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1'-Phthalazine Hydrazone of Diacetyl Monooxime and Its Complexes with Transition Metals: Physicochemical and Theoretical Study

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Abstract—1'-Phthalazine hydrazone of diacetyl monooxime and its Cu(II) and Ni(II) complexes were synthesized. The acid-base properties of the hydrazone were potentiometrically and spectrophotometrically studied, and quantum-chemical calculations of the ionization constants and the energies of possible tautomeric forms and conformations were performed. Complexes of copper(II) prepared by the reaction of the hydrazone with copper(II) acetate, chloride, and bromide were shown to have the dimeric structure with the bidentate-bridging N–O-groups of the oxime fragment, whereas the copper(II) complex prepared from copper(II) nitrate, forms the dimer via the endocyclic nitrogen atoms of the phthalazine fragment.

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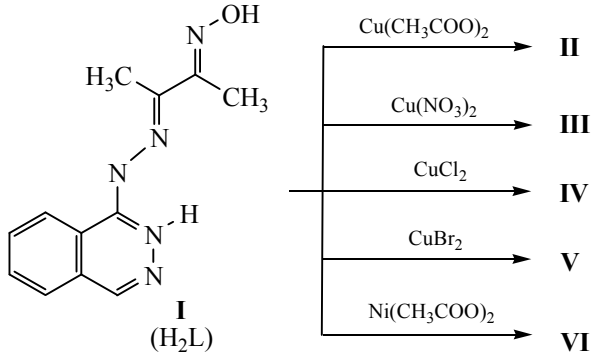
The interest of researchers to 1-hydrazinophthalazine (hydralazine), its derivatives, and their complexes with transition metals is due to biological activity inherent to these compounds, first of all, hypotensive and antitumor activity [1– 4]. A wide series of hydrazones of hydralazine with mono- and.dicarbonyl compounds is described in [5–8], as well as their coordination compounds with some metals [9–15]. There are also numerous data on the hydrazones of diacetyl monooxime and their complexes [16–24]. As the objects for this study we have chosen 1'-phthalazinyl hydrazone of diacetyl monooxime **I** and its complexes with copper(II), nickel(II), and zinc(II). This ligand system is potentially capable to form complexes differing in the size of the metal-chelate ring as well as the nature of the donor atoms; besides, the formation of dimer complexes, in which either the oxime group or the nitrogen atoms of the phthalazine fragment act as a bridge, is possible.

The synthesis of the coordination compounds under consideration was performed by the following scheme:



Hydrazone **I** was identified by the elemental analysis (Table 1), IR (Table 2) and ^{1}H NMR spectroscopy.

In the ^{1}H NMR spectrum of compound **I** in DMSO-d_6 the following signals were registered (δ, ppm): the protons of the oxime group (11.2 s, 1H); NH group of the phthalazine hydrazine fragment (11.11 s, 1H); both signals are suppressed by addition of D_2O; protons of the phthalazine fragment (9.71 s, 1H, H^4; 8.33 d.d 1H, H^8, J 8.5, 1.4 Hz; 7.58–7.70 m 3H, H^5–H^7); methyl group protons (2.24 s, 3H;, 2.13 s, 3H).

Table 1. Elemental analysis of compounds **I–VI**

Comp. no.	Found, %				Formula	Calculated, %			
	C	H	N	M		C	H	N	M
I	58.8	5.33	28.3	–	$C_{12}H_{13}N_5O$	59.2	5.40	28.8	–
II	46.5	4.05	19.0	17.0	$C_{28}H_{30}N_{10}O_6Cu_2$	46.1	4.14	19.2	17.4
III	39.5	3.12	22.1	17.5	$C_{24}H_{24}N_{12}O_8Cu_2$	39.2	3.29	22.8	17.3
IV	42.6	3.62	20.4	18.9	$C_{24}H_{24}Cl_2N_{10}O_2Cu_2$	42.2	3.54	20.5	18.6
V	37.0	3.05	18.5	16.2	$C_{24}H_{24}Br_2N_{10}O_2Cu_2$	37.4	3.14	18.2	16.5
VI	53.2	4.22	25.4	11.0	$C_{24}H_{24}N_{10}O_2Ni$	53.1	4.45	25.8	10.8

