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Protolytic Properties of 8-Quinolylhydrazones of Substituted Salicylaldehydes and Physicochemical Properties of Their Copper(II) Complexes

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Abstract—Acid–base properties of hydrazones derived from 8-hydrazinoquinoline and substituted salicylaldehydes were studied. Under the experimental conditions, only the first step of ionization of the hydrazones is realized. The ionization constants were calculated quantum-chemically. Copper(II) complexes of these hydrazones, $(HL)Cu(X)(CH_3OH)_n$, were isolated (HL^- is the monodeprotonated form of hydrazones, and X^- is the acid residue). According to the data of elemental analysis, IR spectroscopy, conductometry, and magnetochemistry, the majority of the complexes have a binuclear structure. The copper(II) ions in the dimeric complex show antiferromagnetic exchange coupling. The ionization constants of the hydrazones and the exchange parameters strongly depend on the substituent in the salicylaldehyde moiety.

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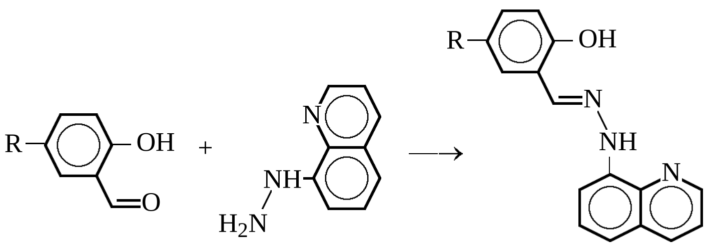
Hydrazones of polyfunctional carbonyl compounds are of particular interest for coordination chemistry of transition metals. Acting as ligands, these compounds readily form complexes with the majority of transition metals [1–3]. Binuclear complexes with such ligand systems are good models for studying exchange effects between paramagnetic centers; particularly convenient in this respect are salicylaldehyde hydrazones whose structure favors the formation of binuclear complexes with many transition metals [2, 3]. The possibility of the bi- or tridentate coordination of salicylaldehyde hydrazones in one of the tautomeric forms predetermines in this case the diversity of forms of the isolated complexes whose structure depends on the synthesis conditions and on the central metal ion [4–8]. Variation of the reaction conditions allows preparation of complexes containing mono- and double-deprotonated hydrazone residues [9–11]. Relatively numerous studies of the magnetic properties of complexes of transition metals, primarily copper(II), with ligands of this type led to some important conclusions allowing prediction of the structure and magnetic properties of the complexes [12–14]. One more reason for the researchers' interest in salicylaldehyde hydrazones is the biological activity of both the free hydrazones and their complexes [1–3, 10, 15–17].

By now, numerous data have been accumulated on the structure and physicochemical properties of complexes based on salicylaldehyde acylhydrazones. It should be noted, however, that coordination compounds of transition metals with salicylaldehyde hetarylhydrazones have been studied to a considerably lesser extent than complexes with acylhydrazones. At the same time, the presence of a heteroaromatic fragment in the ligands significantly affects both the structure of the complexes and their magnetic properties [7, 12–14]. Until now, there have been no systematic studies of the acid–base properties of salicylaldehyde hetarylhydrazones, despite the fact that these properties strongly affect the structure and stability of the coordination compounds of the hydrazones. The goal of this study was to obtain new data on the effect exerted by heterocyclic fragments of hydrazones of substituted salicylaldehydes on the protolytic and complexing properties of the hydrazones, and also on the structure of the complexes formed and on the exchange coupling between the copper(II) ions in the binuclear complexes.

8-Quinolylhydrazones of Substituted Salicylaldehydes

Hydrazones **I** were prepared by the scheme shown below and were identified by elemental analysis and by NMR and IR spectroscopy. The analytical data are given in Table 1.



I, R = H, 5-OCH_3, 3-Br, 5-NO_2, 5,6-benzo.

The following signals, δ, ppm (*J*, Hz), are observed in the ^1H NMR spectra of hydrazones **I**.

