

Novel *N*-benzimidazolyl-2-thione *o*-tosylamino(hydroxy)azomethinic tautomeric ligand systems and their metallochelates

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Dedicated to Prof. V.I. Minkin on the occasion of his 70th birthday

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Abstract

Novel ligand systems –azomethinic derivatives of 1-amino-3-methyl-1,3-dihydrobenzimidazole-2-thione and *o*-tosylamino(hydroxy)benzaldehydes – are synthesized as a result of a multistage procedure and are evaluated. Study of the coordination activity of these compounds has shown that they form complexes ML_2 with transition *d*-elements containing MN_4S_2 and $MN_2O_2S_2$ coordination units in solid and in solution. Electrospray mass-spectrometry results show the possibility of formation of M_2L_2 and M_2L_3 complexes in the vapor phase.

Keywords: 1-Amino-3-methyl-1,3-dihydrobenzimidazole-2-thione, azomethines, metallochelates, electrospray mass-spectrometry

Introduction

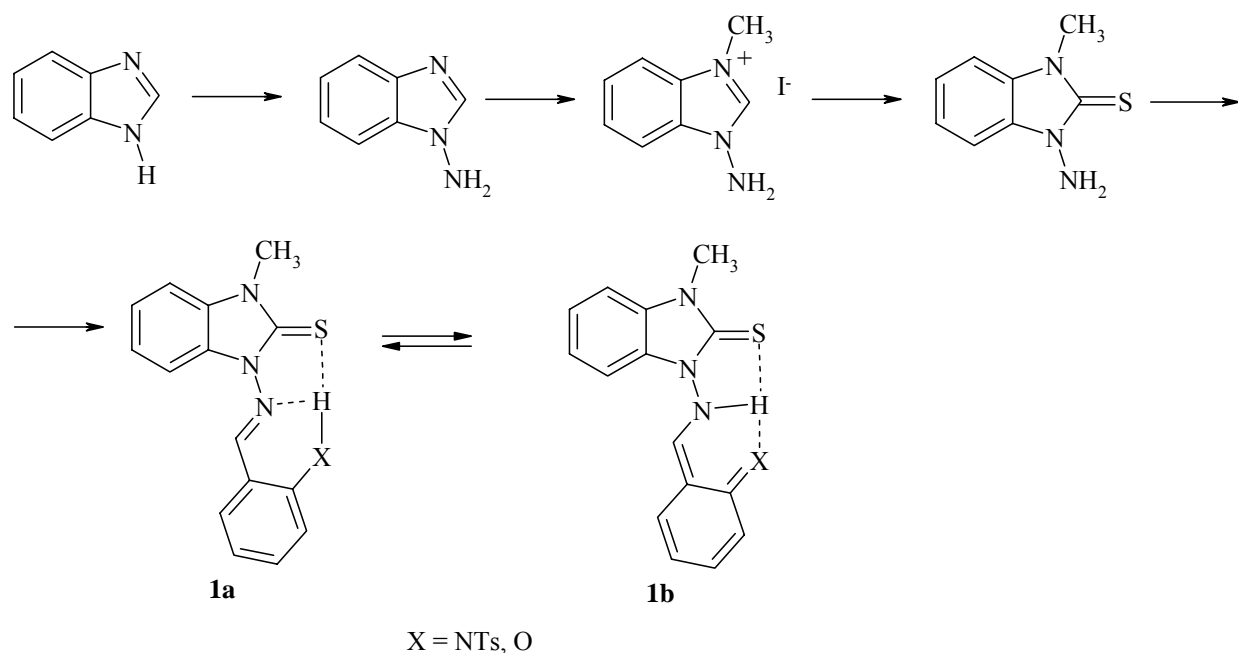
Tautomerism ¹⁻⁴ and complexation ⁵⁻⁹ are prominent aspects of Prof. V.I. Minkin's scientific activity. Representations of various types of elementotropic tautomeric processes, including participation of azomethine andazole derivatives have been advanced, as well as experimentally and theoretically proven by him. ¹⁻⁵

V.I. Minkin has contributed significantly to the development of new synthetic methods of chalcogen-azomethinic chelates,⁵ research of their stereochemistry,⁵ stereodynamics,^{6, 7} a photo-⁸ and quantum⁹ chemistry.

The present article is devoted to the synthesis and investigation of the fine structure of previously undescribed type of tautomeric systems **1** (Scheme 1) - derivatives of 1-amino-2-thiobenzimidazole, containing an *o*-tosylamino(hydroxy)azomethinic fragment at the pyrrole nitrogen atom, and their metallochelates **2**.

