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New Ambidentate Ligands—Azomethin Derivatives of 1-Amino-3-methylbenzimidazoline-2-thion

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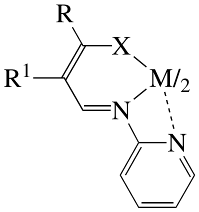
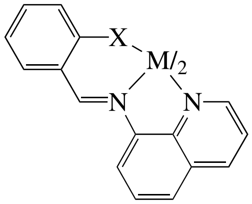
Abstract—Metal chelates ML_2 ($M = Co^{2+}$, Ni^{2+}, Cu^{2+}, Cd^{2+}) are synthesized from azomethin derivative of amino-3-methyl-benzimidazoline-2-thion and 2-*N*-tosylaminobenzaldehyde (HL) and their compositions and structures are determined from the electronic mass spectrometry, IR and electronic spectroscopy and magnetochemistry data.

The complexes based on azomethin ligand systems containing extra coordination-active groups at the imine nitrogen atom are the most extensively studied compounds in the modern coordination chemistry [1–6]. Metal chelates of azomethins are well known that contain at the N atom of the C=N group the azine fragments with endocyclic N-donor atoms involved, for example, in pyridyl (**I**) [6–9] or quinolyl (**II**) [10, 11] cycles. However, chelates based on azomethin ligands with exocyclic donor atoms in the imine substituent are represented only by the thoroughly studied acylhydrazonates (**IIIa**), semi- (**IIIb**), and thiosemicarbazonates (**IIIc**) of metals.[1] At the same time, metal chelates of compounds where the exocyclic donor atom Y (N, O, S, Se) is bonded to the cyclic (including heterocyclic) system are unknown.

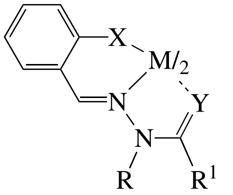
With the aim to study the structures of novel complexes of the Schiff bases with different exoheterocyclic donor fragments, we synthesized for the first time and investigated 1-(2-tosylaminobenzylidene)amino-3-methylbenzimidazoline-2-thion (**IV**, **HL**) containing nucleophilic donor S atom and its metal chelates (**V**).



I: X = NTs, O, S;
Ts = $-SO_2C_6H_4CH_3$-*p*;
R, R^1 = Ar, Het(heteryl).



II: X = NTs, O



III: X = O, NTs, Y = O,
R = H, R^1 = Alk (a);
X = O, Y = O,
R = H, R^1 = NH_2 (b);
X = O, Y = S,
R = H, R^1 = NH_2 (c).

M = Ni, Co, Cu, Zn, Cd

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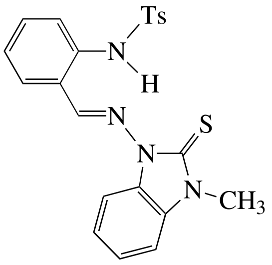
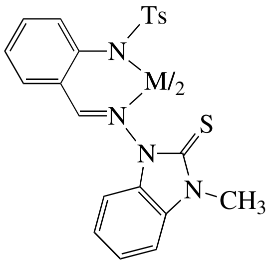
[1] Cambridge Structural Database contains structures of 73 similar metal complexes.



(IV)



(V)

M = Co, Ni, Cu, Cd

EXPERIMENTAL

Mass spectra were obtained by the electrospray ionization (ESI) method on Water/Micromass ZQ (Manchester, Great Britain) mass spectrometer equipped with syringe pump (Harvard Apparatus). The solutions of the samples in methanol were injected in electrospray ionization source by the same pump at flow rate 40 μl/min. The potentials applied to electrospray ionization source were as follows: 3 kV (tube), 0.5 kV (lenses), 4 V (extractor). As in the case of a standard experiment with electrospray ionization, the cone potential was 30 V. The source temperature was 120°C, the temperature of desolvation was 300°C. Nitrogen was used as both the sprayer gas and desolvation gas with flow rates 100 and 300 l/h, respectively.

IR spectra of the samples were recorded on a Nicolet Impact-400 instrument (with essential oil mulls and KBr pellets). The electronic absorption spectra of solutions of the studied compounds in methylene chloride were measured on a UNICAM Helyos Gamma instrument. The ^{1}H NMR spectra of solutions of ligand **IV** and its complex with Cd (**V**(Cd)) in DMSO-D$_6$ were recorded on a Bruker DPX-250 instrument.