Hydrazone **I** with R = H: aromatic protons of the salicylaldehyde moiety: 6.84 d.d (1H, *J* 7.5, 1.6), 6.88 d (1H, *J* 8.2), 7.15 d.d.d (1H, *J* 8.2, 8.0, 1.5), 7.37 d.d (1H, *J* 7.5, 1.5); aromatic protons of the quinoline fragment: 7.25 d (1H, *J* 8.4), 7.29 d (1H, *J* 8.6), 7.44–7.55 m (2H), 8.21 d (1H, *J* 8.3), 8.81 d.d (1H, *J* 4.2, 1.5); CH (azomethine) 8.57 s (1H); NH 10.70 s (1H); OH 10.89 s (1H).

Hydrazone **I** with R = 5-OCH_3: aromatic protons of the salicylaldehyde fragment: 6.78 d (1H, *J* 8.0), 6.72 d.d (1H, *J* 8.8, 2.9), 6.93 d (1H, *J* 2.9); aromatic protons of the quinoline fragment: 7.25 d (1H, *J* 8.1), 7.31 d (1H, *J* 7.4), 7.44–7.52 m (2H), 8.19 d.d (1H, *J* 8.3, 1.4), 8.79 d.d (1H, *J* 4.1, 1.4); CH (azomethine) 8.50 s (1H); NH 10.30 s (1H); OH 10.63 s (1H).

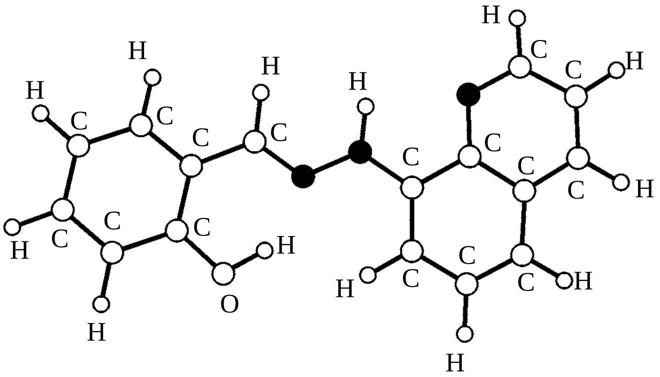
Hydrazone **I** with R = 5,6-benzo: aromatic protons of the naphthyl fragment: 7.26–7.36 m (2H), 7.48–7.56 m (2H), 7.76–7.80 m (1H), 8.24–8.30 m (1H); aromatic protons of the quinoline fragment: 7.18 d (1H, *J* 8.8), 7.28 d (1H, *J* 8.3), 7.48–7.56 m (2H), 7.76 d (1H, *J* 9.4), 8.85 d.d (1H, *J* 4.1, 1.6); CH (azomethine) 9.62 s (1H); NH 10.89 s (1H); OH 12.23 s (1H).

The hydrazones of type **I** can exist in solution in the protonated, molecular, and anionic forms, depending on the acidity. Presumably, in acidic solutions the N atoms of the hydrazide moiety are the protonation sites; ionization of the ligands apparently occurs as successive elimination of the phenolic and hydrazine protons. To evaluate the acid–base properties of hydrazones **I**, we performed potentiometric titration of aqueous-alcoholic solutions of compounds **I** with R = H and OCH_3 (the solubility of the other compounds was insufficient) and of solutions of hydrazones **I** in 70% dioxane (Table 2).

As expected, electron-donor substituents in the salicylaldehyde moiety increase pK_a, and electron-acceptor substituents decrease it. The increase in pK_a in going from aqueous-alcoholic to aqueous-dioxane solutions is due to properties of these solvents. The dependence of pK_a on the substituents suggests that

