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Binuclear Cu(II) and Ni(II) Complexes with Schiff Bases—the Products of Condensation of Amino Alcohols with 2-Phenylhydrazone 1-Phenylbutane-1,2,3-Trione: Synthesis and Magnetic Properties

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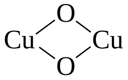
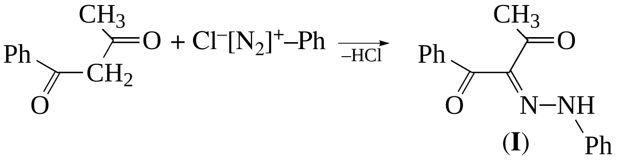
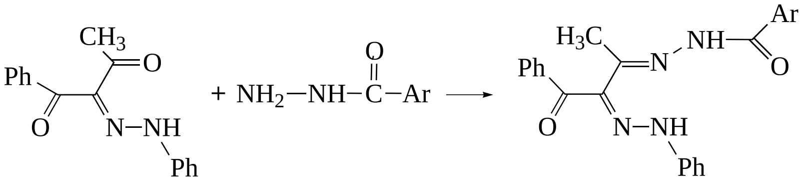
Abstract—The binuclear complexes of Cu^{2+} and Ni^{2+} with a new ligand system obtained through condensation of amino alcohols with 2-phenylhydrazone 1-phenylbutane-1,2,3-trione were synthesized. The compositions and structures of ligands and complexes were determined using elemental analysis, IR and NMR spectroscopy and magnetochemistry. The nickel complexes were found to be diamagnetic; in the copper complexes, substantial antiferromagnetic exchange interaction was observed (for Cu^{2+} complexes with $n = 2$ and 3, 2J is equal to –396 and –393 cm^{-1}, respectively). The structure of the exchange fragment  is discussed.

The β-diketones are known to enter rather easily the azo coupling reaction with aryldiazonium salts to yield hydrazones, which are potential N,N,N- and N,N,O-donor ligands [1–3]. However, all compounds containing these ligands are merely mononuclear metal chelates. It was of interest to synthesize polynuclear complexes with similar ligands through introduction of additional chelatophore groups in arylhydrazones (**I**), which are the products of azo coupling of aryldiazonium salts with β-dicarbonyl compounds. We intended to synthesize these complexes by the following reactions:



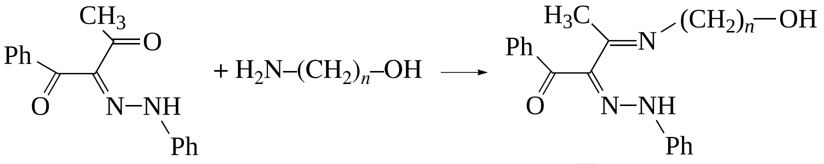
(**I**)

(1)



(2)

However, as follows from further investigations, no condensation occurs between the carbonyl oxygen atom of hydrazones **I** and aromatic hydrazides by reaction (2). This was rather surprising, since in the above-cited works, the condensation of the carbonyl group with less basic nitrogen atom of aromatic or aliphatic amines proceeds almost quantitatively. On the other hand, condensation between hydrazones **I** and amino alcohols (ethanol- and propanolamine) proceeds smoothly, which made it possible to synthesize ligand systems (**II**):



(**II**, H_2L) $n = 2, 3$

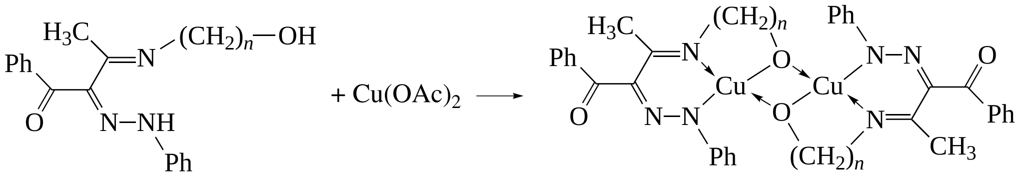
(3)

Table 1. Results of elemental analysis of ligands **II** and complexes **III** and **IV**