The magnetic susceptibility of paramagnetic metal chelates was measured in DMSO-D$_6$ solution by the Evans method.

1-(2-Tosylaminobenzylidene)amino-3-methylbenzimidazoline-2-thion (IV). A solution of 1-amino-3-methylbenzimidazolilne-2-thion (1.79 g, 0.01 mol) [12] and 2-tosylaminobenzaldehyde (2.75 g, 0.01 mol) [13] in glacial acetic acid (15 ml) was refluxed for 2 h. The precipitate formed after cooling was filtered off, washed with ether, and dried at 120°C. The yield was 2.35 g (83%). Colorless needle-shaped crystals were obtained by recrystallization of the precipitate from butanol, mp = 202–204°C.

For $C_{22}H_{20}N_4O_2S_2$

anal. calcd. (%):	C, 60.53;	H, 4.62;	N, 12.83.
Found (%):	C, 60.48;	H, 4.55;	N, 12.87.

^{1}H NMR (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).

Bis[1-(2-tosylaminobenzylideneamino)-3-methylbenzimidazoline-2-thionato]nickel(II) (V(Ni)). A 1N solution of sodium methylate (1 ml) and a hot solution containing $Ni(CH_3COO)_2 \cdot 4H_2O$ (0.05 g, 0.25 mmol) in 5 ml of the same solvent were added to a hot solution of azomethin **IV** (0.218 g, 0.5 mmol) in 20 ml of methanol. The mixture was refluxed for 15 min. The precipitate formed after cooling was filtered off, washed with cold methanol, and dried at 120°C. The yield was 0.190 g (82%). The brown needle-shaped crystals were obtained after recrystallization of precipitate **V** from butanol, mp > 200°C.

For $C_{44}H_{38}N_8O_4S_4Ni$

anal. calcd. (%):	C, 56.84;	H, 4.12;	N, 12.05.
Found (%):	C, 57.02;	H, 4.23;	N, 12.17.

The remaiming metal chelates were prepared following the analogous procedure and using the corresponding metal acetates.

Bis[1-(2-tosylaminobenzylidene)amino-3-methylbenzimidazoline-2-thionato]cobalt(II) (V(Co)). The brown fine needle-shaped crystals were formed in the yield 0.175 g (75%), mp > 200°C.

For $C_{44}H_{38}N_8O_4S_4Co$

anal. calcd. (%):	C, 56.82;	H, 4.12;	N, 12.05.
Found (%):	C, 57.12;	H, 4.20;	N, 12.11.

Bis[1-(2-tosylaminobenzylidene)amino-3-methylbenzimidazoline-2-thionato]copper(II) (V(Cu)). The dark brown prismatic crystals were formed with a yield of 0.210 g (90%), mp > 200°C.

For $C_{44}H_{38}N_8O_4S_4Cu$

anal. calcd. (%):	C, 56.54;	H, 4.10;	N, 11.99.
Found (%):	C, 56.63;	H, 4.18;	N, 12.08.

Bis[1-(2-tosylaminobenzylidene)amino-3-methylbenzimidazoline-2thionato]cadmium(II) (V(Cd)). The yellow finely-crystalline powder was formed, mp > 200°C.

For $C_{44}H_{38}N_8O_4S_4Cd$

anal. calcd. (%):	C, 53.73;	H, 3.89;	N, 11.39.
Found (%):	C, 53.90;	H, 3.95;	N, 11.27.

^{1}H NMR (DMSO-D_6), δ, ppm: 2.25 (6H, s, $2PhCH_3$); 3.8 (6H, s, $2NCH_3$), 6.7–7.75 (24H, m, $24H_{arom}$), 9.40 (2H, s, 2HC=N).

