Russian Journal of General Chemistry, Vol. 74, No. 5, 2004, pp. 772–775. Translated from Zhurnal Obshchei Khimii, Vol. 74, No. 5, 2004, pp. 840–843.

Complex Compounds of Azomethines with an MN_2S_2 Five-membered Coordination Unit: Metal Chelates of 2-{[4-(3,5-Diphenyl-4,5-dihydropyrazol-1-yl)-benzylidene]amino}benzenethiol

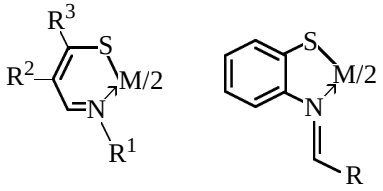
A. S. Burlov, I. G. Borodkina, L. I. Kuznetsova, A. I. Uraev, N. I. Makarova, I. S. Vasil'chenko, G. S. Borodkin, O. Altun, A. Feiizoglu (Abdullaev), and A. D. Garnovskii

Rostov State University, Rostov-on-Don, Russia
Trakai University, Turkey

Received May 27, 2002

Abstract—Chelate complexes of 2-{[4-(3,5-diphenyl-4,5-dihydropyrazol-1-yl)benzylidene]amino}benzenethiol (LH) of the ML_2 composition and with an $M_2N_2S_2$ five-membered coordination unit were obtained. The syntheses were carried out by chemical (from LH and metal acetates) and electrochemical (from LH and zero-valent metals) methods in methanol. The chelate compounds were assigned *cis*-planar (M = Ni) and tetrahedral (M = Co, Zn, Cd) configurations.

Complexes of Schiff bases with an MN_2S_2 coordination unit occupy an important place in the chemistry of azomethine metal chelates in view their peculiar stereochemistry (preferential formation of *cis*-planar and distorted tetrahedral structures) [1–3] and the possibility of creation of models of active centers of nonheme metal proteins [4–8]. Whereas most emphasis in the development of this field of coordination chemistry has been placed on six-membered metal chelates **I** [1–, 5–8], five-membered chelates **II** are equally interesting objects [1–3, 9–25].

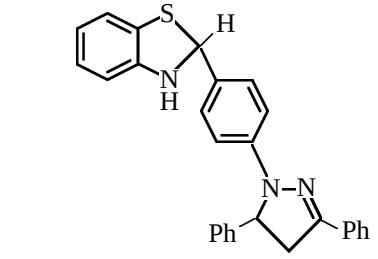


I **II**

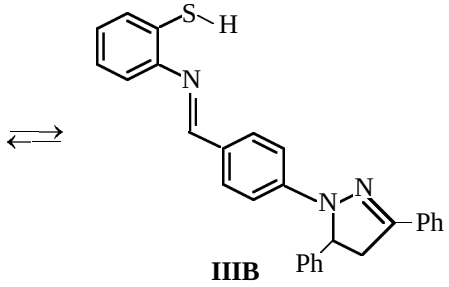
I, R^1, R^2, R^3 = Alk, Ar, Ht; **II**, R = Ar, Ht.

Proceeding with the research initiated in [9, 10], we synthesized for the first time and studied ligand **III** (LH) and metal complexes **IV**, **Va**–**Vc** derived from it.

As would be expected [26–28], ligands **III** in crystal and in solutions exist mainly in the closed benzothiazoline form **A**, which is proved by the ^1H NMR and IR spectra.



IIIA



IIIB

The IR spectrum of compound **III** contains a well-defined band at 3346 cm^{-1}, which relates to stretching vibrations of the secondary amino group, and bands in the region of 1580 cm^{-1} characteristic of the endocyclic C=N bond of the pyrazoline ring [29]. Vibrations of the open form **B** in the region 1620–1660 cm^{-1} (exocyclic azomethine C=N bond) and 2500–2600 cm^{-1} [ν(SH)] are absent from the spectrum.