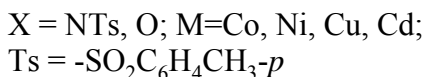
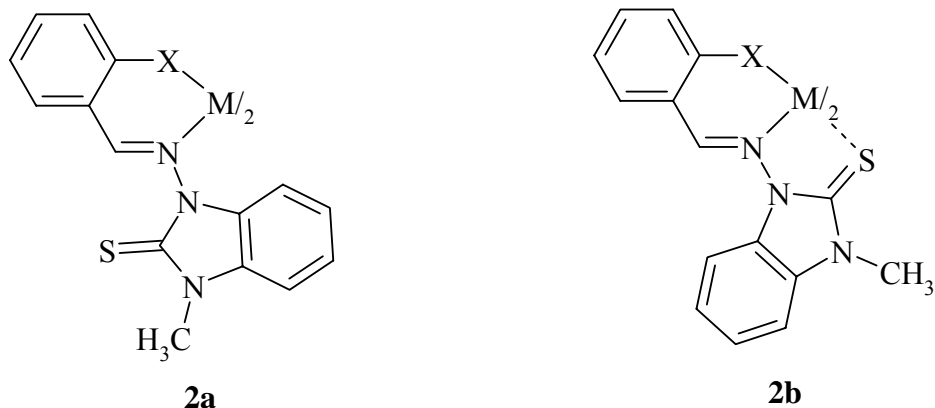
Results and Discussion

The synthesis of type **1** compounds has been carried out following the transformations^{10, 11} described in Scheme 1.



Scheme 1. Synthesis of N-benzimidazolyl-2-thione containing azomethines.

Metallochelates **2** are obtained from boiling methanol solutions of compounds **1** and metals acetates.¹²



^1H NMR analysis (solution in $\text{DMSO}-d_6$) (see Experimental Section) established, that type **1** ligands (X = NTs, O) exist in tautomeric form **1a**. The results obtained are in a good agreement with the literature data specifying primary realization of oxo(thio)tautomers of considered derivatives with an azole fragment^{4, 13} and iminophenolic tautomeric forms for *o*-tosylamino(hydroxy)azomethines.^{1-3, 14-16}

Metallocomplexes, gained on the basis of **1**, by analogy with chelates of 2-amino(oxo-, thio)azoles¹⁷⁻²⁶ and *o*-amino(hydroxy-, mercapto)azomethines^{5, 16, 27} could be represented by formulas **2a** and **2b**. Both of these types are possible considering the elemental analysis data. Electrospray mass-spectrometry indicates mononuclear chelates with structure L_2M (LH - ligand).²⁸

Formations of chelate structures are confirmed by comparison of IR spectra of ligands **1** and complexes **2**. Thus, disappearance of the signals of the HNTs and OH groups (3300 cm^{-1} region) and lower frequencies of azomethinic C=N group (by $15\text{-}25\text{ cm}^{-1}$ from 1597 cm^{-1}) and C=S (by $25\text{-}60\text{ cm}^{-1}$ from 1186 cm^{-1}) are observed. The last fact confirms an octahedral structure **2b** in the described mononuclear complexes. This conclusion is also confirmed by magneto chemical data (**2**: X = NTs, M = Co, $\mu_{\text{eff}} = 4.63\text{ M.B.}$; M = Ni, $\mu_{\text{eff}} = 2.87\text{ M.B.}$) and electron spectroscopy results (**2**: X = NTs, M = Ni; bands at 14580 cm^{-1} ($\epsilon = 25\text{ l/mol}\cdot\text{cm}$) and 9500 cm^{-1} ($\epsilon = 47\text{ l/mol}\cdot\text{cm}$), corresponding to the transitions $^3\text{A}_{2g} \rightarrow ^3\text{T}_{2g}$ and $^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g}$ (F) of nickel(2+) ion in the symmetry O_h). However, the absorption of the C=S group represented by double set of bands in the IR spectrum of copper chelates (**2**: X = NTs, O; M = Cu) may be caused by a pentacoordinated structure with participation of only one sulfur atom of two ligands in the coordination.