Table 1. Analytical data for compounds of types **I**–**IV**

Compound type	R	X	Formula	Found (calculated), %			
				C	H	N	M
I	H	–	$C_{16}H_{13}N_3O$	73.5 (73.0)	5.3 (4.98)	15.4 (16.0)	–
I	5-OCH_3	–	$C_{17}H_{15}N_3O_2$	69.1 (69.6)	5.0 (5.15)	15.3 (14.3)	–
I	5-Br	–	$C_{16}H_{12}BrN_3O$	56.9 (56.2)	3.8 (3.53)	13.5 (12.3)	–
I	5,6-Benzo	–	$C_{20}H_{17}N_3O$	75.7 (76.2)	5.9 (5.43)	12.5 (13.3)	–
I	5-NO_2	–	$C_{16}H_{12}N_4O_3$	62.9 (62.3)	4.1 (3.92)	18.9 (18.2)	–
II	5-NO_2	NO_3	$C_{17}H_{15}CuN_5O_7$	43.3 (43.9)	3.33 (3.25)	15.4 (15.1)	13.8 (13.7)
III	H	NO_3	$C_{34}H_{32}Cu_2N_8O_{10}$	48.9 (48.6)	3.92 (3.84)	13.6 (13.3)	15.0 (15.1)
III	5-OCH_3	NO_3	$C_{36}H_{36}Cu_2N_8O_{12}$	47.6 (48.0)	3.97 (4.03)	12.0 (12.4)	14.0 (14.1)
III	5-Br	NO_3	$C_{34}H_{30}Br_2Cu_2N_8O_{10}$	41.4 (40.9)	3.12 (3.03)	11.8 (11.2)	12.6 (12.7)
III	5,6-Benzo	NO_3	$C_{42}H_{40}Cu_2N_8O_{10}$	54.0 (53.4)	4.34 (4.27)	11.4 (11.9)	13.8 (13.5)
III	5-Br	ClO_4	$C_{34}H_{30}Br_2Cl_2Cu_2N_6O_{12}$	38.6 (38.1)	2.93 (2.82)	7.77 (7.84)	11.7 (11.9)
IV	5-Br	Cl	$C_{34}H_{30}Br_2Cl_2Cu_2N_6O_4$	43.8 (43.2)	3.34 (3.20)	8.74 (8.90)	13.5 (13.5)
IV	5-Br	Br	$C_{34}H_{30}Br_4Cu_2N_6O_4$	40.2 (39.5)	2.99 (2.93)	8.01 (8.13)	12.0 (12.3)



The most favorable conformations of the neutral form and anion of hydrazone **I** with R = H.

the ionization site in the compounds is the phenolic group. Only the first step of the ionization of hydrazones **I** is realized under the experimental conditions; the hydrazine proton is not abstracted in the course of titration to pH 13.

A quantum-chemical calculation of pK_a was performed for aqueous solution, because the set of semiempirical constants describing the solvent in the polarizable continuum model (PCM) is the most developed specifically for aqueous solutions. The results are listed in Table 2.

The values of pK_a were calculated by Eq. (1) for T 298.15 K:

$$\mathrm{p}K_a = \Delta G_w^0/2.303RT. \quad (1)$$

The standard free energy of the ionization in aqueous solution, ΔG_w^0, was determined from the following thermodynamic cycle:

$$\begin{tikzcd}
AH(g) \arrow[r, "\Delta G_g^0"] & A^-(g) \arrow[d, "\Delta G_s(A^-)"'] + & H^+(g) \arrow[d, "\Delta G_s(H^+)"] \\
AH(w) \arrow[u, "-\Delta G_s(AH)"] \arrow[r, "\Delta G_w^0"] & A^-(w) + & H^+(w)
\end{tikzcd}$$

The free energies (G_g) of the molecules and anions in the gas phase (AH, A^-) at T 298.15 K were calculated as the total energies of the optimized geometric structures corresponding to the global minimum on the potential energy surface of the corresponding species (E), taking into account the zero-point vibration energy (E_0) and the free energy of the transition from T 0 K to T 298.15 K ($\Delta G_{0\rightarrow 298}$):

$$G_g = E + E_0 + \Delta G_{0\rightarrow 298}. \quad (2)$$

Table 2. Total energy (E, hartree), zero-point vibration energy (E_0, hartree), free energy of the transition from T 0 K to T 298 K ($\Delta G_{0\rightarrow 298}$, hartree), and energy of solvation (ΔG_s, kcal mol^{-1}) of the neutral (HA) and ionized (A^-) forms; calculated ΔG_w^0 (kcal mol^{-1}) and pK_a of the ionization