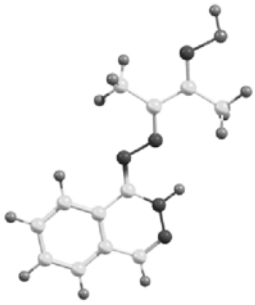
Table 2. IR spectra of compounds **I–VI**

Comp. no.	ν(OH)	ν(NH)	ν(C=N–N=C)	ν(C=N)	ν(N–O)
I	3235	3343	1609	1592, 1531	972
II	–	2800–3600	1639	1613, 1492	760
III	2600–3500	–	1629	1614, 1544	962
IV	–	2800–3600	1649	1618, 1493	764
V	–	2800–3600	1638	1619, 1490	759
VI	2600–3500	–	1629	1600, 1556	950

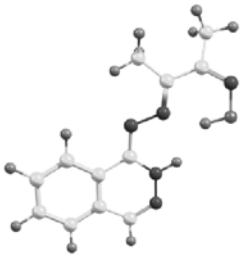
The synthesized compound can exist in solutions and in the solid phase in different tautomeric forms. To estimate their relative stability, we performed calculation of the total energy of possible isomers of the studied hydrazone; the results are given in Fig 1. For preliminary optimization of geometry of the isomers the PRIRODA V.1.91 program was employed [25]; the Perdew-Burke-Ernzerhof (PBE) functional [26] and the orbital basis of the Gauss functions of the TZ quality were used. The final geometry optimization and calculation of the electron absorption spectra by the TDDFT method [27–29] were performed at the B3LYP/6-31G11(d,p) level [30, 31].

According to the results of the quantum-chemical simulation, the most stable is the hydrazono-phthalazone tautomer **Ia**. The hydrazino-phthalazine tautomer **Ic** and the tautomer corresponding to the proton transfer in the oxime group from oxygen to nitrogen are destabilized with respect to **Ia** by ca. 8 kcal mol^{-1}, and the cyclic form **Ig**, by 10 kcal mol^{-1}.

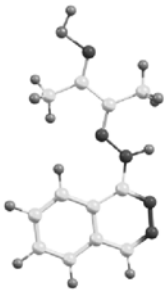
The results of calculations agree well with the optical absorption spectra of compound **I**. The shape of the spectra in different solvents strongly depends on the solvent nature. The most longwave absorption band in ethanol lies at 360 nm; the increase of the solvent polarity results in the red shift of this band by 15 nm in dioxane, 25 nm in methanol, 20 nm in DMSO and DMF. In acetonitrile the position of the band is not changed. In the methylene chloride and chloroform solutions a substantial decrease of intensity and a blue shift of this band is observed. This can be explained by the shift of the prototropic equilibrium from the hydrazono-phthalazone form to the aminohydrazone. In the spectra of compound **I** two overlapping bands at 290–315 nm are also observed, whose shape and position are approximately the same for the ethanol, dioxane, acetonitrile, and dimethylformamide solutions. In the methanol solution, this band has the same shape as in other solvents but suffers a red shift by 25 nm. In the CH_2Cl_2 and $CHCl_3$ solutions this band practically cannot be seen. The position of the third band in the absorption spectrum is widely varied depending on the solvent nature: from 210 nm in the alcohol solution to 255 nm in DMF. Based on these data, it is presumable that in solution the compound