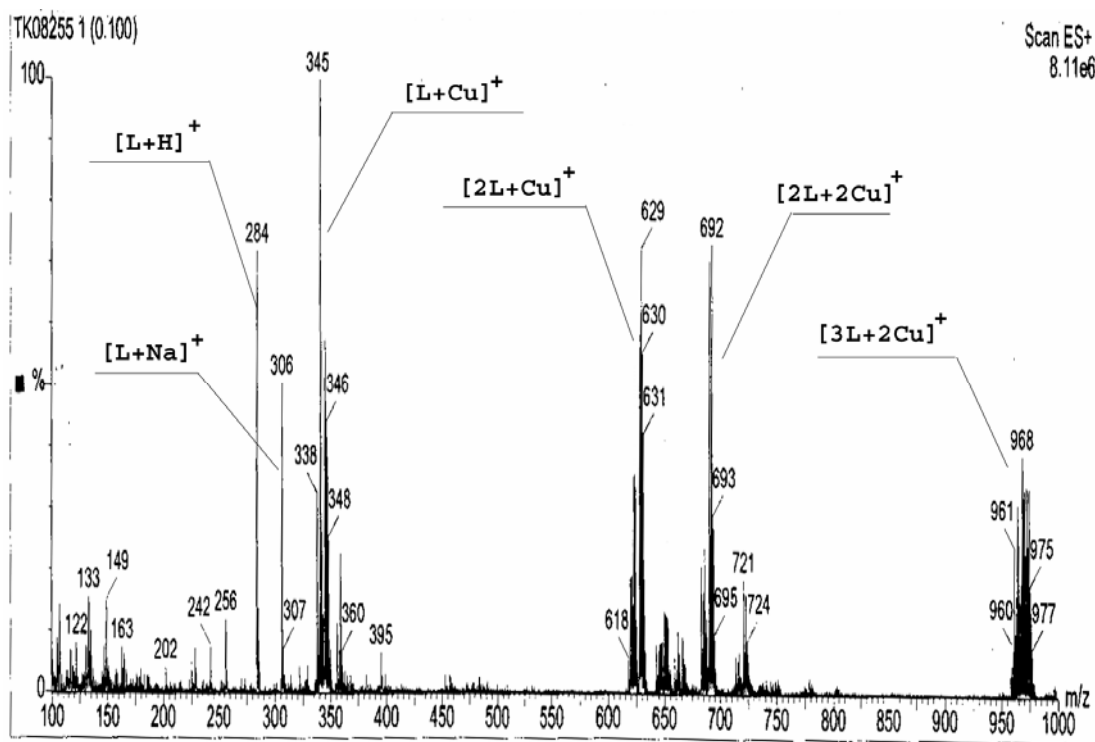
Electrospray mass-spectrometry research has not only allowed²⁸ to detect complexes of ML_2 structure, but also to establish the formation of binuclear complexes for all metallochelates of copper, and in some cases for nickel and cadmium. Besides in electrospray mass-spectra, the ions containing three ligands and two atoms of metal – M_2L_3 , were also detected (Table 1).

Table 1. Peaks containing in mass-spectra of ligands **1** and their complexes **2**

X = NTs	ML ₂ (m/z; int. %)	M ₂ L ₂ (m/z; int. %)	M ₂ L ₃ (m/z; int. %)
Ni		ML ⁺ ion only	
Cu	935; 10	998; 20	
Cd	985; 35		

X = O	ML ₂ (m/z; int. %)	M ₂ L ₂ (m/z; int. %)	M ₂ L ₃ (m/z; int. %)
Co	624; 6		964; 90
Ni	623; 12		962; 45
Cu	629; 70	692; 70	972; 45
Zn	651 (+Na); 90		974; 30
Cd	679; 6	793; 15	1072; 50

The ions mentioned above can be demonstrated by the mass-spectrum (fig. 1) of copper complex **2** (X = O, M = Cu).

**Figure 1.** Mass-spectrum of copper complex **4**.

As we can see in the spectrum (Fig. 1) alongside with the presence of the molecular ion (m/z = 629), there is a set of peaks corresponding to M₂L₂ and M₂L₃ binuclear complexes structures.

The structure of a binuclear M_2L_2 complex can be presented by formula **3**, expanding the number of active coordination centers ($X=NTs, O$).

In similar binuclear complexes, ligands behave as tetradentates which is in a good agreement with literature data, showing an opportunity of participation in coordination interaction of both free electron pairs of sulfur and of the thio-containing azole ligands.¹⁷⁻²⁶

Binuclear structures **4** containing three ligands, can probably be explained by formation of adducts with participation of coordinatively nonsaturated metals in binuclear structures **3**.