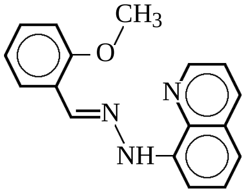
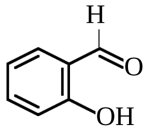
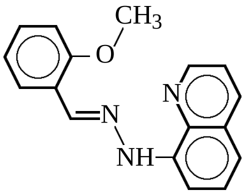
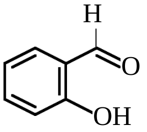
Compound	HA			
	ΔG_s	E	E_0	$\Delta G_{0\rightarrow 298}$
I, R = H	–37.80	–856.714428	0.252844	0.209748
I, R = 5-NO_2	–50.13	–1061.270860	0.255180	0.208296
I, R = 5-OCH_3	–42.64	–971.226285	0.284567	0.238733
I, R = 5-Br	–35.94	–3462.645669	0.243064	0.197308
I, R = 5,6-benzo	–40.01	–1010.285752	0.280082	0.230443
	–43.45	–895.975107	0.298698	0.249949
C_6H_5OH	–18.80	–307.369764	0.102026	0.072916
	–20.61	–420.712779	0.112104	0.080806

Table 2. (Contd.)

Compound	A$^-$				ΔG_w^0	pK_a	pK_a^{exp}
	ΔG_s	E	E_0	$\Delta G_{0\to 298}$			
I, R = H	–83.85	–856.161441	0.238110	0.192965	12.31	9.03	9.72 (ethanol–water) 10.56 (dioxane)
I, R = 5-NO_2	–84.52	–1060.743423	0.241328	0.191449	8.46	6.20	9.44 (dioxane)
I, R = 5-OCH_3	–89.51	–970.670188	0.269708	0.220997	12.77	9.36	10.10 (ethanol–water) 10.62
I, R = 5-Br	–78.59	–3462.101187	0.228554	0.179022	9.57	7.02	9.70 (dioxane)
I, R = 5,6-benzo	–85.37	–1009.741109	0.283955	0.234850	12.26	8.99	10.09 (dioxane)
	–84.25	–895.409821	0.264564	0.219850	25.22	18.50	–
C_6H_5OH	–72.96	–306.805059	0.0877507	0.058727	13.34	9.88	9.88
	–69.34	–420.157580	0.097739	0.065759	12.20	8.95	8.97

The geometry optimization over all the natural coordinates and the calculation of the vibration spectrum in the point of the minimum on the potential energy surface were performed with the PRIRODA program developed by D.N. Laikov [18], using the density functional theory (DFT) with the Perdew–Burke–Ernzerhof's functional [19]. As the calculation basis set we used the three-exponential set of Gaussian functions (r3zv.pbe in designation of the program author). No scaling factors were used for normal mode frequencies.

The most favorable conformation of the neutral forms of all the examined hydrazones is the structure stabilized by two hydrogen bonds. The structure of **I** (R = H) is shown in the figure as example. The preferable conformation of the corresponding anions is different, with the phenyl ring turned by 180° (see figure), whereas the initial conformation is destabilized by approximately 6 kcal mol^{-1} because of the mutual repulsion of the lone electron pairs of phenoxide oxygen and azomethine nitrogen.

The energies of solvation (ΔG_s) of the neutral and ionized species were calculated within the framework of the PCM model [20–24], with the dispersion contribution [25] taken into account using the PC GAMESS program [26] by the DFT method in the B3LYP/6-31G(d,p) approximation. The energies of solvation were calculated after preliminary optimization of the geometry of the molecules and ions in the solvent. The calculated energies of solvation are given in Table 2.

The free energy of the solvated hydrogen ion was taken equal to –268.87 kcal mol^{-1} and was calculated on the basis of the above-given thermodynamic cycle for phenol using the experimental ionization constant pK_a 9.88. The value obtained is close to that used by Liptak and Shields [20] in ab initio calculation

Table 3. Absorption bands in IR spectra of compounds of types **I–IV** (cm^{-1})

Compound	R	X	ν(OH)	ν(NH)	ν(C=N) (azomethine)	ν(C=N) (quinoline)
I	H	–	3320	3200	1630	1590
I	5-OCH_3	–	3320	3190	1630	1590
I	5-Br	–	3310	3190	1635	1595
I	5,6-benzo	–	3320	3195	1630	1590
I	5-NO_2	–	3310	3200	1630	1595
II	5-NO_2	NO_3	–	3195	1610	1585
III	H	NO_3	–	3195	1610	1580
III	5-OCH_3	NO_3	–	3200	1615	1580
III	5-Br	NO_3	–	3195	1610	1580
III	5,6-benzo	NO_3	–	3195	1615	1580
III	5-Br	ClO_4	–	3200	1610	1585
IV	5-Br	Cl	–	3195	1610	1580
IV	5-Br	Br	–	3200	1610	1580

of the ionization constants of substituted phenols, –269.0 kcal mol^{-1}.

