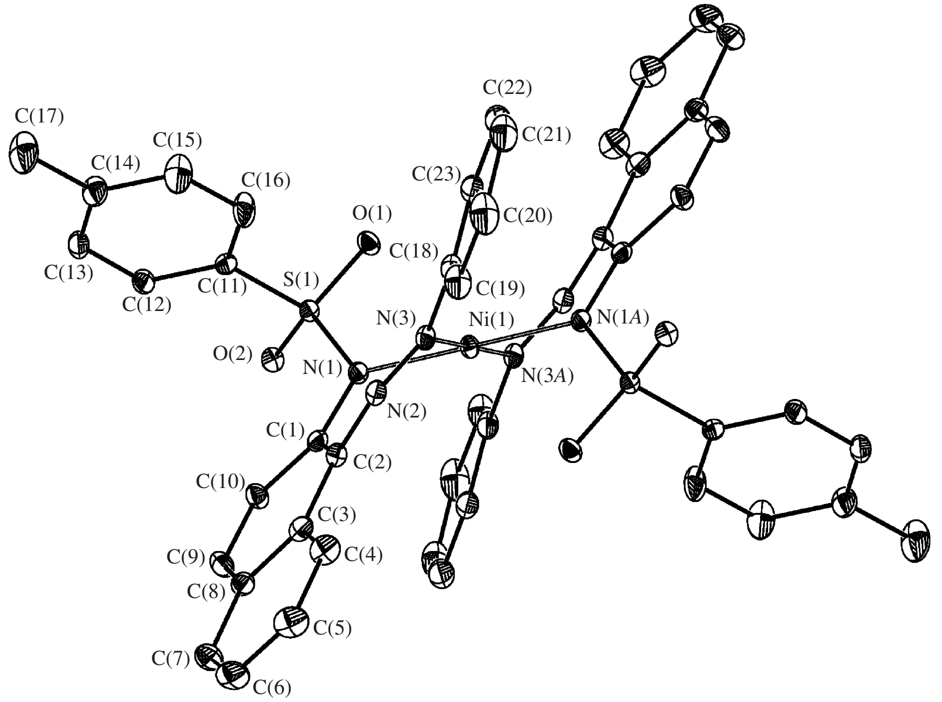


Fig. 1. Structure of complex **Ib** (thermal ellipsoids are given with 50% probability; the same is in Figs. 2 and 3). The hydrogen atoms are omitted.