RESULTS AND DISCUSSION

Metal chelates **V** were obtained by the direct reaction of a ligand (HL) and metal salts according to the following scheme [2, 3]:

$$2LH + M(OAc)_2 \longrightarrow ML_2 + 2AcOH.$$

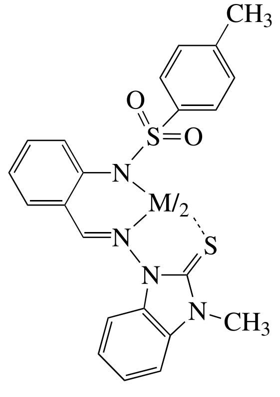
The composition of metal complexes ML_2 (L is the deprotonated ligand) was determined by the elemental analysis, IR (lacking absorption bands of the NH fragment of the HNTs group), ^{1}H NMR (disappearing signal from a proton of the HNTs group, shifts of the remaining signals, lacking signals of the protons of the solvent molecules) [14], and mass spectrometry method (the molecular peaks in mass spectra of chelates correspond to the indicated composition) [15].

The mass spectral data we obtained together with the data [16, 17] made it possible to establish the composition of metal complexes formed and to consider the route of fragmentation and recombination of the fragments of their molecules (and of the molecules of the initial ligand system) under the experimental conditions. Thus, the spectrum of compound **IV** contains, along with a peak of the protonated ligand [HL + H] ($m/z = 437$, $I = 15\%$), the following signals: [HL + Na][2] ($m/z = 459$, $I = 100\%$), [2HL + Na] ($m/z = 895$, $I = 12\%$)[3], where HL is the ligand molecule, m/z is the ratio of a fragment mass to its charge, I is the signal intensity. The spectrum of complex **V**(Ni) contains the following signals: the most intense signal corresponding to [NiL] ($m/z = 493$, $I = 100\%$), the [NaL] signal ($m/z = 459$, $I = 10\%$), and the low-intensity molecular peak due to [NiL_2] ($m/z = 928$).

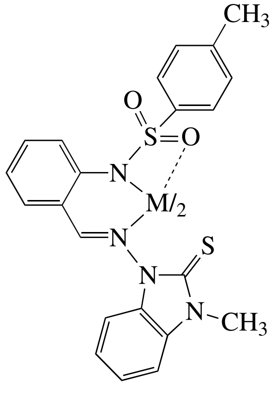
The spectrum of complex **V**(Cu) exhibits the low-intensity molecular peak of [CuL_2 + H] ($m/z = 935$, $I = 8\%$), the intense signal [CuL] ($m/z = 498$, $I = 100\%$), and the signals due to the subsequent destruction of this fragment. In addition to the above signals, one more peak is observed in mass spectrum of compound **V**(Cu) that corresponds to a dimer [Cu_2L_2] ($m/z = 998$, $I = 13\%$) formed, probably, as a result of combination of the **V**(Cu) molecule and the Cu^{2+} ion. The spectrum of chelate **V**(Cd) contains the [LNa] signals ($m/z = 459$, $I = 43\%$), [LCd] ($m/z = 549$, $I = 58\%$), [L_2Cd + H] ($m/z = 985$, $I = 30\%$). An attempt to record mass spectrum of complex **V**(Co) was failure, obviously, due to its low solubility.

The analysis of the low-intensity peaks with $m/z < ML_2$ showed that the fragmentation of metal complexes **V** mainly occurs as a result of detachment of the methyl groups at the N atom of benzimidazole substituent and of different fragments of the tosyl substituent $C_7H_7SO_2$. The main course of destruction of the above chelates is the detachment of the whole deprotonated molecules of the ligand systems.

The ligand system **IV** is potential tridentate and contains, in addition to the chelate-forming N atoms of the tosylamine and azomethin groups (compounds **V**) [18–20], the atoms that can form the donor–acceptor bonds, namely, the S atoms of thiobenzimidazole fragment (complexes **VI**) [21–24] and the O atoms of sulfamide group (complexes **VII**) [25]. Moreover, one should take into account the possibility of formation of pentacoordinated structures ML_2 [23, 25–27], where one of the ligands is bidentate (as in **V**), while the other one is tridentate ligand (as in **VI** or **VII**).



(VI)



(VII)

This work was performed with the aim to determine the composition and the structure of the coordination unit of metal chelates **V** and to study them by IR, UV spectroscopy, and magnetochemistry methods. IR spectra of the ligand system **IV** contain bands due to the stretching vibrations of the NSO_2 (1158 and 1358 cm^{-1}), C=S (1186 cm^{-1}), C=N (1571 cm^{-1}, benzimidazole ring and 1597 cm^{-1}, azomethin fragment), and HNTs (3350 cm^{-1}) groups. The latter band is significantly broadened due to the formation of the intramolecular

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[2] The appearance in all mass spectra of the $[M + Na]^+$ ion can be explained by the presence of sodium in a solvent, glass bottles, tubes used in the experiment, and, possibly, in the spectrometer ionization chamber itself [16].