Thus, the standard Gibbs energy of the ionization in the solution was calculated by formula (3):

$$\Delta G_w = G_g(A^-) + \Delta G_s(A^-) + 287.87 - G_g(HA) - \Delta G_s(HA). \quad (3)$$

The calculated ionization constants and all the terms used in the calculations are given in Table 2. It can be seen that the dissociation of methyl ether of hydrazone **I** (R = H) is difficult (pK_a 18.5); this result is consistent with the fact that only the first step of the ionization of hydrazones **I** is realized under the experimental conditions.

The trends in variation of the pK_a values for hydrazones **I**, calculated theoretically by both procedures, reasonably agree with the experiment (Table 2). To assess the adequacy of the calculation procedure, we additionally calculated pK_a for salicylaldehyde; the value we obtained is close to the experimental value (8.95 and 8.97, respectively).

Table 4. Molar electrolytic conductivity of 0.001 M solutions of complexes of types **II–IV** in methanol

Compound	R	X	λ, $\Omega^{-1} cm^2 mol^{-1}$
II	5-NO_2	NO_3	65
III	H	NO_3	127
III	5-OCH_3	NO_3	111
III	5-Br	NO_3	115
III	5,6-benzo	NO_3	107
III	5-Br	ClO_4	120
IV	5-Br	Cl	12
IV	5-Br	Br	11

Complexes of Cu(II) with 8-Quinolylhydrazones of Substituted Salicylaldehydes

The composition and structure of complexes of acylhydrazones **I** were determined by elemental analysis, conductometry, IR spectroscopy, and magnetochemical measurements. The composition of the complexes formed by reactions of hydrazones **I** with copper(II) nitrate, perchlorate, chloride, and bromide corresponds to the general formula $(HL)Cu(X)(CH_3OH)_n$, where HL^- is the monoprotonated form of the hydrazones and X^- is the acid residue (Table 1).

In the IR spectra of the complexes, compared to those of hydrazones **I**, the stretching band ν(OH) of the phenolic moiety (~3320 cm^{-1} in the spectra of compounds **I**) disappears, whereas the ν(NH) band of the hydrazine moiety (~3200 cm^{-1}) is preserved (Table 3). The ν(C=N) bands of the azomethine and heterocyclic fragments, observed in the spectra of the starting hydrazones at ~1630 and 1590 cm^{-1}, are somewhat shifted toward smaller wavenumbers in the spectra of the complexes. These data indicate that the ligands are coordinated with the copper ions in the monodeprotonated form via phenoxide oxygen atom and azomethine and heterocyclic nitrogen atoms.

With the aim to determine the mode of binding of the acid anions in the isolated complexes, we examined them conductometrically. The molar electrolytic conductivities of 0.001 M solutions of the complexes are given in Table 4. It is well known [27] that the

Table 5. Magnetic properties of complexes of types **II–IV**

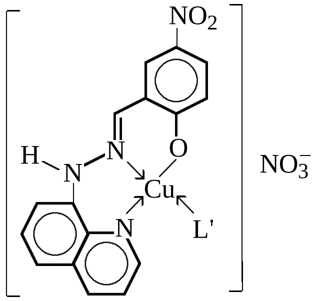
Compound	R	X	T, K	μ_{eff}, BM[a]	$-2J$, cm^{-1}	g	ρ
II	5-NO_2	NO_3	290	1.85	–	–	–
			77.4	1.7			
III	H	NO_3	290	1.61	55	2.00	0.02
			77.4	1.49			
III	5-OCH_3	NO_3	292	1.59	74	2.00	0.03
			77.4	1.35			
III	5-Br	NO_3	290	1.71	59	2.01	0.02
			77.4	1.44			
III	5,6-benzo	NO_3	290	1.65	69	2.00	0.01
			77.4	1.37			
III	5-Br	ClO_4	295	1.77	62	2.10	0.03
			77.4	1.41			
IV	5-Br	Cl	298	1.71	34	2.00	0.01
			77.4	1.58			
IV	5-Br	Br	298	1.42	142	2.00	0.03
			77.4	0.88			