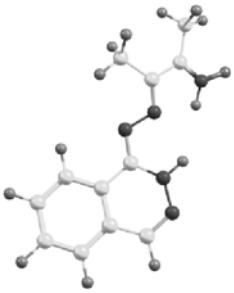
Ia *E* –814.19808462
Δ*E* 0.0



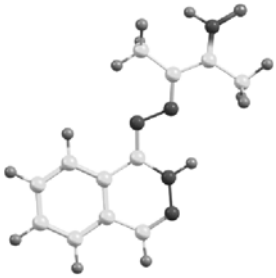
Ib *E* –814.19049100
Δ*E* 4.8



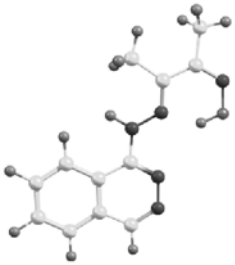
Ic *E* –814.18619111
Δ*E* 7.5



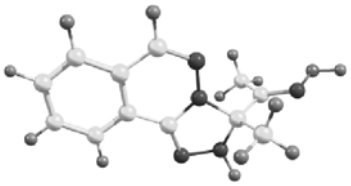
Id *E* –814.18526728
Δ*E* 8.0



Ie *E* –814.18565026
Δ*E* 7.8



If *E* –814.16959592
Δ*E* 17.9



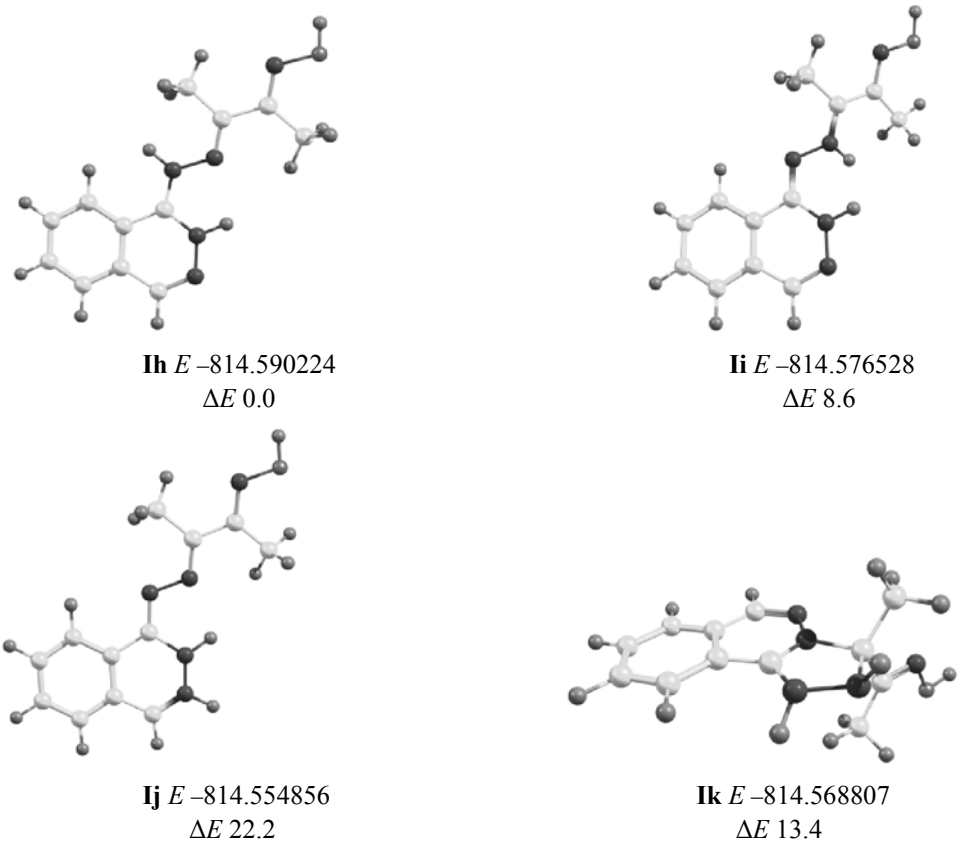
Ig *E* –814.1812508
Δ*E* 10.6

Fig. 1. Total energies (au) of the isomeric structures of compound **I** calculated at the B3LYP/6-311G(d,p) level; Δ*E* (kcal mol^{-1}) is given with respect to the most stable conformation.

exists in the form of two tautomers: more polar diazine form **Ia** and less polar hydrazine form **Ic** which is stabilized in nonpolar solvents.

An important factor determining the complexing ability of a ligand is its protolytic properties [32, 33]. We have studied the protolytic equilibria in the water-ethanol solution of hydrazone **I** by potentiometric and spectrophotometric methods. The analysis of the potentiometric titration curve is indicative of protonation of the molecule of hydrazone; the calculated basicity constant K_b = 3.40. No deprotonation was detected in the alkaline medium up to pH = 12.5. The data of spectrophotometric study confirm the presence of a single equilibrium connected with the protonation of the ligand and the formation of a cation in the range pH 2–12. In neutral and alkaline region the absorption spectra of the solutions practically coincide, the longwave absorption band lying at 360 nm. In the acidic medium (for pH < 6.9) a blue shift of the longwave absorption band to 345–340 nm is observed. The position of the band at 290 nm practically does not depend on the pH of the solution.