The presence of a chiral center in the pyrazoline fragment of ligand **III** results in the observation in the

1070-3632/04/7405-0772

IR spectra, magnetic characteristics, and elemental analyses of azometine **III** and complexes **IV, Va–Vc**

Comp. no	M_{ef}, BM	IR spectrum, ν(C=N), cm^{-1}	Color	mp, °C	Found, %					Formula	Calculated, %				
					C	H	N	S	M		C	H	N	S	M
III	[a]	[b]	Light yellow	170–171	77.16	5.54	9.89	7.39	–	$C_{28}H_{23}N_3S$	77.56	5.34	9.69	7.40	–
IV	[a]	1620 m	Red-brown	>250 (decomp.)	72.99	4.70	9.95	6.91	6.55	$C_{56}H_{44}N_6NiS_2$	72.80	4.80	9.10	6.94	6.35
Va	4.35	1624 m	Brown	>250 (decomp.)	72.75	4.82	8.70	7.15	6.58	$C_{56}H_{44}CoN_6S_2$	72.78	4.80	9.10	6.94	6.38
Vb	[a]	1625 m	Orange	>250 (decomp.)	72.30	4.74	9.00	6.93	7.12	$C_{56}H_{44}N_6S_2Zn$	72.26	4.77	9.04	6.98	7.03
Vc	[a]	1620 m	″	>250 (decomp.)	68.30	4.65	8.74	6.71	11.64	$C_{56}H_{44}CdN_6S_2$	68.79	4.54	8.60	6.56	11.50

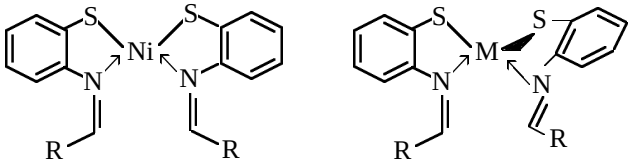
[a] Diamagnetic. [b] ν(NH) 3346s.

^{1}H NMR spectra ($CDCl_3$) of anisochronous CH_2 proton signals at δ (ppm) 3.17 d.d (J_{HH} 17.2, J_{HH} 7.0 Hz) and 3.83 d.d (J_{HH} 17.2, J_{HH} 12.3 Hz) The pyrazoline CHPh proton signal is observed at δ 5.22 d.d (J_{HH} 12.3, J_{HH} 7.0 Hz). The thiazoline CH and NH proton signals are observed at δ 6.29 s and 4.22 s, respectively. Aromatic protons appear as multiplets at δ 6.50–7.80 m (18H).

Chelates **IV**, **Va**–**Vc** of the ML_2 composition [M = Co(II), Ni(II), Zn(II), and Cd(II)] (see table) were synthesized chemically and electrochemically from compound **III** (see Experimental). The IR spectra of the chelates contain well-defined absorption bands at 1620–1625 cm^{-1}, corresponding to stretching vibrations of coordinated C=N bond [10].

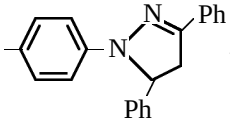
The ^{1}H NMR spectra of the Ni(II), Zn(II), and Cd(II) complexes preserve the general pattern characteristic of the ligand, but the NH signal at δ 4.22 disappears and the signal of the HC=N proton (δ 8–9) appears.

Together the above evidence allows us to assign structures **IV** and **V** to the complexes described for the first time. In these structures, the azomethine ligand system is stabilized by coordination (cf. [28]).



IV

Va–**Vc**

R =  ; M = Co (**a**), Zn (**b**), Cd (**c**).

The ^{1}H NMR evidence allows the diamagnetic nickel complex to be assigned a slightly tetrahedrally distorted planar configuration in solution, which is evidenced by the fact that the chemical shifts of aromatic proton signals span an extended range (δ 6.0–9.0). This result is consistent with the diamagnetism of the nickel chelate in the crystal phase, we revealed by Faraday's method, as well as published data based on X-ray diffraction data for complexes **II** (M = Ni) [13, 18, 23, 30, 31]. Similar complexes

Va–**Vc** were assigned a tetrahedral configuration, based on the magnetic moment (M_{ef} 4.35 BM) for the cobalt chelate and published data for the zinc and cadmium complexes [32, 33].

Thus, the example of new azometine chelates with account for published data [9–28] was used to show that the character of polyhedra that are realized in complexes with MN_2S_2 five-membered coordination unit is determined by the electronic configuration of the metal and does not depend on the nature of the substituent in the aldehyde fragment of the ligand system.

EXPERIMENTAL

The IR spectra were taken on a Specord IR-71 instrument in mineral oil. The ^{1}H NMR spectra were obtained on a Varian Unity-300 spectrometer (300 MHz) in $CDCl_3$ against internal HMDS. Magnetic measurements were carried out by Faraday's method at 304 K on an installation assembled at the Rostov State University [34].