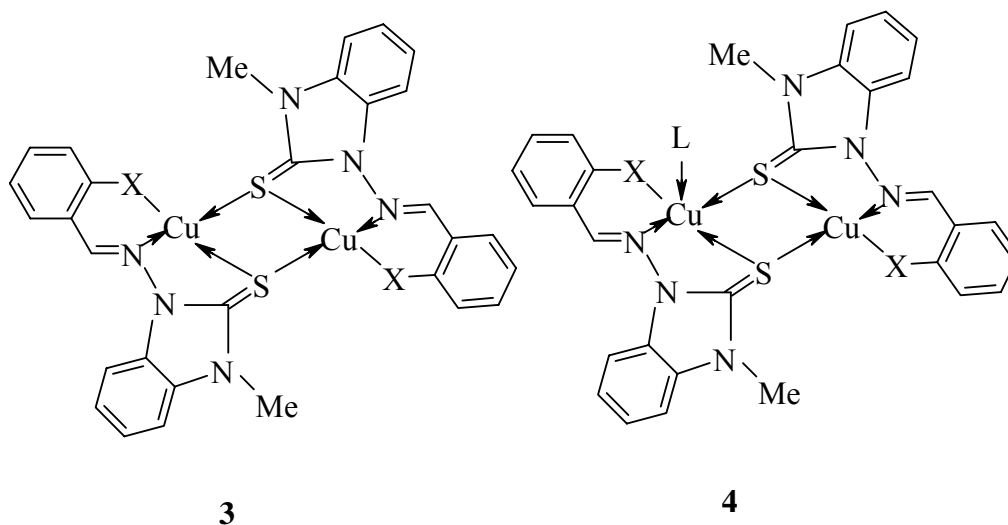


Table 1 shows the dependence between ion composition, ligand nature and electron configuration of the complex-forming metals.

Thus, *o*-tosylamino(hydroxy)azomethinic derivatives of 1-amino-2-thio-3-methylbenzimidazole during complexation with *d*-metals in solution act as bi- and tridentate ligands forming ML_2 complexes, opening a novel way for the introduction of a chalcogen atom in the coordination sphere. From the other hand these systems may play the role of mono-, bi- and tridentate ligands in vapor phase forming M_2L_2 and M_2L_3 complexes.

Experimental Section

General Procedures. 1H NMR spectra (DMSO- d_6) were registered on Varian UNITY-300 (300 MHz, internal 2H standard) and Bruker DPX-250 (250 MHz, internal 2H standard) spectrometers. Mass-spectra (electrospray ionization method)²⁹ were obtained on a mass-spectrometer Water/Micromass ZQ (Manchester, UK) equipped Harvard Apparatus. Methanolic solutions of complex samples were introduced with the flow speed 20 of $\mu L/min$. Capillary potential was 3 kV, lens potential – 0.5 kV, extractor potential – 4 V. The source temperature was 120 °C and the temperature of desolvation was 300 °C. Nitrogen was both used as spray gas and desolvating

gas. IR spectra as Nujol mulls or KBr pellets were registered on Nicolet Impact-400. The electron spectra of the solutions of complexes in CH_2Cl_2 were measured on UNICAM Helyos Gamma. Magnetic susceptibilities of chelates were measured by Evans method.

1-(2-Tosylaminobenzilideneimino)-3-methyl-1,3-dihydrobenzoimidazole-2-thione (1: X = NTs). A solution of 1.79 g (0.01 mol) of 1-amino-3-methylbenzimidazoline-2-thione¹⁰ and 2.75 g (0.01 mol) of 2-tosylaminobenzaldehyde¹¹ was boiled in 15 ml of glacial acetic acid during 2 hours. The precipitate formed after cooling was filtered off, washed with ether and dried at 120 °C. Yield 2.35 g (83 %). Colorless needlelike crystals, m. p. 202-204 °C (from butanol). Found, %: C 60.48; H 4.55; N 12.87. For $\text{C}_{22}\text{H}_{20}\text{N}_4\text{O}_2\text{S}_2$ calculated, %: C 60.53; H 4.62; N 12.83. ¹H NMR spectrum (DMSO- d_6); δ (ppm): 2.27 (3H, s, PhCH_3); 3.80 (3H, s, NCH_3); 7.20 – 8.00 (12H, m, H_{arom}); 9.97 (1H, s, HC=N); 10.65 (1H, s, HNTs).