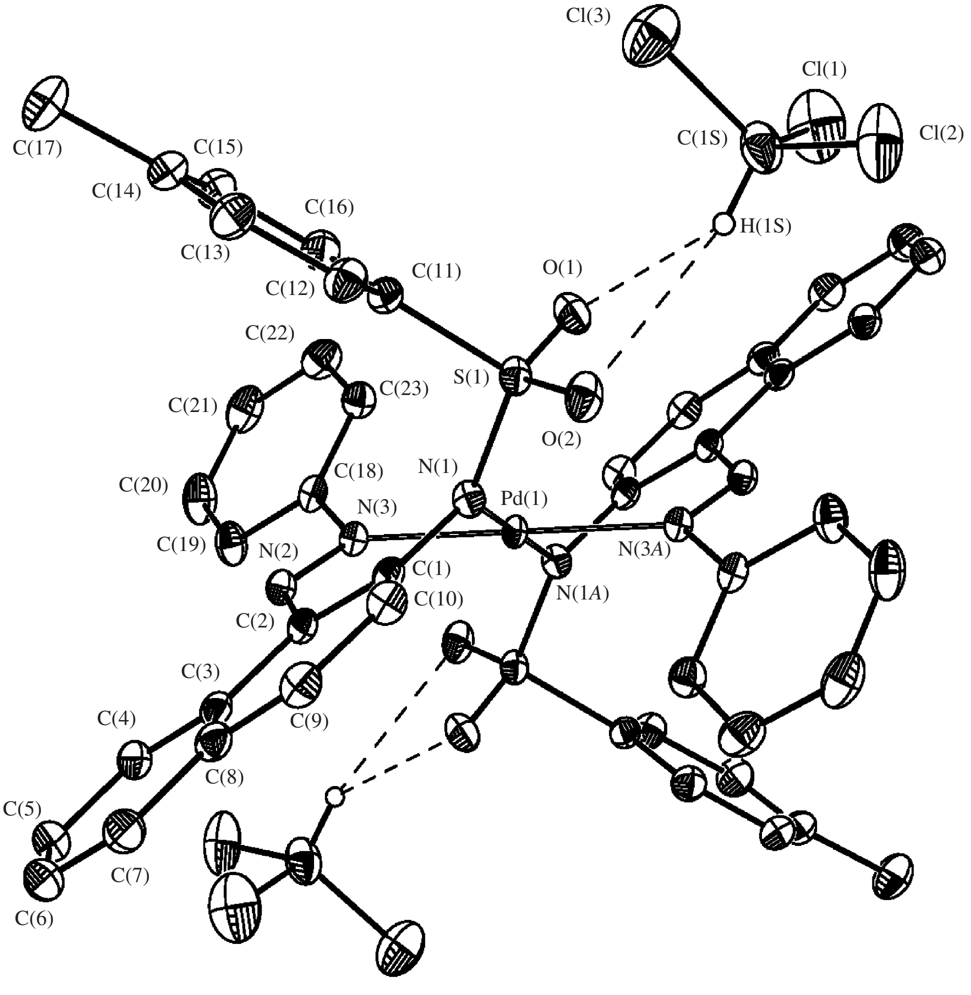


Fig. 2. Structure of complex **Id**. The hydrogen atoms are omitted.

Table 4. Selected bond lengths and bond angles in structures LH, **Ib**, and **Id**

Bond	*d*, Å		
	LH	Ib	Id
M–N(1)		1.882(2)	2.013(1)
M–N(3)		1.895(2)	2.022(1)
S(1)–O(2)	1.434(1)	1.435(2)	1.443(1)
S(1)–O(1)	1.436(1)	1.436(2)	1.445(1)
S(1)–N(1)	1.628(1)	1.628(2)	1.629(1)
S(1)–C(11)	1.757(1)	1.764(2)	1.763(1)
N(1)–C(1)	1.392(2)	1.385(3)	1.384(1)
N(2)–N(3)	1.268(2)	1.268(2)	1.266(1)
N(2)–C(2)	1.402(2)	1.382(3)	1.381(1)
N(3)–C(18)	1.423(2)	1.441(3)	1.434(1)
C(1)–C(2)	1.409(2)	1.404(3)	1.414(2)
Angle	ω, deg		
N(1)MN(3A)*		94.52(8)	97.11(4)
N(1)MN(3)		85.48(8)	82.89(4)
O(2)S(1)O(1)	119.71(7)	117.74(9)	116.89(6)
O(2)S(1)N(1)	110.61(7)	112.71(9)	113.35(6)
O(1)S(1)N(1)	103.39(7)	104.88(9)	104.90(5)
O(2)S(1)C(11)	108.41(7)	107.6(1)	107.81(6)
O(1)S(1)C(11)	108.36(7)	108.8(1)	108.97(6)
N(1)S(1)C(11)	105.42(7)	104.3(1)	104.16(6)
C(1)N(1)S(1)	129.63(11)	121.7(2)	121.36(8)
C(1)N(1)M		117.8(1)	118.79(8)
S(1)N(1)M		120.2(1)	119.63(6)
N(3)N(2)C(2)	117.51(13)	119.9(2)	121.7(1)
N(2)N(3)C(18)	115.39(13)	114.0(2)	113.8(1)

* The atoms were obtained from basis atoms by symmetric transformations $1 - x + 1, -y + 1, -z + 1$ and $1 - x, -y, -z + 1$ for **Ib** and **Id**, respectively.

complexes have C_i symmetry, the molecules occupy specific positions with the symmetry center coinciding with the metal atom. Complex **Id** is a crystal solvate with two $CHCl_3$ molecules, whereas **Ib** crystallizes without solvation molecules.

