ISSN 1070-3632, Russian Journal of General Chemistry, 2009, Vol. 79, No. 4, pp. 826–832. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © I.N. Shcherbakov, L.D. Popov, S.I. Levchenkov, A.N. Morozov, V.A. Kogan, A.D. Vikrishchuk, 2009, published in Zhurnal Obshchei Khimii, 2009, Vol. 79, No. 4, pp. 663–669.

Specificity of Complex Formation of Benzoin (Phthalazin-1-yl)hydrazone with Copper(II) and Nickel(II): Physicochemical Study and Quantum-Chemical Simulation

I. N. Shcherbakov[a], L. D. Popov[a], S. I. Levchenkov[b], A. N. Morozov[a], V. A. Kogan[a], and A. D. Vikrishchuk[b]

[a] *Southern Federal University, ul. Zorge 7, Rostov-on-Don, 344090 Russia*
e-mail: physchem@yandex.ru

[b] *Southern Research Center, Russian Academy of Sciences, Rostov-on-Don, Russia*
e-mail: s.levchenkov@gmail.com

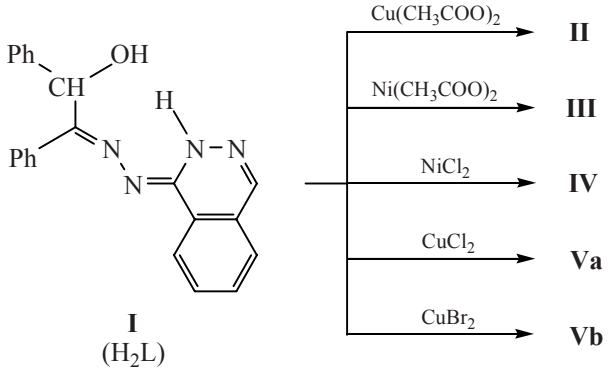
Received May 30, 2008

Abstract—Benzoin (phthalazin-1-yl)hydrazone and its complexes with copper(I), copper(II), and nickel(II) were synthesized. Acid–base properties of benzoin (phthalazin-1-yl)hydrazone were studied, and its ionization constants and energies of possible conformers were calculated by quantum-chemical methods. The structure of the isolated complexes was determined on the basis of their elemental compositions, IR spectra, and data of thermogravimetric, conductometric, and magnetochemical measurements. Copper(II) acetate with benzoin (phthalazin-1-yl)hydrazone forms dinuclear complex, nickel(II) acetate and chloride produce mononuclear octahedral complexes, and copper(II) halides give rise to copper(I) complexes with the oxidized hydrazone.

DOI: 10.1134/S1070363209040240

Benzoin hydrazones belong to a fairly poorly explored group of ligand systems. The hydroxy group in benzoin and its condensation products may be regarded as alcoholic rather than phenolic (as in salicylaldehyde hydrazones); therefore, it is considerably less acidic. However, unlike α-diketone hydrazones, semicarbazones and acylhydrazones derived from benzoin are capable of coordinating metal ions as both singly and doubly deprotonated species [1–4]. Benzoin hetarylhydrazone complexes have not been reported; on the other hand, the available published data indicate that the presence of a heteroaromatic fragment in a ligand molecule could strongly affect both structure and magnetic properties of complexes based thereon [5–8]. As subjectes for study we selected benzoin (phthalazin-1-yl)hydrazone (**I**) and its copper(II) and nickel(II) complexes.

As shown in [9, 10], hydrazones derived from phthalazin-1-ylhydrazine exist as the corresponding 1,2-dihydrophthalazin-1-ylidene tautomers; this was also confirmed by X-ray analysis of some hydrazones and their complexes [11, 12]. The complexes were synthesized according to the scheme shown below.



