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Tetradentate 5,7-Dichloro-8-hydroxy-2-quinolylhydrazones

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Abstract—Chromogenic tetradentate 5,7-dichloro-8-hydroxy-2-quinolylhydrazones of 5-methylfurfural, 2-thiophenecarboxaldehyde, and phenylglyoxylic acid have been prepared. Mass spectrometry data of the prepared hydrazones are presented. Spectral properties of the prepared products and their chromogenic reactions with selected heavy metal ions have been studied. High selectivity of the hydrazone of 5-methylfurfural with respect to lead ion has been demonstrated.

Keywords: quinolylhydrazones, complex formations, spectroscopy, lead

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Synthesis of new chromogenic organic compounds capable of colored complexes formation with heavy metal ions (in particular, with lead ions) is an essential part of development of highly selective monitoring systems to detect these ions in water at the level of the maximum permissible concentration [1, 2]. A number of sensitive reagents for lead detection have been known; however, they are not sufficiently selective [3–7]. 5,7-Dichloro-8-hydroxy-2-quinolylhydrazones of acetaldehyde, benzaldehyde, and acetone bearing an $[NO_2]$ coordination cavity are of special interest [7]. Complex formation reactions of these compounds with lead ions cause red shift of the electron absorption bands but are generally not selective. Applying polydentate ligands with more rigid molecular structure is among the approaches to enhance the complex formation selectivity [8].

This work aimed to prepare a series of 5,7-dichloro-8-hydroxy-2-quinolylhydrazones containing $[N_2O_2]$ or $[N_2OS]$ coordination and to study their chromogenic reactions with lead ions.

5,7-Dichloro-8-hydroxy-2-quinolylhydrazones of 5-methylfurfurol (**I**), 2-thiophenecarbaldehyde (**II**), and phenylglyoxylic acid (**III**) were prepared via condensation of 2-hydrazino-3,5-dichloro-8-quinolol [9] with the corresponding oxo compounds (Scheme 1).

Scheme 1.

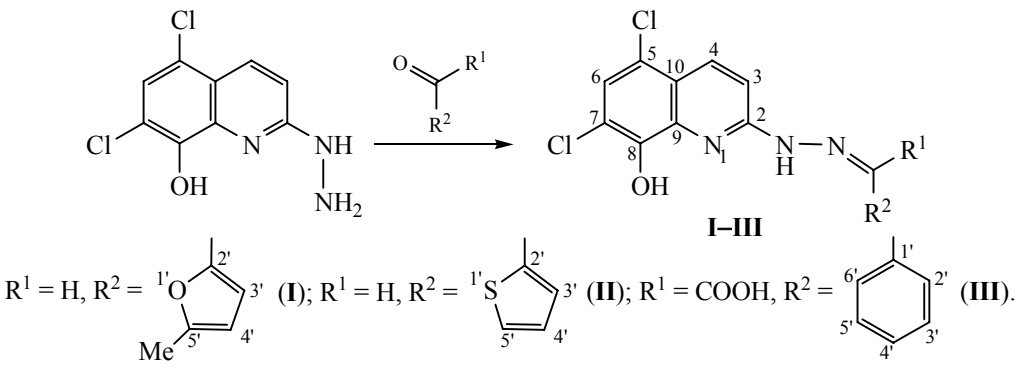

Table 1. IR spectral parameters (ν, cm^{-1}) of hydrazones **I–III**

Assignment	I	II	III
O–H	3410 br	3400 br	3440 br
N–H	3340	3280	3400 br
OH_{bound} (COOH)	–	–	3200–3150 br
C=O (COOH)	–	–	1660 s.sh
$C=N_{arom}$	1660 s.sh	1648 s.sh	1644 s
$C=C_{arom}$	1608 w, 1556	1608, 1556	1620 s.br, 1592 s.br
	1508 s, 1480 s	1508 s, 1480 s	1556 s, 1520 s.br, 1496 s
C=NN	1536 s	1532 s	1532 s.sh
C–N	1380 s, 1320	1392, 1324	1388, 1316
C–C, C–O	1280, 1256	1280, 1256	1280 sh, 1268, 1228
C–S	–	1352	–
C–Cl	852, 844	860, 852	868, 860
$\gamma(C–H_{CCC–Ph})$	–	–	696
$\delta(C–H_{arom})$	1448 s	1432 s	1444 s

Hydrazones **I–III** were fine-crystalline light-yellow compounds. Their chemical composition was confirmed by elemental analysis. MALDI mass spectra of all hydrazones contained the M^+, $[M + H]^+$, and $[M + Na]^+$ ion peaks.