[3] The signals from the products of complex **IV** decomposition have low intensity and correspond to the fragments [HL–2O–CH_2] ($m/z = 390$), [HL–C_7H_9–SO] ($m/z = 295$).

hydrogen bond with azomethin N atom. In IR spectra of all metal chelates **V**, the band due to vibrations of the HNTs group is lacking, which suggests the formation of a chelate compound. In the spectra of metal chelates, the band due to the stretching vibrations of the C=S group is noticeably shifted (by 25–60 cm^{-1}) toward long waves, as compared to its position in the spectrum of the ligand, which indicates the formation of the bond between the S atom of benzimidazolthion fragment and the metal atom (type **VI**). The bands from the SO_2 group of the tosyl fragment are only slightly shifted, which can be explained by the lacking coordination of the O atom of this group to the central metal ion (type **VI**).

The important characteristics that can be used in order to determine the structure of the coordination unit in the Ni(II) and Co(II) complexes are the parameters of their electronic absorption spectra in visible and near-IR regions and the values of the effective magnetic moments (μ_{eff}). The electronic absorption spectra of metal chelate **V**(Ni) in visible and near-IR regions contain two bands at 14580 cm^{-1} (ε = 25 l/mol cm) and 9500 cm^{-1} (ε = 47 l/(mol cm)) due to transitions $^3A_{2g} \longrightarrow {}^3T_{2g}$ and $^3A_{2g} \longrightarrow {}^3T_{1g}(F)$ of the Ni^{2+} ion with the O_h symmetry, respectively.[4] The μ_{eff} value of this compound in DMSO solution is equal to 2.87 μ_B, which is typical of the Ni^{2+} ion involved in the octahedral ligand surrounding. The spectral data (3830 cm^{-1} (ε = 21 l/(mol cm)) and 9340 cm^{-1} (ε = 42 l/(mol cm)) and the value μ_{eff} (4.75 μ_{eff}) **V**(Co) also indicate the octahedral structure of its ligand surrounding.

Thus, the results of the study obtained by different physicochemical methods for metal chelates **V** confirm that these complexes have the octahedral surrounding of a central atom. The coordination involves the N atoms of the tosylamine and azomethin groups and the S atoms of thiobenzimidazole fragments of two molecules of deprotonated ligands, i.e., these metal chelates have structure **VI** with the MN_4S_2 coordination core. At the same time, the unambiguous conclusion on the structure of complex **V**(Cu) can be done only after supplementary investigations (for instance, by X-ray diffraction method), since this chelate can, in potential, exhibit the pentacoordinated structure (of the tetragonal pyramid) [26, 27].