Hydrazone **I** was identified by the data of elemental analysis (Table 1) and IR and ^{1}H NMR spectroscopy. The following absorption bands were observed in the IR spectrum of hydrazone **I**: slightly broadened band at 3269 cm^{-1} was assigned to stretching vibrations of the O–H group, N–H bond gave a band at 3325 cm^{-1}, stretching vibrations of the azomethine C=N bond appeared at 1677 cm^{-1}, two bands at 1591 and 1570 cm^{-1}

Table 1. Colors, melting points, elemental analyses, and molar conductivities of compounds **I–V**

Comp. no.	Color	mp, °C	Found/calculated, %				Formula	λ, Ω^{-1} cm^3 mol^{-1}
			C	H	N	*M*		
I	Yellow	218	73.7/74.6	4.99/5.12	16.1/15.8	–	$C_{22}H_{18}N_4O$	–
II	Brown	>250	62.5/63.5	4.09/3.88	13.8/13.5	14.9/15.3	$C_{22}H_{16}CuN_4O$	3.0
III	Brown–green	>250	57.3/56.8	4.50/4.77	12.8/12.0	13.7/12.6	$C_{22}H_{22}NiN_4O_4$	8.6
IV	Yellow	>250	66.9/66.6	5.35/5.10	13.1/13.5	7.30/7.08	$C_{46}H_{42}NiN_8O_4$	4.6
Va	Yellow	>250	50.2/49.9	3.02/2.79	15.1/15.5	16.9/17.6	$C_{15}H_{10}ClCuN_4O$	6.8
Vb	Yellow	>250	43.9/44.4	2.70/2.48	14.2/13.8	15.4/15.7	$C_{15}H_{10}BrCuN_4O$	7.5

corresponded to C=N bonds in the heterocyclic fragment, and stretching vibrations of the C–O bond had a frequency of 1254 cm^{-1} [13–16].

The ^{1}H NMR spectrum of hydrazone **I** in DMSO-d_6 contained the following signals, δ, ppm: 7.24–7.69 (10H, Ph), 6.58 d (1H, OH, J = 6.3 Hz), 6.9 d (1H, CH, J = 6.3 Hz), 11.78 s (1H, NH), 8.27 d (1H, 8-H, J = 7.8 Hz), 7.89 m (3H, 5-H, 6-H, 7-H), 8.00 br.s (1H, 4-H). The chemical shift of the hydroxy proton suggests a weak acidity of the hydroxy group; nevertheless, both NH and OH signals disappeared upon addition of D_2O. The downfield position of the NH signal confirms the assumed structure of hydrazone **I** as 1,2-dihydrophthalazin-1-ylidene tautomer.

The electronic absorption spectra of hydrazone **I** displayed a distinct dependence of the spectral pattern on the solvent nature and pH value. A 20-nm blue shift of the long-wave absorption maximum (λ 350 nm) was observed in aqueous ethanol at pH < 5; this means that the hydrazone molecule is protonated [1–3]; no deprotonation occurred in the pH range from 5 to 12.

Analysis of the IR and NMR spectra of hydrazone **I** led us to presume that its deprotonation should involve proton abstraction from the phthalazine rather than benzoin fragment. This distinguishes compound **I** from well studied salicylaldehyde hydrazones and related structures in which the OH group is deprotonated much more readily than the NH group [1, 3, 4]. The same follows from the ionization constants of hydrazone **I**, calculated by quantum-chemical method according to the procedure described in [17]: the pK_{a1} and pK_{a2} values were estimated at 10.89 and 20.67, respectively, and the first ionization step corresponds to proton abstraction from the NH group (Table 2). According to the calculations, the most favorable conformer of neutral hydrazone **I** has structure **A** stabilized by two hydrogen bonds (Fig. 1).

Coordination compounds based on hydrazone **I** were synthesized according to the scheme given above. Their structure was determined on the basis of their elemental compositions (Table 1) and conductometric (Table 1), IR spectral, and magnetochemical data (Table 3).

Complex **II** obtained from hydrazone **I** and copper(II) acetate had a composition of 1:1 (CuL, Table 1). Its thermogravimetric analysis revealed no endothermic effects in the temperature range from 120 to 180°C; i.e., no inner-sphere solvent molecules were present in complex **II** [13, 18]. Thermooxidative decomposition of the ligand occurs at 240–400°C. Measurement of the electric conductivity of a 0.001 M solution of complex **II** in DMF showed that it is a nonelectrolyte [19].