2-{[4-(3,5-Diphenyl-4,5-dihydropyrazol-1-yl) benzylidene]amino}benzenethiol (III). To a methanol solution (30 ml) of 3.26 g of 1-(4-formyl)-3,5-diphenyl-2-pyrazoline obtained by the procedure in [35], 1.25 g of *o*-aminothiophenol was added, and the mixture was refluxed for 1 h. After cooling, yellow crystals formed and were filtered off, recrystallized from methanol, and dried in a vacuum oven at 100°C. Yield 75%.

Metal 2-{[4-(3,5-diphenyl-4,5-dihydropyrazol-1-yl)benzylidene]amino}benzenethiolates (IV), Va–Vc. *a*. To a solution of 0.86 g azomethine **I** in 20 ml of methanol, 0.001 mol of corresponding metal acetate in 20 ml of methanol was added, and the mixture was refluxed for 2 h. After cooling, a precipitate formed and was filtered off, washed with methanol (3×5 ml), recrystallized from toluene or methanol–chloroform (2 : 1), and dried in a vacuum oven at 150°C.

b. The synthesis was carried out by anodic dissolution of metal (Ni, Co, Zn, or Cd) in methanol [22, 36, 37]. A platinum electrode was used as a cathode and tetraethylammonium perchlorate as a conductive additive. Current strength 20 mA, voltage 20 V, synthesis time 2–3 h. The load of the electrolyzer was 0.001 mol of the ligand in 30 ml of methanol. The precipitate that formed was filtered off and recrystallized from benzene–methanol (1 : 3) or chloroform–methanol (1 : 2). Yield 80–85%.

ACKNOWLEDGMENTS

The work was financially supported by the Russian Foundation for Basic Research (project nos. 00-03-32538 and 00-15-97320).

REFERENCES

1. Garnovskii, A.D., Nivorozhkin, A.L., and Minkin, V.I., *Coord. Chem. Rev.*, 1993, vol. 126, nos. 1–2, p. 1.
2. Garnovskii, A.D., *Koord. Khim.*, 1993, vol. 19, no. 5, p. 394.
3. Garnovskii, A.D. and Vasil'chenko, I.S., *Usp. Khim.*, 2002, vol. 71, no. 11, p. 1064.
4. Solomon, E.Y., Baldwin, M.Y., and Lovery, M.D., *Chem. Rev.*, 1992, vol. 92, no. 4, p. 521.
5. Nivorozhkin, A.L., Uraev, A.I., Burlov, A.S., and Garnovskii, A.D., *Ross. Khim. Zh.*, 1996, vol. 40, nos. 4–5, p. 162.
6. Mandal, S., Das, G., Singh, R, Shukla, R., and Bharadway, P.K., *Coord. Chem. Rev.*, 1997, vol. 160, p. 191.
7. Uraev, A.I., Nivorozhkin, A.L., Bondarenko, G.I., Lysenko, K.A., Korshunov, O.Yu., Vlasenko, V.G., Vasil'chenko, I.S., Shuvaev, A.T., Kurbatov, V.P., Antipin, M.Yu., and Garnovskii, A.D., *Dokl. Ross. Akad. Nauk*, 1999, vol. 367, no. 1, p. 67.
8. Uraev, A.I., Nivorozhkin, A.L., Bondarenko, G.I., Lysenko, K.A., Korshunov, O.Yu., Vlasenko, V.G., Shuvaev, A.G., Kurbatov, V.P., Antipin, M.Yu., and Garnovskii, A.D., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2000,, no. 11, p. 1892.
9. Kochin, S.G., Garnovskii, A.D., Kogan, V.A., Osipov, O.A., and Sushko, T.G., *Zh. Neorg. Khim.*, 1969, vol. 14, no. 5, p. 1428.
10. Garnovskii, A.D., Kogan, V.A., Osipov, O.A., Kochin, S.G., Kuznetsova, L.I., and Mitina, G.K., *Zh. Obshch. Khim.*, 1971, vol. 41, no. 6, p. 1370.
11. Lindoy, L.F., Bush, D.H., and Goedken, V., *Chem. Commun.*, 1972, no. 12, p. 683.
12. Uhlemann, E. and Pohl, V., *Z. Anorg. Allg. Chem.*, 1973, vol. 397, no. 2, p. 162.
13. D'yachenko, O.A., Atovmyan, L.O., Aldoshin, S.M., Kogan, V.A., Kochin, S.G., and Osipov O.A., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1975, no. 5, p. 2130.
14. Kawamoto, T. and Kushi, J., *Chem. Lett.*, 1992, no. 4, p. 297.
15. Kawamoto, T., Kuma, H., and Kushi J., *Chem. Commun.*, 1996, no. 23, p. 2121.
16. Kawamoto, T., Nagasava, I., Kuma, H., and Kushi, J., *Inorg. Chem.*, 1996, vol. 35, no. 9, p. 2427.
17. Erkan, F., Ulku, D., Ancin, N., Ostas, S.C., and