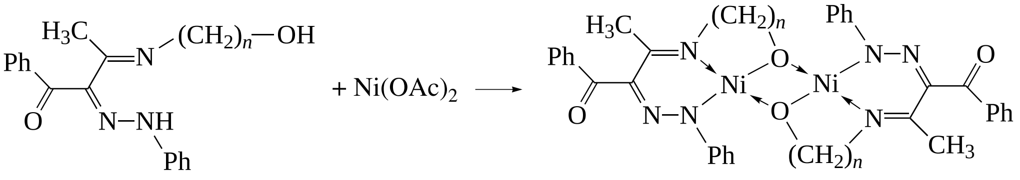
Compound	*n**	Empirical formula	Composition (found/calcd), %			
			C	H	N	M
II	2	$C_{18}H_{19}N_3O_2$	70.1/69.9	5.9/6.1	13.9/13.6	
II	3	$C_{19}H_{21}N_3O_2$	70.4/70.6	6.6/6.5	12.8/13.0	
III	2	$C_{36}H_{36}N_6O_4Cu_2$	57.8/58.1	4.6/4.8	11.1/11.3	17.4/17.2
III	3	$C_{38}H_{40}N_6O_4Cu_2$	58.8/59.0	5.4/5.2	10.7/10.9	16.8/16.6
IV	2	$C_{36}H_{36}N_6O_4Ni_2$	58.6/58.9	4.9/5.1	11.6/11.4	16.5/16.1
IV	3	$C_{38}H_{40}N_6O_4Ni_2$	60.1/60.4	5.2/5.0	10.9/11.1	15.6/15.4

* *n* is the number of (CH_2) groups.

The formulas of these ligands evidence that they can be considered as tridentate dibasic systems similar to those that were described in [4–6] and were used to synthesize the binuclear complexes of transition metals in the first period of the Periodic Table. We obtained a series of new Cu^{2+} and Ni^{2+} complexes (**III**, **IV**) with ligands **II**.



(**III**), *n* = 2, 3 (4)



(**IV**), *n* = 2, 3 (5)

The composition and structure of all ligands and complexes were determined using elemental analysis, IR and NMR spectroscopy and magnetochemistry. The NMR spectra of ligands **II** (*n* = 2, 3) exhibited signals with integrated intensities corresponding to the total number of their protons: a singlet at 2.5 ppm (3H) from the methyl group protons, singlet signals at 3.6 (2H) and 3.8 ppm (3H) from two (*n* = 2) or three (*n* = 3) methylene group protons, respectively, a singlet at 5 ppm (1H) from the NH proton of the hydrazine group, a multiplet signal at 7–8 ppm from the protons of two benzene rings, and a singlet at 15 ppm (1H) from the hydroxyl proton.

Reactions of ligands **II** with copper(II) or nickel(II) acetates (reactions (4) and (5), respectively) resulted in ML complexes, where L^{2-} is a doubly deprotonated form of the ligand (Table 1). Coordination was confirmed by the fact that the alcohol OH and hydrazine NH stretching vibration bands, which were observed in the spectra of free ligands at 3400 and 3200 cm^{-1}, respectively, disappeared from the spectra. The effective magnetic moments of copper chelates (per one copper atom) even at room temperature were noticeably smaller than a purely spin value (1.73 μ_B, Table 2). When the temperature was lowered to liquid nitrogen temperature, the effective magnetic moment (μ_{eff}) further lowered, thus suggesting a strong antiferromagnetic exchange interaction between two copper atoms in dimeric complex **III**. The magnetic properties of complex **III** were explained in terms of the isotropic Heiselberg–Dirac–van Vleck model using a modified Bleaney–Bowers equation, which accounts for a small amount of paramagnetic impurities in the dimeric sample [9]. The calculated exchange parameters (2*J*) (Table 2) are in good agreement with the exchange parameters of the binuclear copper(II) complexes with polydentate ligands based on the products of condensation of aminoethanol and aminopropanol with substituted salicylaldehyde derivatives [6]. Rather large (in absolute value) parameters of antiferromagnetic exchange inter-

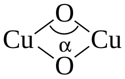
Table 2. Magnetic properties of binuclear complexes **III**