Suggested structures of the prepared hydrazones were confirmed by IR spectroscopy data (Table 1). Absorption bands at 1660–1648 and 1608–1656 cm^{-1} were assigned to the stretching vibrations of conjugated C=N and C=C bonds in the quinoline fragment, respectively. Wide absorption band with maximum at 3440–3400 cm^{-1} corresponded to the stretching vibrations of the quinoline OH group involved in the intramolecular hydrogen bond. Strong absorption band of the hydrazone C=N stretching vibrations was observed at 1536–1532 cm^{-1} for all prepared compounds. A special feature of hydrazone **III** containing carboxy and phenyl groups was the presence of absorption bands due to COOH stretching vibrations at 3600 and 1660 cm^{-1}, $C=C_{arom}$ stretching vibrations at 1644–1620 cm^{-1}, and $C–H_{CCC–Ph}$ bending vibrations at 696 cm^{-1}.

The above-mentioned IR spectral data coincided with ^1H and ^{13}C NMR spectroscopy results (Table 2). In particular, ^1H NMR spectra of all hydrazones contained the following signals characteristic of the quinoline group: a singlet of the proton adjacent to the two chlorine substituents (C^6–H) at 7.74–8.40 ppm, doublets of the C^2–H and C^3–H protons at 7.60–8.33 ppm as well as NH (3.40–3.44 ppm) and OH (10.39–11.30 ppm) signals. The number of signals in ^{13}C NMR spectra of the hydrazones coincided with the number of carbon atoms in the molecules, thus confirming the products purity. The signals chemical shifts were consistent with the ^1H NMR chemical shifts and with the acceptor properties of the substituents.

Complex formation of the prepared hydrazones with Cd(II), Co(II), Cu(II), Hg(II), Ni(II), Pb(II), and Zn(II) cations was studied by photometry of the solutions. The electron absorption spectra (Table 3 and Fig. 1) revealed that potentially tetradentate hydrazones **I–III** formed orange-colored complexes (the absorption band maximum being of 460–470 nm) with lead ions in alkaline solution (pH 10). The complexes formation was accompanied with a red shift Δλ of the absorption band. Reactions of hydrazone **I** with other studied cations did not result in the color change. On the contrary, hydrazone **II** formed orange-colored compounds with the above-listed cations. Hydrazone **III** gave light-brown compounds with Co(II) and Ni(II) cations.

Stoichiometry of the hydrazones interaction with lead ions to give colored complexes was determined applying the isomolar series method (Fig. 2). The results showed that ligands **I** and **II** bearing a single proton-donor group each formed the PbL_2 complexes (L standing for the ligand molecule) (Fig. 2, curves *1*, *2*). Ligand **III** containing two proton-donor groups formed the 1 : 1 complex (Fig. 2, curve *3*).

To conclude, ligand **I** with the $[N_2O_2]$ coordination cavity revealed relatively high selectivity in the chromogenic reaction with lead cations. The other

Table 2. ^{1}H and ^{13}C NMR spectral parameters of hydrazones **I–III**

Comp. no.	δ, ppm (*J*, Hz)	δ_C, ppm
I	8.31 d (1H, C^4H, *J* 8.0), 8.02 s (1H, C^6H), 7.62 d (1H, C^3H, *J* 9.2), 7.43 s (1H, =CH), 6.72 d (1H, $C^{4'}H$, *J* 3.2), 6.25 d (1H, $C^{3'}H$, *J* 2.4), 2.36 s (3H, Me), 3.40 s (1H, NH), 11.30 s (1H OH_{bound})	155.64 (C^8), 146.91 (C^2), 148.79 (C=N), 139.15 (C^9), 135.12 (C^4), 123.29 (C^6), 120.72, 120.35 (C^5, C^{10}), 116.67 (C^7), 111.42 (C^3), 154.20, 132.57, 113.89, 108.91 ($C^{2',3',4',5'}$), 14.02 (Me)
II	8.33 d (1H, C^4H, *J* 9.2), 8.40 s (1H, C^6H), 7.60 d (1H, C^3H, *J* 5.6), 7.63 s (1H, =CH), 7.60, 7.60 d (1H, $C^{4'}H$), 7.38 d (1H, $C^{5'}H$, *J* 3.2), 7.13, 7.12, 7.11 t (1H $C^{4'}H$, *J* 4.4), 3.40 s (1H NH), 11.46 s (1H OH_{bound})	155.57 (C^8), 146.92 (C^2), 140.18 (C=N), 139.14 (C^9), 135.24 (C^4), 123.41 (C^6), 120.81, 120.41 (C^5, C^{10}), 116.76 (C^7), 111.23 (C^3), 137.35, 129.43, 128.34, 128.00 ($C^{2',3',4',5'}$)
III	8.44 d (1H, C^4H, *J* 9.2), 7.88 d (1H, C^3H, *J* 10), 7.74, 7.76 (2H, $C^{2'}H$, $C^{6'}H$), 7.74 s (1H, C^6H), 7.57 s (1H, =CH), 7.46, 7.45, 7.42, 7.42, 7.40 m, 7.39, 7.35, 7.33 t (5H, Ph), 12.45 s (1H, COOH), 3.44 s (1H, NH), 10.39 s (1H, OH_{bound})	164.72 (COOH), 154.82 (C^8), 147.92 (C^2), 138.46 (C=N), 136.12 (C^9), 136.00 (C^4), 125.07 (C^6), 122.00, 119.89 (C^5, C^{10}), 117.02 (C^7), 111.12 (C^3), 128.90–128.49 ($C^{1',2',3',4',5',6'}$)