1-(2-Hydroxybenzilideneimino)-3-methyl-1,3-dihydrobenzoimidazole-2-thione (1: X = NTs). was synthesized by a similar procedure using the 2-hydroxybenzaldehyde. Colorless needlelike crystals, m. p. 202-203 °C (from *n*-butanol). Found, %: C 63.66; H 4.54; N 14.76. For $\text{C}_{15}\text{H}_{13}\text{N}_3\text{OS}$ calculated, %: C 63.58; H 4.62; N 14.83. ¹H NMR spectrum (DMSO- d_6); δ (ppm): 3.80 (3H, s, NCH_3); 6.90 – 7.60 (8H, m, H_{arom}); 10.20 (1H, s, HC=N); 10.97 (1H, s, OH).

Bis[1-(2-tosylaminobenzilidene-imino)-3-methyl-1,3-dihydrobenzoimidazole-2-thionato] nickel(2⁺) (2: X = NTs, M = Ni). 1 ml of 1N solution of sodium methylate was added to the hot solution of 0.218 g (0.5 mmol) of azomethine **1** (X = NTs) in 20 ml of methanol after that the hot solution of 0.055 g (0.25 mmol) of nickel diacetate tetrahydrate in 5 ml of the same solvent was added to the reaction mixture. After refluxing during 15 min, the mixture was cooled and the precipitate was filtered off and washed with 5 ml of cold methanol. Yield 0.190 g (82 %). Brown crystals, m. p. > 200 °C. Found, %: C 57.02; H 4.23; N 12.17. For $\text{C}_{44}\text{H}_{38}\text{N}_8\text{O}_4\text{S}_4\text{Ni}$ calculated, %: C 56.84; H 4.12; N 12.05.

All complexes on the base of ligands **2** (X = NTs, O) were obtained by the similar method. All species have m. p. > 200 °C.

Table 2. Yields and analytical data on metallochelates **3**

	M	Yield, g (%), color	Brutto-formula	Found, % / Calc., %
X = NTs	Cu	0.210 (90), brown	C ₄₄ H ₃₈ N ₈ O ₄ S ₄ Cu	C 56.63 / 56,54
				H 4.18 / 4,10
				N 12.08 / 11,99
	Co	0.175 (75), brown	C ₄₄ H ₃₈ N ₈ O ₄ S ₄ Co	C 57.12 / 56.82
				H 4.20 / 4.12
				N 12.11 / 12.05
Cd	0.215 (87), yellow	C ₄₄ H ₃₈ N ₈ O ₄ S ₄ Cd	C 53.90 / 53,73	
			H 3,95 / 3,89	
			N 11,27 / 11,39	
X = O	Ni	0.259 (83), brown	C ₃₀ H ₂₄ N ₆ O ₂ S ₂ Ni	C 57,73 / 57,80
				H 3,90 / 3,88
				N 13,29 / 13,48
	Cu	0.239 (76), brown	C ₃₀ H ₂₄ N ₆ O ₂ S ₂ Cu	C 57,51 / 57,36
				H 3,74 / 3,85
				N 13,29 / 13,38
	Co	0.206 (66), brown	C ₃₀ H ₂₄ N ₆ O ₂ S ₂ Co	C 57,84 / 57,78
				H 3,92 / 3,88
				N 13,39 / 13,48
	Zn	0.274 (87), yellow	C ₃₀ H ₂₄ N ₆ O ₂ S ₂ Zn	C 57,28 / 57,19
H 3,76 / 3,84				
N 13,25 / 13,34				
Cd	0.250 (74), yellow	C ₃₀ H ₂₄ N ₆ O ₂ S ₂ Cd	C 53,29 / 53,22	
			H 3,65 / 3,57	
				N 12,35 / 12,41

Table 3. ¹H NMR spectra of complexes **3** (δ, ppm)

	M	CH ₃	H _{arom}	HC=N	
X = NTs	Cd	2.25 (6H, s, 2PhCH ₃)	3.80 (6H, s, 2NCH ₃)	6.70 – 7.75 (24H, m)	9.40 (2H, s)
X = O	Zn	3.25	6.80 – 7.50	8.37	
X = O	Cd	3.30	7.10 – 7.60	8.80	

Conclusions

During the synthesis of chelates of Schiff bases containing chalcogen atoms in the coordination sphere^{5, 12, 27} the novel azomethinic complexes with a benzimidazolyl-2-thione fragment were obtained and characterized. *o*-Tosylamino(hydroxy)azomethinic derivatives of 1-amino-2-thio-3-

methylbenzimidazole undergo complexation with *d*-metals in solution, acting as bi- and tridentate ligands forming ML_2 complexes, opening a novel way to introduce a chalcogen atom in the coordination sphere. From the other hand these systems may play the role of mono-, bi- and tridentate ligands in the vapor phase forming M_2L_2 and M_2L_3 complexes.

Acknowledgments

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