[a] The effective magnetic moments were calculated per copper ion.

number of ions formed by dissociation of a complex and hence the coordination mode of the acido ligands (inner- or outer-sphere) can be determined from the molar electrolytic conductivity of 0.001 M solutions. Our results show that the dimeric complexes prepared by the reactions of copper(II) nitrate and perchlorate with 8-quinolylhydrazones of substituted salicylaldehydes are ternary electrolytes with outer-sphere nitrate and perchlorate anions. Complexes of copper(II) chloride and bromide with 8-quinolylhydrazone of 5-bromosalicylaldehyde, on the contrary, are nonelectrolytes, i.e., the halide ions are fairly tightly bound to the metal ions [28].

The magnetic susceptibility of the complexes in the solid phase was measured by the Faraday method. The magnetic moment of the complex prepared by the reaction of 8-quinolylhydrazone of 5-nitrosalicylaldehyde with copper(II) nitrate is 1.85 BM at room temperature, and it does not noticeably change on cooling to the boiling point of liquid nitrogen (Table 5). These data suggest that the complex is monomeric [29].

The whole set of the available data allow us to ascribe structure of type **II** to the complex formed by the reaction of 8-quinolylhydrazone of 5-nitrosalicylaldehyde with copper(II) nitrate. The formation of monomeric complexes can be attributed in this case to the deficiency of the electron density on the phenoxide oxygen atom, due to electron-withdrawing properties of the nitro group. Similar results were obtained previously for copper complexes with the monodeprotonated form of 5-nitrosalicylaldehyde acylhydrazones [30, 31]:



II, L' = CH_3OH.

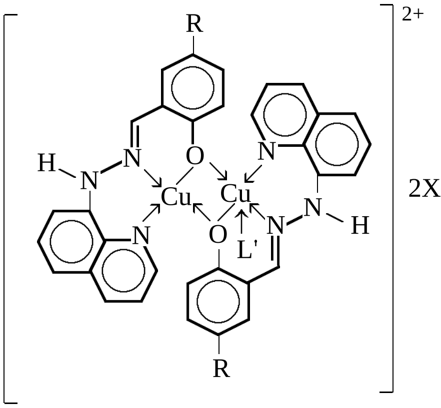
The magnetic moments of all the other isolated copper(II) complexes are appreciably lower than the spin-only value and decrease on cooling. These data unambiguously indicate that this group of complexes has a dimeric structure. The temperature dependence of the magnetic susceptibility of the dimeric complexes was adequately interpreted within the framework of the Heisenberg–Dirac–van Vleck isolated exchange cluster model [32, 33]. The parameters of the antiferromagnetic exchange coupling $2J$ were calculated with the modified Bleaney–Bowers equation (4) taking into account the presence of a certain amount of a paramagnetic impurity in the complex [32, 33]:

$$\chi'_m = \frac{2N_A g^2 \beta^2}{3kT}\left[(1-\rho)(1+\frac{1}{3}\exp\left(\frac{-2J}{kT}\right)^{-1} + \rho S(S+1)\right] + N_\alpha, \quad (4)$$

where χ'_m is the molar magnetic susceptibility corrected for the diamagnetism of the atoms using the Pascal additive scheme [19]; ρ, mole fraction of a paramagnetic impurity; N_α, temperature-independent paramagnetism taken as 60×10^{-6} for the Cu(II) ion; N_A, Avogadro number; k, Boltzmann constant; T, temperature, K; g, Landé factor (g-factor); β, Bohr magnetone; and S, total spin of a paramagnetic impurity.

The magnetic data for the complexes are given in Table 5.

It is well known that only phenoxide oxygen atoms can act as bridging atoms in all the dimeric copper complexes of this type [8, 14]. A significant effect of substituent R on the strength of the exchange coupling in the complexes prepared from copper nitrate indirectly confirms this mode of dimerization. Available data allow us to ascribe with confidence structures of types **III** and **IV** to the dimeric complexes of copper with 8-quinolylhydrazones of substituted salicylaldehydes.