A comparison of the key geometric parameters of complexes **Ib** and **Id** has shown that their structures are almost identical (Table 4). Thus in both **Ib** and **Id**, the M–N(3) distance is somewhat shorter than M–N(1). The six-membered metal rings MN_3C_2 are nonplanar having a *twist*-boat conformation. Slight deviations from the ring plane are observed in both complexes for the metal atom (1.02 Å for Ni(1) and 1.04 Å for Pd(1)) and for the N(2) atom (0.24 and 0.23 Å, respectively) which deviate from the mean planes (the mean root-square deviations are 0.02 and 0.01 Å) to the opposite directions. The folding angle along the N(1)–N(3) line is 45.9° for **Ib** and 48.4° for **Id**. In both complexes, the phenyl group is not conjugated with the lone pair of N(3) (the C(19)C(18)N(3)N(2) torsion angles are 29.8° and 33.6°, respectively), which is apparently due to steric repulsion between the SO_2 group and the neighboring ligand.

The insignificant elongation of the S–O bonds in **Id** is obviously related to the presence of C–H···O interactions with a solvation $CHCl_3$ molecule. The hydrogen atom H(1S) is involved in the formation of bifurcated unsymmetrical H-bond with the O(1) and O(2) oxygen atoms (H(1S)···O(1) 2.19 Å, C(1S)H(1S)O(1) 134°, H(1S)···O(2) 2.56 Å, C(1S)H(1S)O(1) 149°) (Fig. 2).

Note that the naphthalene fragment in **Ib** is somewhat distorted. The deviations of C(1) and C(10) atoms from the plane through the other ring atoms are 0.107 and 0.08 Å, whereas in complex **Id** the maximum deviation observed for C(1) is only 0.04 Å. The ring distortion and, as a result, some shortening of the C(1)–C(2) bond in **Ib** (Table 4) is apparently caused by steric repulsion of the substituents at N(1) and N(3*A*) atoms in both complexes, the repulsion being stronger for shorter M–N bonds.

To analyze how the metal coordination affects the bond length distribution in the ligand, X-ray diffraction of LH was carried out. The structure is shown in Fig. 3.

An abnormally strong intramolecular H-bond N(1)–H(1N)···N(3) (N(1)···N(3) 2.559(1) Å; N(1)H(1N)···N(3) 139°) is formed in the ligand with closure of a six-membered ring. According to the Cambridge Crystallographic Data Centre, the distance between the hydrogen donor and acceptor in six-membered H-bonded rings in structures of this type usually exceeds 2.6 Å. Only the structure of 2,4-bis(phenylazo)aniline [20] with N···N distance shorter (2.532 Å) than that in LH is known.

In LH, unlike the metal rings in **Ib** and **Id**, the H-bonded ring is planar. Moreover, the plane of the phenyl group at N(3) is coplanar to the H-bonded ring, which in turn decreases the N(3)–C(18) bond length to 1.423(2) Å.

However, the bond lengths and bond angles in the N(1)C(1)C(2)N(2)N(3) fragment in LH and in complexes **I** almost do not differ (Table 4). The greatest change is observed for the N(2)–C(2) bond, which is probably due to deviation of N(2) from the ring plane in the complexes (see above). Thus, the effects of M(II) coordination and strong H-bond in LH on the bond length distribution in the ring are similar. Moreover, the slight variation of the bond lengths upon ring distortion