Table 2. Total energies (E), energies of zero-point vibrations (E_0), differences in the Gibbs energies at 0 and 298 K ($\Delta G_{0\to298}$), and energies of solvattion (ΔG_s) of neutral (**A**), singly deprotonated (**B**) and doubly deprotonated (**C**) forms of hydrazone **I** and calculated ΔG_c^0 and pK_a values of structures **A** and **B**

Species	ΔG_s, kcal mol^{-1}	E, hartree	E_0, hartree	$\Delta G_{0\to298}$, hartree	ΔG_c^0, kcal mol^{-1}	pK_a
A	–15.95	–1143.642041	0.356799	193.60	–14.9	10.89
B	–63.68	–1143.082478	0.341025	183.85	–28.2	20.67
C	–181.45	–1142.383435	0.323762	170.89		

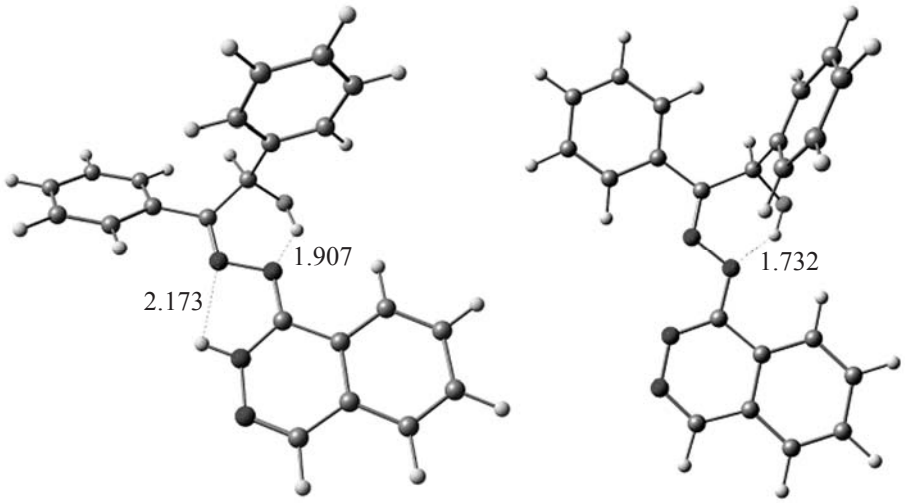
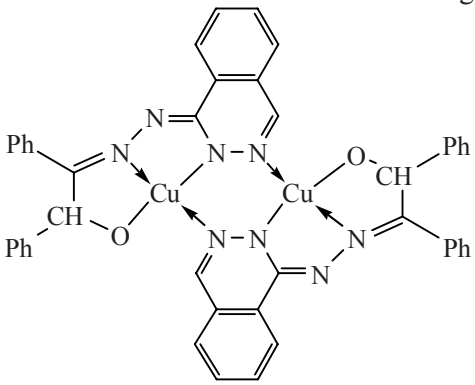


Fig.1. Preferential conformations of the neutral (**A**) and singly deprotonated forms (**B**) of hydrazone **I**.

The IR spectrum of complex **II** lacked absorption bands typical of OH and NH stretching vibrations, while the band belonging to the azomethine C=N bond slightly displaced to lower frequencies (1655 cm^{-1}); the positions of absorption bands due to heterocyclic C=N bonds and C–O remained almost unchanged.



II

Table 3. Magnetic properties of complexes **II–V**

Compound no.	Temperature, K	μ_{eff},[b] B.M.
II[a]	293, 77.4	1.88, 1.28
III	293, 77.4	2.96, 2.90
IV	293, 77.4	2.90, 2.87
Va	295	Diamagnetic
Vb	295	Diamagnetic

[a] Exchange parameter $2J = -93$ cm^{-1}; $g = 2.20$. [b] Calculated per copper ion.

Measurement of the magnetic susceptibility of complex **II** in the solid phase by the Faraday method showed that its magnetic moment decreases from 1.85 B.M. at room temperature to 1.28 B.M. at –196°C (nitrogen boiling point). These data suggest the existence of moderate antiferromagnetic exchange interaction; therefore, complex **II** is a dimer. We succeeded in satisfactorily interpreting the temperature dependence of magnetic susceptibility of complex **II** in terms of the Heisenberg–Dirac–Van Vleck isolated exchange cluster model [20–23]. The antiferromagnetic exchange coupling parameter $2J$ was calculated using modified Bleaney–Bowers Eq. (1) which takes into account the presence of some paramagnetic impurity in the complex [20, 21].

$$\chi'_M = \frac{2N_A g^2 \beta^2}{3kT}\left\{(1-f)\left[1+\frac{1}{3}\exp\left(\frac{-2J}{kT}\right)^{-1} + fS(S+1)\right\} + N_\alpha. \quad (1)$$

Here, χ'_M is the molar magnetic susceptibility corrected for diamagnetism of atoms according to the Pascal model [20], f is the mole fraction of a paramagnetic impurity, and N_α is the temperature-independent paramagnetism which was assumed to be equal to 60×10^{-6} for Cu(II) ion.