To elucidate the nature of the cation formed, we performed a nonempirical calculation of the energies of possible protonation products of compound **I** (Fig. 2). From all potentially proton acceptor centers of the hydrazone, the most preferable center of protonation is the exocyclic (α-hydrazine) nitrogen atom of the diazine fragment **Ih**. These assumptions were confirmed by comparison of the experimental and calcu-



Ih E –814.590224
ΔE 0.0

Ii E –814.576528
ΔE 8.6

Ij E –814.554856
ΔE 22.2

Ik E –814.568807
ΔE 13.4

Fig. 2. Total energies (au) of the isomeric structures of monoprotonated hydrazone **I** calculated at the B3LYP/6-311G(d,p) level; ΔE (kcal mol^{-1}) is given with respect to the most stable conformation.

lated nonempirically (by the TDDFT method) the characteristics of the absorption spectra of the hydrazone and its protonated and.deprotonated forms.

We have also performed quantum-chemical calculations of the pK_a values by calculation of the free energies of the monodeprotonated, molecular, and mono-protonated forms in aqueous solution (Table 3). The free energy in the gas phase at 298 K was determined as the sum of the total energy E, the zero-point energy E_0, and the variation caused by heating from 0 to 298 K $\Delta G_{0\to298}$:

$$G_g = E + E_0 + \Delta G_{0\to298}. \quad (1)$$

For the reaction of protonation of hydrazone **I** the calculations give the values of ΔG_{298} = –2.82 kcal mol^{-1} and pK_b = 2.07. For acidic dissociation of hydrazone **I** we obtained the values ΔG_{298} = –18.21 kcal mol^{-1} and pK_a = 13.35. The theoretical value of pK_b is in good agreement with the experimental; the large value of pK_a is confirmed by the absence of notable dissociation of hydrazone **I** up to pH = 12.5.

To study the complexing ability of compound **I** we have synthesized and investigated its complexes with various salts of some transition metals. The measurement of magnetic susceptibility of the copper(II) coordination compounds **II–IV** in the temperature range 298–77.4 K has shown that effective magnetic moments for all complexes decrease with temperature. This fact suggests the presence of rather strong exchange interaction of the antiferromagnetic type in the complexes and points to the binuclear structure of the compounds (Table 4). The temperature dependence of the magnetic susceptibility of the copper(II) complexes was satisfactorily interpreted within the Heisenberg–Dirac–van Vleck isolated exchange cluster model [34, 35]. Parameter ^2J of the antiferromagnetic exchange interaction was calculated by the Bleaney–Bowers Eq. (2), taking into account the presence of some fraction of paramagnetic admixture in the complex:

$$\chi'_M = 2N_A g^2\beta^2/3kT \times\{(1-f)[1+1/3\exp(-2J/kT)]^{-1} + f\cdot S(S+1)\} + N_\alpha, \quad (2)$$

Table 3. Total energies (E), zero-point energies (E_0), variation of free energy from 0 K to 298 K ($\Delta G_{0\to298}$, kcal mol^{-1}), free energy at 298 K ($G_g = E + E_0 + \Delta G_{0\to298}$), free energy of solvation (ΔG_s,), and free energy in solution at 298 K (G_s) of monoanion, neutral molecule, and monocation of hydrazone **I**

Hydrazone form	E, au	E_0, au.	$\Delta G_{0\to298}$, kcal mol^{-1}	G_g, au	ΔG_s, kcal mol^{-1}	G_s, au
HL^-	–813.6346920	0.228553	153.524	–813.1614828	–57.56	–813.2532106
H_2L	–814.1980846	0.243032	162.893	–813.6954659	–9.69	–813.7109079
H_3L^+	–814.59022400	0.256662	172.003	–814.0594576	–47.46	–814.1350899

where χ'_M is the molar magnetic susceptibility corrected for diamagnetism using the additive Pascal scheme; f is the molar fraction of paramagnetic admixture; N_α is the temperature-independent paramagnetism accepted for ion Cu(II) to be 60×10^{-6}.