hydrazones, in particular, compound **II**, participated in similar chromogenic reactions with other studied cations.

EXPERIMENTAL

Electron absorption spectra of the hydrazones (2×10^{-4} mol/L) in the absence of metal ions and in the presence of 1×10^{-3} mol/L of lead(II) ions were recorded using a USER Supervisor 6705 spectrophotometer (China) in 2 : 2 : 1 DMF–ethanol–water medium. Absorbance of the isomolar series solutions was measured in a 10 mm quartz cell using an Ekspert-003 light diodes miniphotometer (Russia). ^{1}H and ^{13}C NMR spectra of the solutions in DMSO-d_6 were recorded with a Bruker 400 AMX spectrometer at 400 MHz with TMS as internal reference. MALDI mass spectra were obtained using an Ultraflex II instrument (firm Bruker). Used matrix is dihydroxybenzoic acid (DHB), concentration 1 g/L, the ratio of the matrix: analyte 10 : 1. IR spectra at 3800–400 cm^{-1} (KBr pellets) were recorded using a Specord M 80 spectrometer. Elemental analysis was performed using a Carlo Erba 1106 device. Reaction of hydrazones with metals was carried out using state standard samples of solutions of 1 mg/cm^3 ions on the State Register: Cd(II) – 7773-2000, Co(II) – 7784-2000, Cu(II) – 7764-2000, Ni(II) – 7785-2000, Hg(II) – 7343-96, Zn(II) – 7770-2000 (firm EAA "Ecoanalytics," Moscow).

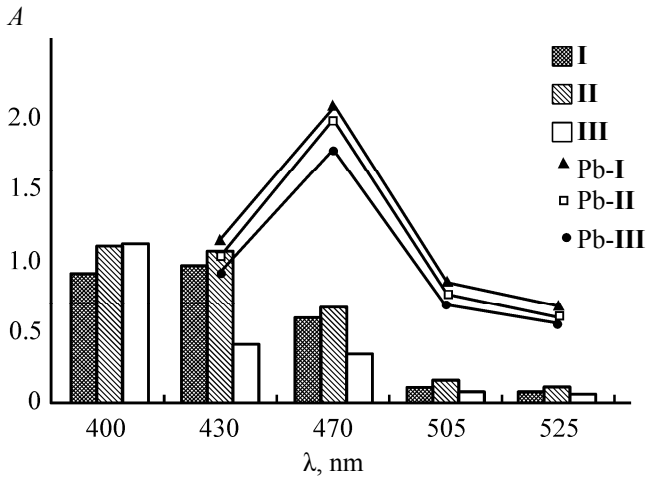

Fig. 1. Photometry response of solutions of the hydrazones in the absence of metal ions and in the presence of excess of lead(II) ions as function of the wavelength.

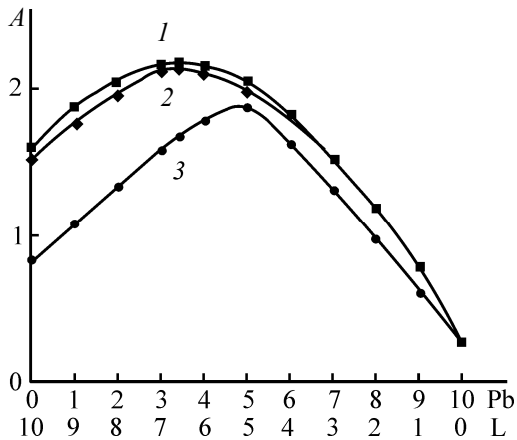

Fig. 2. Absorbance of isomolar series of solutions of Pb(II) and the hydrazone (*1*) **I**, (*2*) **II**, and (*3*) **III**. Σ[Pb] + [hydrazone] = 0.65×10^{-3} mol/L, pH 10, λ 470 nm.