The presence of several donor centers in the ligand molecule provides the possibility for several mode of dimerization of the complexes, in particular through nitrogen atoms in the phthalazine fragment with

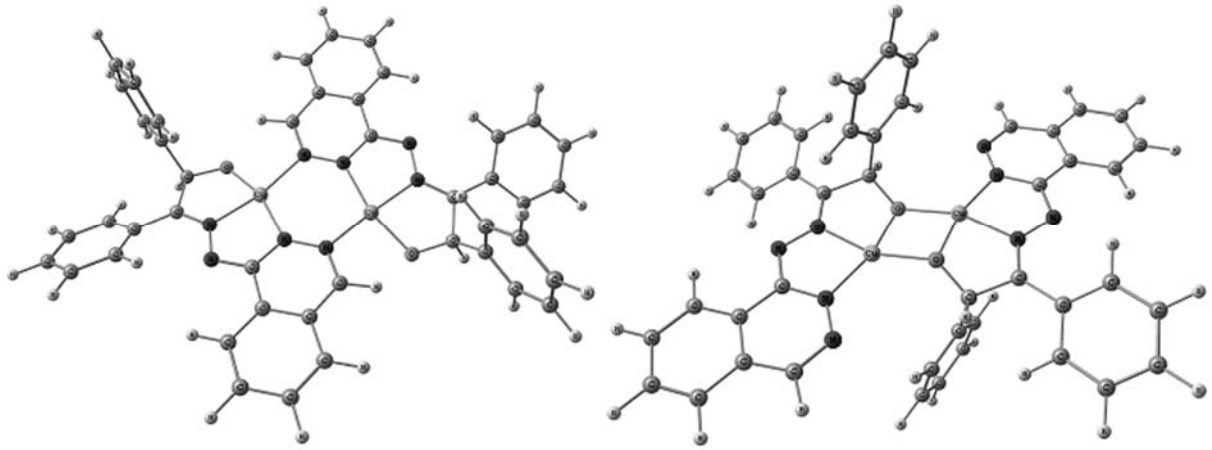
formation of six-membered $Cu_2(NN)_2$ exchange entity (**D**) or through oxygen atoms in the benzoin fragment with formation of four-membered Cu_2O_2 exchange entity (**E**). The energies of isomeric structures **D** and **E** were calculated in terms of the density functional theory (DFT). The results are shown in Fig. 2. It is seen that dimerization through the phthalazine nitrogen atoms (structure **D**) is more favorable (by 2.35 kcal mol^{-1}).

The exchange parameter $2J$ in complex **II** is -93 cm^{-1}. On the other hand, some dimeric copper complexes with bridging nitrogen atoms belonging to phthalazine or pyridazine fragment showed strong antiferromagnetic exchange characterized by a $2J$ value of -300 to -450 cm^{-1} [24, 25]. The low exchange parameter suggests that the exchange moiety in dimeric complex **II** is nonplanar [7, 8]. In fact, DFT calculations showed that the planes of the monomer fragments are turned with respect to each other by an angle of about 15° due to steric repulsion of hydrogen atoms in position *4* of the phthalazine rings and donor oxygen atoms.

The reaction of hydrazone **I** with nickel(II) acetate and chloride gave complexes $NiL(H_2O)_3$ (**III**) and $Ni(HL)_2(MeOH)_3$ (**IV**), respectively (here, L^{2-} and HL^- are, respectively, doubly and singly deprotonated hydrazone **I** species). Both these complexes are nonelectrolytes (Table 1); their effective magnetic moments are 2.96 and 2.90 B.M., respectively, and are almost independent of temperature. Thermogravimetric analysis of complexes **III** and **IV** revealed endothermic effects in the temperature range from 120–160°C with weight loss corresponding to elimination of inner-sphere water or methanol molecules, res-pectively [13, 18]; thermooxidative decomposition of the ligand was observed at 240–400°C.