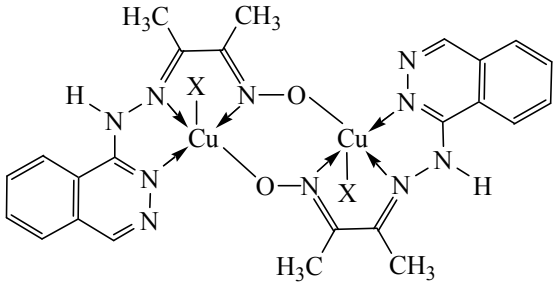
The exchange parameters ^2J in copper(II) complexes **II**, **IV**, and **V** prepared by the reaction of hydrazone **I** with copper(II) acetate, chloride, and bromide, respectively, are equal to –89, –84, and –38 cm^{-1}. Close values of the exchange parameters were reported earlier for binuclear copper(II) complexes with acylhydrazones of salicylaldehyde, in which the bridging function was performed by the α-oxyazine oxygen atom of the hydrazide fragment [36–38]. In this case, the exchange fragment cannot be planar; the distortion of the exchange fragment decreases the degree of overlap of magnetic orbitals of the paramagnetic centers; the consequence is a decrease in the contribution of the antiferromagnetic component into the total effect of the exchange interaction [39–41].

In the IR spectra of the studied compounds a wide band in the range 2800–3600 cm^{-1} is observed; this is indicative of the fact that at least one of exchangeable protons is not abstracted. From the presence of bands of medium intensity in the spectrum of complex **II** in the range 1657–1639 cm^{-1} it is possible to conclude on incorporation of acetate ions into the coordination sphere of copper ions. The stretching vibrations frequency of the diazine fragment increases from 1608 cm^{-1} in the free ligand to 1628–1639 cm^{-1} in the complex, whereas the C=N$_{oxime}$ band shifts from 1592 to 1613–1619 cm^{-1}. The band at 1531 cm^{-1} shifts to 1490–1492 cm^{-1}. Such transformation of the IR spectra upon complexation and similarity of the shape of spectra for all three complexes is indicative of the same type of coordination of the copper(II) ion with the ligand with the formation of a dimeric structure, in which the role of the bridge play the N–O groups.

Table 4. Magnetic properties of complexes **II–VI**

Comp. no.	T, K	μ_{eff}, MB[a]	$-^2J$, cm^{-1}	g
II	293	1.74	89	2.14
	77.4	1.29		
III	293	1.60	295	2.20
	77.4	0.69		
IV	293	1.70	84	2.08
	77.4	1.30		
V	293	1.74	38	2.00
	77.4	1.55		
VI	293	2.96	–	–
	77.4	2.90		

[a] (μ_{eff}) calculated to one metal ion.

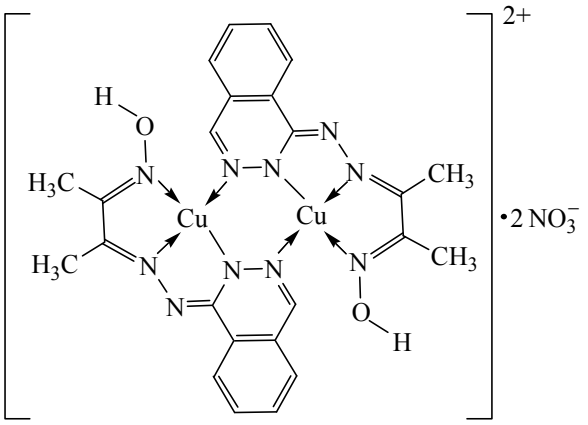


X = CH_3COO (**II**), Cl (**IV**), Br (**V**).

Weaker exchange interaction in complex **V** is explained by larger distortion of the coordination node of the copper ion due to the interaction with the bromide ion and, as a result, a decrease in the overlap of magnetic orbitals of the copper ion.

In complex **III** prepared by the reaction of hydrazone **I** with copper(II) nitrate the antiferromagnetic exchange interaction is notably stronger ($^2J = –295$ cm^{-1}). The only possible explanation of

such drastic differences in magnetic properties can be the assumption on different type of dimerization [38, 42–43]. It may be assumed that in complex **III** the bridge function perform the nitrogen atoms of the phthalazine fragments, and the complex has the following structure:



III

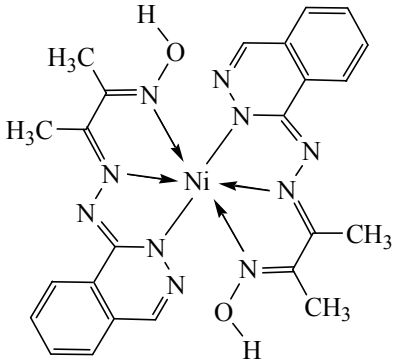
In this case the exchange fragment must be close to planar [12, 13, 44], that favors effective overlap of magnetic $d_{x^2-y^2}$ orbitals of copper(II) ions with the orbitals of the bridging heterocyclic nitrogen atoms [39–41]. The position of the N–O group stretching vibrations band in the IR spectrum of compound **III** is slightly changed, from 972 to 962 cm^{-1}, which along with a high value of the exchange parameter is indicative of the formation of a dimer structure in which the bridge function is played by the phthalazine fragments of the ligands.