Sun, M., *Acta Crystallogr., Sect. C*, 1996, vol. 52, no. 9, p. 1141.

18. Kawamoto, T., Kuma, H., and Kushi, J., *Bull. Chem. Soc. Jpn.*, 1997, vol. 70, no. 6, p. 1599.
19. Hossain, M., Ghosh, S., and Chattopadhyay, S.K., *Trans. Met. Chem.*, 1997, vol. 22, no. 5, p. 497.
20. Kawamoto, T. and Kushi, J., *Inorg. Chim. Acta.*, 1997, vol. 265, nos. 1–2, p. 163.
21. El-Bindari, A.L., *Synth. React. Inorg. Metalloorg. Chem.*, 1998, vol. 28, no. 10, p. 1743.
22. Kharisov, B.I., Blanko, L.M., Garnovskii, A.D., Burlov, A.S., Kuznetsova, L.I., Korovina, L.V., Garnovskii, D.A., and Dieck, T., *Polyhedron.*, 1998, vol. 17, nos. 2–3, p. 381.
23. Kawamoto, T. and Kushi, J., *J. Chem. Soc., Dalton Trans.*, 2000, no. 18, p. 3022.
24. Zhang, C., Guzei, I.A., and Espenson, J.H., *Inorg. Chem.*, 2001, vol. 40, no. 10, p. 2437.
25. Tyler, L.A., Olmstead, M.M., and Mascharak, P.K., *Inorg. Chem.*, 2001, vol. 40, no. 21, p. 5408.
26. Fulop, F., Mattinen, J., and Philaja, K., *Tetrahedron*, 1990, vol. 46, no. 18, p. 6545.
27. Valters, R.E., Fulop, F., and Korbouis, D., *Adv. Heterocycl. Chem.*, 1996, vol. 66, p. 1.
28. Minkin, V.I., Garnovskii, A.D., Elguero, J., Katritzky, A.R., and Denisko, O.V., *Adv. Heterocycl. Chem.*, 2000, vol. 76, p. 157.
29. Bellamy, L.J., *The Infra-red Spectra of Complex Molecules*, New York: Wiley, 1957.
30. Kawamoto, T., and Kushi, J., *Chem. Lett.*, 1992, p. 893.
31. Kawamoto, T. and Kushi, J., *J. Chem. Soc., Dalton Trans.*, 1992, no. 18, p. 3137.
32. Minkin, V.I. and Nivorozhkin, L.E., *Mendeleev Chem. J.*, 1996, vol. 40, nos. 4-5, p. 12.
33. Minkin, V.I. and Nivorozhkin, L.E., *Ross. Khim. Zh.*, 1996, vol. 40, nos. 4–5, p. 12.
34. Kurbatov, V.P., Hohlov, A.V., Garnovskii, A.D., Osipov, O.A., and Khulkhachieva, L.A., *Koord. Khim.*, 1979, vol. 5, no. 3, p. 351.
35. Kutelya, L.A. and Shevchenko, A.E., USSR Inventor's Certificate no. 717 046, *Byull. Izobret.*, 1980, no. 7.
36. Garnovskii, A.D., Kharisov, B.I., Scopenko, V.Y., Blanko-Jerez, L.M., Kokozay, V.N., Khuzarov, A.S., Garnovskiy, D.A., Burlov, A.S., and Pavlenko, V.A., *Direct Synthesis of Coordination and Organometallic Compounds*, Garnovskii, A.D. and Kharisov, B.I., Eds., Amsterdam: Elsevier, 1999.
37. Garnovskii, A.D., Vasil'chenko, I.S., and Garnovskii, D.A., *Sovremennye aspekty sinteza metallokompleksov. Osnovnye ligandy i metody* (Modern Aspects of Synthesis of Metal Complexes. Main Ligands and Methods), Rostov-on-Don: Lab. Perspekt. Obraz., 2000.