According to the IR data, nickel(II) acetate and chloride coordinate, respectively, doubly and singly deprotonated ligand. The IR spectrum of **IV** contains a broad absorption band at 3370 cm^{-1} due to coordinated methanol molecules and a band at 3251 cm^{-1} due to stretching vibrations of the OH group in the ligand. In the IR spectrum of **III** we observed only a broad band with its maximum at 3391 cm^{-1}, which was assigned to coordinated water molecules.

The assumed structures of nickel(II) complexes **III** and **IV** are shown below.



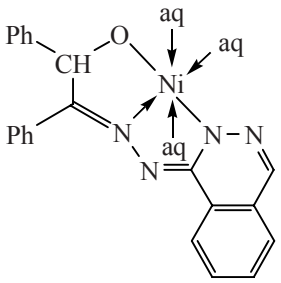
D

E = –5593.158149 au,
ΔE= 0.0 kcal mol^{-1}

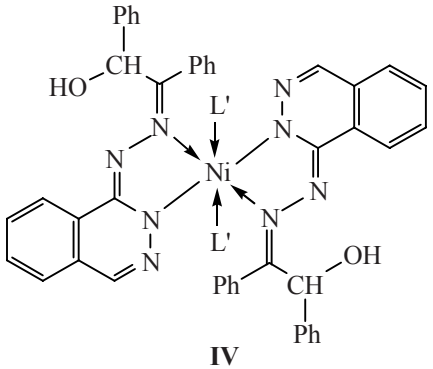
E

E = –5593.154408 au,
ΔE = 2.35 kcal mol^{-1}

Fig. 2. Probable structures (**D**, **E**) of dinuclear copper(II) complex with hydrazone **I**; total energies (E) and relative stabilities (ΔE) are given.



III



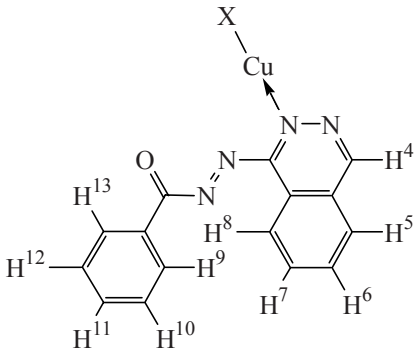
IV

L' = CH_3OH.

Hydrazone **I** reacted with copper(II) chloride and bromide in a quite different mode than with copper(II) acetate or nickel(II) chloride. After addition of copper (II) halide to a solution of hydrazone **I**, the mixture turned colorless, and a weakly colored solid separated. Its elemental composition, IR spectrum, and magnetic properties sharply differed from those found for the other examined complexes. The complexes obtained from hydrazone **I** and copper(II) chloride and bromide had the compositions $C_{15}H_{10}ClCuN_4O$ and $C_{15}H_{10}BrCuN_4O$, respectively. According to the data of thermogravimetric analysis, the complexes contained no solvent molecules. Measurement of the conductivity of their 0.001 M solutions in DMF showed that these complexes are nonelectrolytes; this means that the halide ions therein are coordinated in non-ionogenic mode [19].

The IR spectra of the complexes contained an absorption band at 1710 cm^{-1}, which was absent in the spectrum of initial hydrazone **I**; this band may be attributed to stretching vibrations of carbonyl group. By contrast, no band at 1250 cm^{-1} typical of C–O stretching vibrations was observed. The complexes were diamagnetic, i.e., copper(II) ion was reduced to copper(I). Therefore, we were able to examine them by ^{1}H NMR spectroscopy. The ^{1}H NMR spectra of both complexes were very similar, indicating formation of the same oxidation product from hydrazone **I**. The spectra displayed signals belonging to 10 protons. The above findings allowed us to presume that the complexation products of hydrazone **I** with copper(II) chloride and bromide have structure **V**.