Table 3. Parameters of electronic absorption spectra of hydrazones **I**–**III** and their complexes with lead(II) ions

Ligand L	λ_{max}, nm (log ε)		Δλ, nm
	L	PbL_n	
I	433 (3.65)	468 (4.39)	35
II	441 (3.67)	468 (4.26)	27
III	400 (3.92)	460 (4.15)	60

5-Methylfurfurol 5,7-dichloro-8-hydroxy-2-quinolylhydrazone (I). A mixture of 1.23 g (5 mmol) of 2-hydrazino-3,5-dichloro-8-quinolol, 0.88 g (8 mmol) of 5-methylfurfurol (firm Merck, for synthesis), 60 mL of DMF, and 40 mL of ethanol was stirred during 3 h. The product was precipitated from the reaction mixture with water, re-precipitated from DMF with water, washed with ethanol, and sequentially recrystallized from chloroform and chloroform–acetone mixture. Yield 0.92 g (54%), light-yellow fibrous crystals, mp 226–229°C (decomp.). Mass spectrum, *m*/*z* (I_{rel}, %): 336 (100) $[M + H]^+$, 338 (69) isotope, 340 (16) second isotope, 358 (39), 360 (24), 362 (5) $[M + Na]^+$. M_{calc} 336.18. Found, %: C 54.09; H 3.35; Cl 20.67; N 12.86. $C_{15}H_{11}Cl_2N_3O_2$. calculated, %: C 53.59; H 3.30; Cl 21.09; N 12.50. Spectral data are given in Tables 1–3.

2-Thiophenecarbaldehyde 5,7-dichloro-8-hydroxy-2-quinolylhydrazone (II) was obtained similarly from 5 mmol of 2-hydrazino-3,5-dichloro-8-quinolol and 8 mmol of 2-thiophenecarbaldehyde (firm Merck, for synthesis). The product was reprecipitated from DMF with water, washed with ethanol, and recrystallized from chloroform. Yield 1.05 g (62%), mp 238–241°C (decomp.). Mass spectrum, *m*/*z* (I_{rel}, %): 338 (100) $[M + H]^+$, 340 (69) isotope, 342 (17) second isotope, 360 (20), 362 (13), 364 (3) $[M + Na]^+$. M_{calc} 338.22. Found, %: C 49.74; H 2.78; Cl 20.51; N 12.25; S 10.77. $C_{14}H_9Cl_2N_3OS$. Calculated, %: C 49.72; H 2.68; Cl 20.06; N 12.42; S 10.48. Spectral data are given in Tables 1–3.

Phenylglyoxylic acid 5,7-dichloro-8-hydroxy-2-quinolylhydrazone (III) was obtained similarly from 5 mmol of 2-hydrazino-3,5-dichloro-8-quinolol and 8 mmol of phenylglyoxylic acid. The product was poorly soluble in organic solvents; it was twice washed with boiling chloroform and ethanol. Yield 1.58 g (84%), mp 225–228°C (decomp.). Mass spectrum, *m*/*z* (I_{rel}, %): 376 (100) $[M + H]^+$, 378 (69) isotope, 380 (69) second isotope, 398 (25), 400 (16), 364 (4) $[M + Na]^+$. M_{calc} 376.20. Found, %: C 55.01; H 3.12; Cl 18.34; N 10.75. $C_{17}H_{11}Cl_2N_3O_3$. Calculated, %: C 54.28; H 2.95; Cl 18.85; N 11.17. Spectral data are given in Tables 1–3.

Determination of metal : ligand ratio in complexes of hydrazones I–III with lead(II) ions by means of photometry. The isomolar series of solutions was prepared, containing constant total concentration of lead(II) ions and the ligand. The starting solutions of lead(II) acetate (firm Roschim-reactive, Moscow, State All-Union standart 1027-67, 99%) in bidistilled water (1 mmol/L) and of the hydrazone in DMF (1 mmol/L) were introduced into a beaker in the 0 : 10, 1 : 9, 2 : 8, 3 : 7, 3.4 : 6.8, 4 : 6, 5 : 5, 6 : 4, 7 : 3, 8 : 2, 9 : 1, or 10 : 0 volume ratio. The mixture was diluted with DMF ("chemically pure" grade) (half of the mixture volume), 50 μL of sodium hydroxide solution was added to pH 10, and the solution absorbance was measured at 470 nm.

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