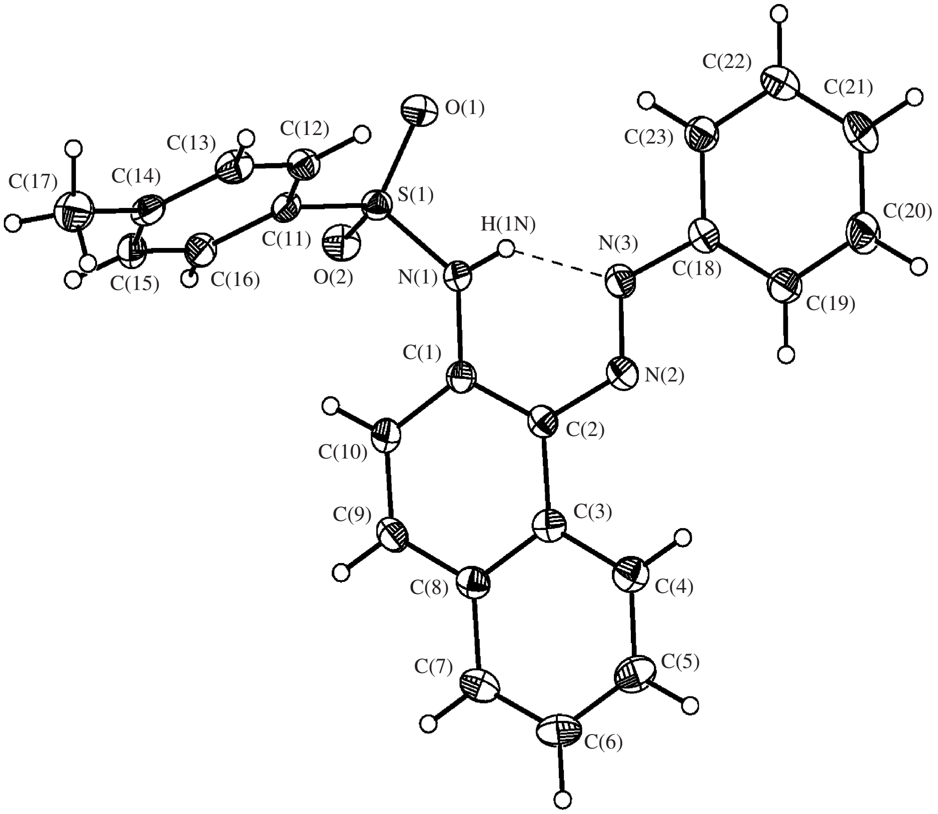


Fig. 3. Structure of the ligand LH.

indicate that the geometric parameters in this system depend little on the degree of flattening of metal rings.

As shown previously [21–23], similar tosylaminoazo compounds and their metal complexes are effective additives to lubrication oils improving lubricating properties (loading, antiwear, and antifriction characteristics). Therefore, compounds prepared and described in this work may prove useful for the development of new effective lubricating compositions for various industry branches.

Thus, the X-ray diffraction studies of **Ib** and **Id** showed that replacement of the benzene ring by a naphthalene ring in the azo compound LH results in structures with two six-membered metal rings rather than a five- and a six-membered ring [6, 7]. We would like to emphasize in this connection that back in 1967, Price noted the possibility of formation of two-membered metal rings in azoamino complexes [24]. This fact is included in the classical handbook [25], although it was not confirmed by X-ray diffraction either in the study cited [24] or in other X-ray diffraction works [10, 12].

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REFERENCES

1. Dyachenko, O.A., Atovmyan, L.O., and Aldoshin, S.M., *J. Chem. Soc., Chem. Commun.*, 1975, no. 2, p. 105.
2. Kogan, V.A., Kharabaev, N.N., Osipov, O.A., and Kochin, S.G., *Zh. Strukt. Khim.*, 1981, vol. 22, no. 1, p. 126.
3. Kogan, V.A., Kochin, S.G., Antsyshkina, A.S., et al., *Mendeleev Commun.*, 1997, p. 239.
4. Kochin, S.G., Antsyshkina, A.S., Sadikov, G.G., et al., *Dokl. Akad. Nauk*, 1997, vol. 355, no. 6, p. 777 [*Dokl.* (Engl. Transl.), vol. 355, no. 6, p. 178].
5. Kogan, V.A., Kochin, S.G., Antsyshkina, A.S., et al., *Mendeleev Commun.*, 1999, p. 82.
6. Garnovskii, A.D., Vasil’chenko, I.S., and Garnovskii, D.A., *Sovremennye Aspekty Sinteza Metallokompleksov. Osnovnye Ligandy I Metody* (Modern Aspects of the Synthesis of Metal Complexes. Key Ligands and Methods), Rostov-on-Don: LaPO, 2000, vol. 355.