In the ^{1}H NMR spectrum of complex **Va** in DMSO-d_6 all signals were broadened due to the presence of a small amount of a paramagnetic impurity. Protons in



V, X = Cl (**a**), Br (**b**).

the phthalazine fragment of **Va** resonated at δ, ppm: 9.05 s (1H, 4-H), 8.74 br.s (1H, 8-H), 8.18 d (1H, 5-H, J = 6.7 Hz), 8.02 d.d (1H, 7-H, J = 7.6 Hz), 7.86 d (1H, 6-H, J = 7.6 Hz); phenyl proton signals: 8.39 br.s (2H, 9-H, 13-H), 7.50 m (3H, 10-H, 11-H, 12-H). ^{1}H NMR spectrum of **Vb**, ppm: 9.18 s (1H, 4-H), 8.61 d (1H, 8-H, J = 7.9 Hz), 8.26 d (1H, 5-H, J = 7.6 Hz), 8.09 d.d (1H, 7-H, $J_1 = J_2$ = 7.6 Hz), 7.96 d.d (1H, 6-H, $J_1 = J_2$ = 7.5 Hz); 8.34 d (2H, 9-H, 13-H, J = 7.2 Hz), 7.60 m (3H, 10-H, 11-H, 12-H).

However, the obtained data did not allow us to unambiguously determine which donor centers in the hydrazone residue are involved in coordination to copper(I) ion. The position of the carbonyl absorption band (1710 cm^{-1}) suggests that the carbonyl oxygen atom is not coordinated to copper(I); therefore, the donor center is either azomethine or heterocyclic nitrogen atom or both these simultaneously. Presumably, the hydrazone residue in complexes **Va** and **Vb** acts as a unidentate ligand, and the coordination number of copper ion is equal to 2.

A probable reason for the observed differences in the reactivities of hydrazone **I** toward copper(II) and nickel(II) acetates, on the one hand, and copper(II) halides, on the other, is as follows. Copper(II) and nickel(II) acetates are involved in coordination with doubly deprotonated hydrazone. It is well known that the nature of metal salt determines the degree of ligand deprotonation in complex formation with salicylaldehyde hydrazones: metal salts derived from strong acids give rise to complexes containing singly deprotonated hydrazone species as ligand, whereas complexes obtained from metal salts with weak acids contain doubly deprotonated ligand species [4, 26, 27]. Presumably, oxidation of the benzoin fragment with copper(II) ion occurs upon coordination with the ligand with non-ionized hydroxy group, which is possible in the reaction of hydrazone **I** with copper(II) chloride and bromide. Analogous process is likely to occur in the reactions of hydrazone **I** with copper(II) nitrate and perchlorate; the latter, being salts of strong acids, should also stabilize singly deprotonated hydrazone species. In these reactions we obtained samples containing mixtures of copper(II) and copper(I) complexes, but we failed to isolate pure diamagnetic complexes suitable for NMR study.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Varian Unity 300 (300 MHz) spectrometer with Fourier transform using DMSO-d_6 as solvent and hexamethyldisiloxane as internal reference. The IR spectra were measured on a Varian Scimitar instrument in the frequency range from 400 to 4000 cm^{-1}; samples were prepared as suspensions in mineral oil and fluorinated hydrocarbons. The electronic absorption spectra were obtained on a Unicam Helios Gamma spectrophotometer in the λ range from 195 to 1100 nm; acetone, acetonitrile, dioxane, DMSO, DMF, methanol, ethanol, carbon tetrachloride, and chloroform were used as solvents ($c = 10^{-5}$ M); cell path length 1 cm.

Thermal gravimetric analysis of the complexes was performed on a Diamond TG/DTA instrument (Perkin–Elmer, Japan). Samples were heated to 650°C at a rate of 10 deg/min. The molar conductivities of 0.001 M solutions of the complexes in DMF were measured using an R-38 rheocord bridge.

The specific magnetic susceptibilities were determined by the relative Faraday method in the temperature range from 80 to 300 K at a magnetic field strength of 9000 Oe; the setup was calibrated against $HgCo(CNS)_4$. The temperature dependences of the magnetic susceptibilities of the dinuclear complexes were interpreted in terms of the Heisenberg–Dirac–Van Vleck isotropic exchange model [20–23]. The exchange coupling parameters for the dinuclear copper complexes were calculated using Bleaney–Bowers equation (1).

Quantum-chemical calculations of the ligands and coordination compounds were performed in terms of the density functional theory (DFT) with Perdew–Burke–Ernzerhof potential [29] using PRIRODA software [30]. A three-exponent sent of Gauss functions was used as calculation basis set. The geometric parameters of model structures were optimized with respect to all natural coordinates without symmetry constraints. No scaling factor was applied to normal vibration frequencies.