The presence of nitrate ions in the crystals of the complex is confirmd by the existence of a wide strong absorption peak in the IR spectrum at 1420 cm^{-1}. It is also indirectly confirmed by the data of derivatography: at 210°C the derivatogram of the complex shows an endothermic effect followed by a large loss of the mass, apparently, due to intramolecular oxidation by the nitrate ions. The assumption on the outer-sphere location of the nitrate ions is based on the measurement of electro-conductivity of 0.001 M solution of the complex in DMF: the value of λ equal to 113 $\Omega^{-1}cm^2\,mol^{-1}$ allows to assign the complex to triple electrolytes [45].

The effective magnetic moment of complex **VI** having the 1 : 2 composition (metal : ligand) is practically independent of the temperature (the decrease in $\mu_{eff.}$ upon cooling to the boiling temperature of liquid nitrogen does not exceed the doubled error of determination, which in our case is ±0.05 MB). The value of μ_{eff} is close to the spin only value for two unshared electrons ($S = 1$) with the octahedral coordination arrangement of the nickel(II) atom. In the IR spectrum of complex **VI** the stretching vibration bands ν(C=N–N=C) and ν(C=N) suffer a longwave shift relative to their position in the spectrum of hydrazone **I** (Table 2); a strong peak corresponding to the Ni–N bond vibrations appears at 574 cm^{-1}.

No endothermic effects are observed on the derivatogram of the complex in the range of 120–180°C that points to the absence of solvent molecules in the inner sphere of the complex [46, 47].

These data allow to conclude that the nickel(II) complex with hydrazone **I** has a distorted octahedral structure **VI**:



VI

EXPERIMENTAL

^{1}H NMR spectra were registered in DMSO-d_6 on a Varian Unity 300 (300 MHz) instrument; internal reference HMDS. IR spectra were taken on a Varian Scimitar instrument in the range 400–4000 cm^{-1} in KBr as well as in mineral oil or the oil of fluorinated hydrocarbons. Absorption spectra in the visible and UV regions were registered on a Varian Cary 5000 spectrophotometer for 10^{-5} M. solutions in acetone, acetonitrile, dioxane, DMSO, DMF, methanol, ethanol, CCl_4, CH_2Cl_2, and $CHCl_3$ in 1 cm cells. Thermal analysis of the complexes was performed on a Diamond TG/DTA instrument (Perkin Elmer). The samples were heated to 650°C at the rate 10 deg min^{-1}. Molar electroconductivity of 0.001 M methanol solutions of the complexes was measured using the reochord bridge P-38. Specific magnetic susceptibility was determined by the relative Faraday method on the device manufactured on the Chair of Physical and Colloid Chemistry of RSU, in the temperature range

80–300 K. The temperature of the sample was measured by the copper-constantan thermocouple. The device was calibrated by the use of complex $HgCo(CNS)_4$.

Hydrazone **I** was prepared from commercial 1-hydrazinophthalazine hydrochloride and diacetyl monooxime. To the solution of 0.03 mol of 1-hydrazinophthalazine hydrochloride in 30 ml of ethanol the equivalent amount of anhydrous sodium acetate was added, and the mixture was refluxed for 10 min. Then, to the reaction mixture 0.03 mol of diacetyl monooxime was added and the refluxing was continued for 4–5 h. After that, 80 ml of distilled water was added to the reaction mixture and the mixture was left for 24 h. The yellow precipitate formed was filtered off, washed with distilled water and ethanol and purified by crystallization from the 1:1 mixture DMF–propanol. Amorphous yellow-orange powder, mp 245–246°C, yield 72%.

Complex compounds were prepared as follows. To the boiling suspension of 1 mmol of the ligand in 15 ml of anhydrous methanol the hot solution of the corresponding salt in 5 ml of anhydrous methanol was added, and the mixture was refluxed for 5 h. The precipitated hydrazone was filtered off and washed with hot methanol. The complexes were purified by refluxing in methanol for 1 h, then dried in a vacuum at 100°C. The data of elemental analysis of the complexes are given in Table 1.

ACKNOWLEDGMENTS

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