ACKNOWLEDGMENTS

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REFERENCES

1. Garnovskii, A.D., Garnovskii, D.A., Vasil'chenko, I.S., *et al.*, *Usp. Khim.*, 1997, vol. 66, no. 5, p. 434.
2. Garnovskii, A.D., Vasil'chenko, I.S., and Garnovskii, D.A., *Sovremennye aspekty sinteza metallokompleksov* (Modern Aspects of the Synthesis of Metal Complexes), Rostov-on-Don: LaPO, 2000.
3. *Synthetic Coordination and Organometallic Chemistry*, Garnovskii, A.D. and Kharisov, B.I., Eds., New York: Basel: Marcel Dekker, 2003.
4. Garnovskii, A.D. and Vasil'chenko, I.S., *Usp. Khim.*, 2002, vol. 71, no. 11, p. 1064.
5. Garnovskii, A.D., Uflyand, I.E., Vasil'chenko, I.S., *et al.*, *Ross. Khim. Zh.*, 2004, vol. 48, no. 1, p. 55.
6. Garnovskii, A.D. and Vasil'chenko, I.S., *Usp. Khim.*, 2005, vol. 74, no. 3, p. 211.
7. Castineiras, A., Castro, J.A., Duran, M.L., *et al.*, *Polyhedron*, 1989, vol. 8, no. 21, p. 2543.
8. Hokeler, T., Kilic, Z., Isikan, A., *et al.*, *J. Mol. Struct.*, vol. 523, nos. 1–3, p. 61.
9. Erxeleben, A., *Inorg. Chem.*, 2001, vol. 40, no. 2, p. 208.
10. Vasil'chenko, I.S., Antsyshkina, A.S., Burlov, A.S., *et al.*, *Zh. Neorg. Khim.*, 1999, vol. 44, no. 8, p. 1278 [*Russ. J. Inorg. Chem.* (Engl. Transl.), vol. 44, no. 8, p. 1205].
11. Borodkina, I.G., Uraev, A.I., Borodkin, G.S., *et al.*, Abstracts of Papers, *VII Mezhd. Simpozium po Magnitnomu Rezonansu* (VII Int. Symp. on Magnetic Resonance), Rostov-on-Don, 2004, p. 258.
12. Kuz'menko, V.V., Kuz'menko, T.A., Pozharskii, A.F., and Kryshtalyuk, O.V., *Khim. Geterotsikl. Soedin.*, 1990, no. 12, p. 1689.
13. Chernova, N.I., Bolotin, B.M., Nurmukhametov, R.N., *et al.*, *Reaktivy i osobo chistye veshchestva. Tr. IREA*, 1973, vol. 35, no. 1, p. 57.
14. Borodkina, I.G., *Cand. Sci. (Chem.) Dissertation,* Rostov-on-Don: Rostov State Univ., 2004.
15. Borisenko, R.R., *Cand. Sci. (Chem.) Dissertation*, Rostov-on-Don: Rostov State Univ., 2004.
16. Sanders, J.K.M. and Brady, P.A., *New J. Chem.*, 1998, vol. 22, no. 5, p. 411.
17. Henderson, B and McIndoe, J.S, *Comprehensive Coordination Chemistry II*, McCleverty, J.A. and Meyer, T.Y., Eds., Elsever, 2003, vol. 2, p. 387.
18. Garnovskii, A.D., Alekseenko, V.A., Kogan, V.A., *et al.*, *Koord. Khim.*, 1977, vol. 3, no. 4, p. 500.

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[4] The band due to the third electron transition of the Ni^{2+} ion with symmetry O_h ($^3A_{2g} \longrightarrow {}^3T_{1g}(P)$) is overlapped by the bands due to more intense intraligand transitions and should lie at about 26200 cm^{-1} according to the calculations.

19. Vazquez, M., Bermejo, M.R., Fondo, M., *et al.*, *Eur. J. Inorg. Chem.*, 2001, no. 7, p. 1863.
20. Vazquez, M., Bermejo, M.R., Fondo, M., *et al.*, *Eur. J. Inorg. Chem.*, 2003, no. 6, p. 1128.
21. Ramaprabhu, S., Lucken, E.A., and Bernardinelli, G., *J. Chem. Soc., Dalton Trans.*, 1995, no. 1, p. 115.
22. Castro, R., Romero, Y., Garcia-Vazquez, J.A., *et al.*, *Inorg. Chim. Acta*, 1996, vol. 345, no. 2, p. 119.
23. Garnovskii, A.D. and Sadimenko, A.P., *Adv. Heterocycl. Chem.*, 1998, vol. 72, p. 1.
24. Minkin, V.I., Garnovskii, A.D., Elguero, J., *et al.*, *Adv. Heterocycl. Chem.*, 2000, vol. 76, p. 157.
25. Garnovskii, D.A., Sadikov, G.G., Antsyshkina, A.S., *et al.*, *Kristallografiya*, 2003, vol. 48, no. 3, p. 471 [*Crystallogr. Rep.* (Engl. Transl.), vol. 48, no. 3, p. 426].
26. Garnovskii, A.D., Antsyshkina, A.S., Anpilova, E.L., *et al.*, *Zh. Neorg. Khim.*, 2003, vol. 48, no. 12, p. 1993 [*Russ. J. Inorg. Chem.* (Engl. Transl.), vol. 48, no. 12, p. 1835].
27. Garnovskii, A.D., Kharisov, B.I., Anpilova, E.L., *et al.*, *Polyhedron*, 2004, vol. 23, no. 11, p. 1909.