The energies of solvation (ΔG_s) of neutral and ionized species were calculated in terms of the polarized continuum model (PCM) [31, 32] with account taken of dispersion contribution using PCGAMESS program [33] (DFT, B3LYP/6-311G(*d*,*p*). The energies of solvation were calculated after preliminary optimization of geometric parameters of molecules and ions in solution. The calculated energies of solvation are given in Table 2. The equilibria involving isomeric structures **D** and **E** of copper(II) complex **II** were examined assuming triplet electronic states.

Hydrazone (I) was synthesized from commercial benzoin and phthalazin-1-ylhydrazine hydrochloride. A hot solution of 0.01 mol of benzoin was added to a hot suspension of 0.01 mol of phthalazin-1-ylhydrazine hydrochloride in 50 ml of methanol. After 5 min, an equivalent amount of sodium acetate was added, and a bright yellow solid immediately began to separate. The mixture was heated for 3 h under reflux and left overnight, and the precipitate was filtered off, washed first with two portions of warm water and then with hot methanol, and recrystallized from methanol–DMF (2:1). Yield 65%, bright yellow amorphous powder, mp 218–219°C. The product was poorly soluble in alcohol, chloroform, and dioxane and insoluble in water and benzene.

Complexes of transition metals with hydrazone I. A hot solution of 0.001 mol of the corresponding copper(II) or nickel(II) salt in methanol was added to a hot suspension of 0.001 mol of hydrazone **I** in 20 ml of

methanol. The mixture changed its color, and hydrazone **I** dissolved. The mixture was heated for 3 h under reflux, and the precipitate was filtered off, washed with hot methanol, and recrystallized from dioxane or methanol–DMF. The elemental compositions, melting points, and colors of the complexes, as well as molar conductivities of their 0.001 M solutions in DMF, are collected in Table 1.

ACKNOWLEDGMENTS

This study was performed under financial support by the Russian Foundation for Basic Research (project no. 08-03-91316-IND_a) and by the Southern Federal University (internal project).