T, K	289	258	238	218	197	163	142	121	100	82
$n = 2$, $2J = -396$ cm^{-1}, $g = 2.00$, $f^* = 0.11$, $r^{**} = 1.74\%$										
$\mu_{\rm eff}^{\rm exp}$***, $\mu_{\rm B}$	1.20	1.10	1.04	0.98	0.92	0.80	0.71	0.65	0.61	0.58
$\mu_{\rm eff}^{\rm calcd}$, $\mu_{\rm B}$	1.18	1.10	1.05	0.99	0.92	0.79	0.72	0.65	0.61	0.58
$n = 3$, $2J = -392$ cm^{-1}, $g = 2.02$, $f = 0.08$, $r = 1.98\%$										
$\mu_{\rm eff}^{\rm exp}$, $\mu_{\rm B}$	1.17	1.10	1.04	0.98	0.82	0.75	0.67	0.60	0.54	0.50
$\mu_{\rm eff}^{\rm calcd}$, $\mu_{\rm B}$	1.17	1.11	1.05	0.99	0.83	0.75	0.66	0.59	0.53	0.51

* f is a fraction of paramagnetic impurities.

** r is the root-mean-square error.

*** The $\mu_{\rm eff}^{\rm exp}$ values were determined by the relative Faraday method (the $\mu_{\rm eff}$ values were calculated per one copper atom in binuclear molecule); $\mu_{\rm eff}^{\rm calcd}$ were calculated within the framework of a modified Bleany–Bower equation using the determined exchanged parameter $2J$.

action apparently indicate that the structure of the exchange fragment  is close to planar and the bond angle $\alpha \geq 100°$ [8]. Unfortunately, we had no possibility to carry out X-ray diffraction analysis of metal chelates obtained, because their single crystals were not available.

Ligands **II** react with nickel(II) acetate to give coordination compounds NiL (Table 1). The IR spectra of these complexes are similar to those of metal chelates **III**. They are diamagnetic, which points to a planar structure of their coordination cores and agrees well with diamagnetism of nickel chelates containing the ligands obtained through condensation of amino alcohols with N-tolylsubstituted derivatives of salicylaldehyde [5]. These data confirm that the nickel(II) complexes synthesized have binuclear structure **IV**.

Thus, this study evidenced that the Schiff bases synthesized in this work through the condensation of monoethanol- and monopropanolamine with 2-phenylhydrazon 1-phenylbutane-1,2,3-trione act as tridentate dibasic ligands and form with Cu^{2+} and Ni^{2+} ions binuclear complexes with a planar coordination core N_2O_2.

EXPERIMENTAL

2-Phenylhydrazone 1-phenylbutane-1,2,3-trione (I) was synthesized using the known procedure [10].

Ligands II were obtained by boiling equimolar mixture of hydrazone **I** and amino alcohol in methanol for 2 h. The precipitate formed after cooling was further filtered off, recrystallized from a heptane–ethylacetate (2 : 1) mixture, and dried in air. The results of elemental analysis are presented in Table 1.

Complexes III, IV were obtained using the following procedure. A hot solution of copper(II) acetate (0.001 mol) in 15 ml methanol (or of nickel(II) acetate in 5 ml methanol) was added to a solution of ligand (0.001 mol) in 10 ml methanol and boiled for 10 min with stirring. The precipitate that was formed after cooling was filtered off and washed with hot methanol. The results of elemental analysis of these complexes are given in Table 1.

IR spectra were recorded on an UR-20 instrument in the 700–4000 cm^{-1} range; the samples were prepared in the form of suspensions in mineral oil.

^{1}H NMR spectra were taken on a UNITY-300 spectrometer with DMSO-d_6 as a solvent and tetramethylsilane as a standard.

Magnetic susceptibility was determined by the relative Faraday method over the temperature range of 78–300 K using a setup designed at the Chair of Physical and Colloidal Chemistry, Rostov State University. $Hg[Co(CNS)_4]$ was used as a standard for calibration. The exchange parameters were calculated from the temperature dependence of magnetic susceptibility within the framework of the dimeric Heiselberg–Dirac–van Vleck model using a modified Bleaney–Bowers equation [9]; also, the program minimizing root-mean-square error was used.

ACKNOWLEDGMENTS

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