7. *Synthetic Coordination and Organometallic Chemistry*, Garnovskii, A.D. and Kharisov, B.I., Eds., New York: Marcel Dekker, 2003.
8. Kogan, V.A. and Shcherbakov, I.N., *Ross. Khim. Zh.*, 2004, vol. 48, no. 1, p. 69.
9. Kogan, V.A., Antsyshkina, A.S., Sadikov, G.G., et al., *Zh. Neorg. Khim.*, 2004, vol. 49, no. 12, p. 1988 [*Russ. J. Inorg. Chem.* (Engl. Transl.), vol. 49, no. 12, p. 1844].
10. Garnovskii, A.D. and Vasil'chenko, I.S., *Usp. Khim.*, 2005, vol. 74, no. 3, p. 211.
11. Kogan, V.A., Lyubchenko, S.N., Shcherbakov, I.N., et al., *Koord. Khim.*, 2005, vol. 31, no. 8, p. 563 [*Russ. J. Coord. Chem.* (Engl. Transl.), vol. 31, no. 8, p. 533].
12. Aldoshin, S.M., D'yachenko, O.A., and Atovmyan, L.O., *Koord. Khim.*, 1980, vol. 6, no. 6, p. 954.
13. Witt, O.N. and Schmitt, G., *Ber. Dtsch. Chem. Ges.*, 1894, vol. 27, no. 3, p. 2370.
14. Garnovskii, A.D., Antsyshkina, A.S., Sadikov, G.G., et al., *Zh. Neorg. Khim.*, 1998, vol. 43, no. 11, p. 1852 [*Russ. J. Inorg. Chem.* (Engl. Transl.), vol. 43, no. 11, p. 1723].
15. Kharisov, B.I., Garnovskii, A.D., and Tsivadze, A.Yu., *J. Coord. Chem.*, 2007, vol. 60, p. 435.
16. Kurbatov, V.P., Khokhlov, A.V., Garnovskii, A.D., et al., *Koord. Khim.*, 1979, vol. 5, no. 3, p. 351.
17. Bruker SMART. Bruker Molecular Analysis Research Tool. Version 5.059, Madison (WI, USA), Bruker AXS, 1998.
18. Sheldrick, G.M., *SADABS. Version 2.01. Bruker/Siemens Area Detector Absorption Correction Program*, Madison (WI, USA): Bruker AXS, 1998.
19. Sheldrick, G., *M SHELXTL Version 5.10. Structure Determination Software Suite*, Madison (WI, USA): Bruker AXS, 1998.
20. Buzykin, B.I., Sorokin, M.Yu., Fassakhov, R.Kh., et al., *Zh. Obshch. Khim.*, 1998, vol. 68, no. 12, p. 1968 [*Russ. J. Gen. Chem.* (Engl. Transl.), vol. 68, no. 12, p. 1885].
21. Barchan, G.P., Chigarenko, G.G., Kogan, V.A., et al., USSR Inventor's Certificate No. 810778, *Byull. Izobret.*, 1981, no. 9.
22. Barchan, G.P., Chigarenko, G.G., Bolotnikov, V.S., et al., USSR Inventor's Certificate No. 910741, *Byull. Izobret.*, 1982, no. 9.
23. Burlov, A.S., Uraev, A.I., Lysenko, K.A., et al., *Koord. Khim.*, 2006, vol. 32, no. 9, p. 714 [*Russ. J. Coord. Chem.* (Engl. Transl.), vol. 32, no. 9, p. 686].
24. Price, R., Metal Complexes of Azo-Dyestuffs, *J. Chem. Soc., A*, 1967, no. 12, p. 2048.
25. Price, R., *The Chemistry of Synthetic Dyes*, Venkataraman, K.M., Ed., New York: Academic, vol. 3.