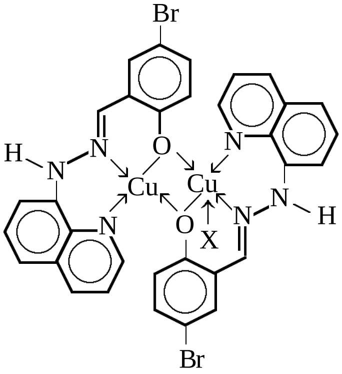
III, L' = CH_3OH, X = NO_3^-, ClO_4^-.

The parameters of the exchange coupling between copper ions in dimeric complexes **III** and **IV** (Table 5) appeared to be considerably lower than the expected values. In all the previously described dimeric complexes with phenoxide oxygen bridging atoms, the parameters of the antiferromagnetic exchange coupling range from –250 to –400 cm^{-1} [12–14, 34]. In our case, the exchange coupling is considerably weaker: In complexes of type **III**, the exchange parameters range from –55 to –79 cm^{-1}, and in complexes of type **IV** they are –34 and –142 cm^{-1} for X = Cl and Br, respectively.

Close exchange parameters were obtained previously for binuclear copper(II) complexes with salicylaldehyde acylhydrazones, in which the oxygen atom of the α-oxy azine group of the hydrazide moiety is the bridging atom [4, 12–14, 34, 35]. In this case, the exchange fragment cannot be planar; distortion of the exchange fragment decreases the overlap of the magnetic orbitals of the paramagnetic centers; as a result, the contribution of the antiferromagnetic constituent to the total effect of exchange coupling decreases [21, 36–39]. As for complexes of types **III** and **IV**, it can be assumed that significant distortions of the exchange fragment result from the participation of the heterocyclic nitrogen atom of the 8-hydrazinoquinoline moiety in the coordination, giving rise to appreciable steric strains in the binuclear molecule.

EXPERIMENTAL

The starting 8-hydrazinoquinoline dihydrochloride was prepared from 8-quinolinol as described in [40].



IV, X = Cl, Br.

Hydrazones derived from 8-hydrazinoquinoline and substituted salicylaldehydes were prepared as follows.

A solution of 0.003 mol of appropriate aldehyde in a minimal amount of ethanol was added to a refluxing suspension of 0.003 mol of 8-hydrazinoquinoline dihydrochloride in 20 ml of ethanol. After 10 min, an equivalent amount of anhydrous sodium acetate in a minimal amount of ethanol was added. The mixture was refluxed for 3 h, after which 20 ml of distilled water was added. The mixture was left overnight. The precipitated hydrazone was filtered off, washed with water and alcohol, and recrystallized from ethanol–dimethylformamide.

Complexes of copper(II) with hydrazones of type **I** were prepared as follows: A hot methanol solution of 0.011 mol of copper(II) nitrate, perchlorate, chloride, or bromide was added to a suspension of 0.010 mol of hydrazone in methanol; in so doing, the hydrazone dissolved immediately. The mixture was refluxed with stirring for 15 min. The resulting solution was slowly evaporated. The precipitated complex was filtered off, washed with methanol, and recrystallized from methanol.

The acidity measurements and potentiometric determination of the ionization constants of acylhydrazones were performed with an I-120M pH meter.

The ^{1}H NMR spectra were recorded in DMSO-d_6 on a Varian Unity 300 spectrometer (300 MHz) in the pulse Fourier mode; internal reference HMDS. The IR spectra were recorded on an IKS-35 spectrometer in the range 700 – 4000 cm^{-1}; samples were prepared as mulls in mineral oil or perfluorinated oil. The molar electrolytic conductivity of 0.001 M solutions of complexes in methanol was measured with an R-38 slidewire bridge.

The specific magnetic susceptibilities were determined by the relative Faraday method on an installation fabricated at the Chair of Physical and Colloidal Chemistry, Rostov State University, in the temperature range 80 – 300 K. The sample temperature was measured with a copper–constantan thermocouple. The installation was calibrated against $HgCo(CNS)_4$. The parameters of exchange coupling in the binuclear copper complexes were calculated within the framework of the Heisenberg–Dirac–van Vleck isotropic model using the modified Bleaney–Bowers equation (4) taking into account the presence of a certain amount of a paramagnetic impurity in the complex [32, 33].

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