REFERENCES

1. Parpiev, N.A., Yusupov, V.G., Yakimovich, S.I., and Sharipov, Kh.G., *Atsilgidrazony i ikh kompleksy s perekhodnymi metallami* (Acylhydrazones and Their Complexes with Transition Metals), Tashkent: Fan, 1988.
2. Kogan, V.A., Zelentsov, V.V., Larin, G.M., and Lukov, V.V., *Kompleksy perekhodnykh metallov s gidrazonami. Fiziko-khimicheskie svoistva i stroenie* (Transition Metal Complexes with Hydrazones. Physicochemical Properties and Structure), Moscow: Nauka, 1990.
3. Mahapatra, B.B., Mahapatra, B.K., and Guru, S., *J. Inorg. Nucl. Chem*., 1977, vol. 39, no. 12, p. 2291.
4. Akinchan, N.T., Akinchan, R., West, D.X., and Yang, Y.-H., *Transition Met. Chem*., 1994, vol. 19, no. 2, p. 135.
5. Tupolova, Yu.P., Lukov, V.V., Kogan, V.A., Popov, L.D., Tkachev, V.V., and Chekhlov, A.N., *Zh. Neorg. Khim*., 2003, vol. 48, no. 11, p. 1780.
6. Abramenko, V.L., Garnovskii, A.D., and Abramenko, Yu.V., *Koord. Khim*., 1994, vol. 20, no. 1, p. 39.
7. Kogan, V.A. and Lukov, V.V., *Koord. Khim*., 1993, vol. 19, no. 6, p. 476.
8. Kogan, V.A. and Lukov, V.V., *Koord. Khim*., 1997, vol. 23, no. 1, p.18.
9. Nakashima, K., Shimada, K., and Akiyama, S., *Chem. Pharm. Bull*., 1985, vol. 33, no. 4, p. 1515.
10. Bystrykh, N.N., Buzykin, B.I., Stolyarov, A.P., Flegontov, S.A., Zverev, V.V., and Kitaev, Yu.P., *Khim. Geterotsikl. Soedin*., 1976, no. 3, p. 402.
11. Paolucci, G., Stelluto, S., Sitran, S., Ajo, D., Benetollo, F., Polo, A., and Bombieri, G., *Inorg. Chim. Acta*, 1992, vol. 57, no. 1, p. 193.
12. Giorgi, G., Ponticelli, F., Chiasserini, L., and Pellerano, C., *J. Chem. Soc., Perkin Trans. 2*, 2000, p. 2259.
13. Samus', N.M., Tsapkov, V.I., and Kravchenko, V.N., *Russ. J. Gen. Chem*., 1997, vol. 67, no.12, p. 1929.
14. Paolucci, G., Stelluto, S., Sitran, S., Ajo, D., Benetollo, F., Polo, A., and Bombieri, G., *Inorg. Chim. Acta*, 1992, vol. 57, no. 1, p. 193.
15. Odashima, T., Yamada, M., Yonemori, N., and Ishii, H., *Bull. Chem. Soc. Jpn*., 1987, vol. 60, no. 9, p. 3225.
16. Moshon, M.C., Gallego, M.C., and Perez, A.G., *Talanta*, 1986, vol. 33, no. 7, p. 627.
17. Popov, L.D., Levchenkov, S.I., Shcherbakov, I.N., and Kogan, V.A., *Russ. J. Gen. Chem*., 2007, vol. 77, no. 7, p. 1284.
18. Kukushkin, Yu.N., Khodzhaev, O.F., Budanova, V.F., and Parpiev, N.A. *Termoliz koordinatsionnykh soedinenii* (Thermolysis of Coordination Compounds), Tashkent: Fan, 1986.
19. Geary, W.J., *Coord. Chem. Rev*., 1971, vol. 7, no. 1, p. 81.
20. Kalinnikov, V.T. and Rakitin, Yu.V., *Vvedenie v magnetokhimiyu* (Introduction to Magnetochemistry), Moscow: Nauka, 1980.
21. Rakitin, Yu.V. and Kalinnikov, V.T., *Sovremennaya magnetokhimiya* (Modern Magnetochemistry), St. Petersburg: Nauka, 1994.
22. Rakitin, Yu.V., *Itogi Nauki Tekh. Stroen. Mol. Khim. Svyaz'*, 1986, vol. 10, p. 132.
23. Kalinnikov, V.T., Rakitin, Yu.V., and Novotortsev, V.M., *Usp. Khim*., 2003, vol. 72, no. 12, p. 1123.
24. Tandon, S.S., Thompson, L.K., and Hynes, R.C., *Inorg. Chem*., 1992, vol. 31, no. 11, p. 2210.
25. Brooker, S., Davidson, T.C., Hay, S.J., Kelly, R.J., Kennepohl, D.K., Pliege, P.G., Moubaraki, B., Murray, K.S., Bill, E., and Bothe, E., *Coord. Chem. Rev*., 2001, vols. 216–217, p. 3.
26. Levchenkov, S.I., Shcherbakov, I.N., Lukov, V.V., and Kogan, V.A., *Koord. Khim*., 1997, vol. 23, no. 4, p. 293.
27. Lukov, V.V., Levchenkov, S.I., Shcherbakov, I.N., and Kogan, V.A., *Koord. Khim*., 1997, vol. 23, no. 7, p. 544.
28. Levchenkov, S.I., Lukov, V.V., Shcherbakov, I.N., and Kogan, V.A., *Koord. Khim*., 1998, vol. 24, no. 5, p. 354.
29. Perdew, J.P., Burke, K., and Ernzerhof, M., *Phys. Rev. Lett*., 1996, vol. 77, no. 18, p. 3865.
30. Laikov, D.N., *Chem. Phys. Lett*., 1997, vol. 281, nos. 1–3, p. 151.
31. Miertus, S., Scrocco, E., and Tomasi, J., *Chem. Phys*., 1981, vol. 55, no. 1, p. 117.
32. Cammi, R. and Tomasi, J., *J. Comput. Chem*., 1995, vol. 16, no. 12, p. 1449.
33. Granovsky, A., *PC GAMESS version 7.0*, *http://classic.chem.msu.su/gran/gamess/index.html*; Nemukhin, A.V., Grigorenko, B.L., and Granovsky, A.A., *Moscow Univ. Chem. Bull*., 2004, vol. 45, no. 2, p. 75.