ISSN 1070-3632, Russian Journal of General Chemistry, 2019, Vol. 89, No. 3, pp. 546–548. © Pleiades Publishing, Ltd., 2019.
Russian Text © G.G. Gondolova, S.Z. Ismailova, P.A. Fatullaeva, A.A. Mejidov, 2019, published in Zhurnal Obshchei Khimii, 2019, Vol. 89, No. 3, pp. 479–482.

LETTERS TO THE EDITOR

Co(II), Ni(II), and Cu(II) Complexes of *N*-(2-Hydroxybenzamido)phthalimide

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Received September 13, 2018; revised September 13, 2018; accepted September 27, 2018

Abstract—Co(II), Ni(II), and Cu(II) complexes with *N*-(2-hydroxybenzamido)phthalimide (LH_2) were synthesized and studied by IR, electron absorption, EPR spectroscopy, and thermogravimetry. In the case of Cu(II) ions, binuclear Cu_2L_2 complexes are formed, in which the ligand acts as a dianion, while Co(II) and Ni(II) ions form $M(LH)_2$ complexes.

Keywords: *N*-(2-hydroxybenzamido)phthalimide, copper complexes, nickel complexes, cobalt complexes

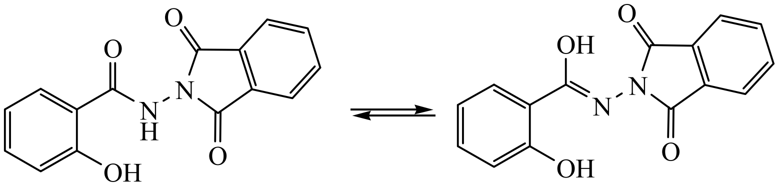
DOI: 10.1134/S1070363219030307

Compounds based on hydrazides of carboxylic acids and their metal complexes possess anti-tuberculosis [1–2], anti-cancer [3–5], anti-malarial [6], and antimicrobial [7, 8] activity. Phthalimide derivatives of hydrazides are known to exhibit antimicrobial activity [9, 10]. Earlier we have synthesized Fe(II) and Mn(II) complexes with *N*-(2-hydroxybenzamido)phthalimide (LH_2) based on salicylhydrazide and phthalic anhydride [11]. In continuation of the work on synthesis and study of salicylhydrazide and phthalic anhydride derivatives and their complexes with metals, in this work we have synthesized Co(II), Ni(II), and Cu(II) complexes with *N*-(2-hydroxybenzamido)phthalimide and studied them by IR, electronic absorption, EPR spectroscopy and thermogravimetry.

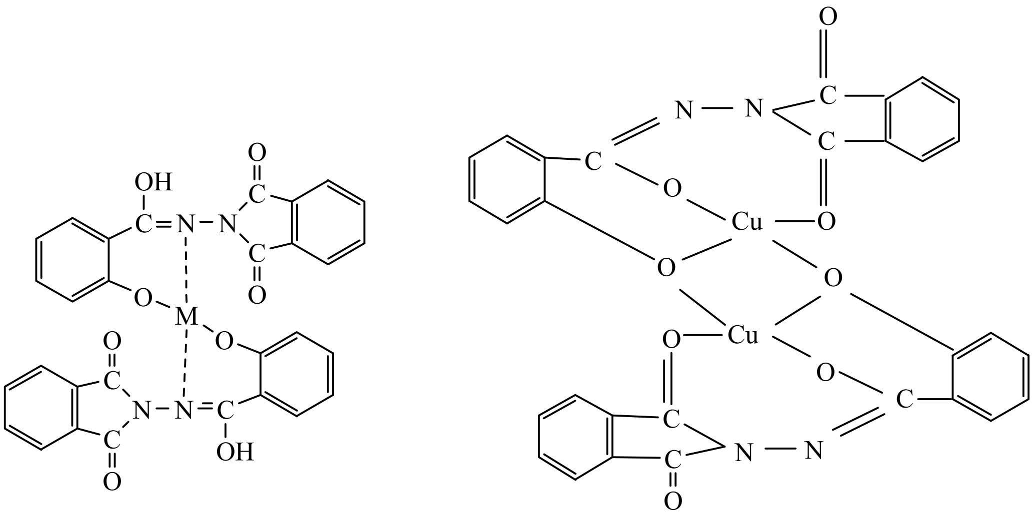
N-(2-hydroxybenzamido)phthalimide was synthesized by reacting salicylhydrazide with phthalic anhydride in a DMF solution at 85°C within 3.5 h [11]. As shown earlier, this ligand is able to play the roles of mono- and dianions as a result of its existence in the keto- and enol forms (Scheme 1). Oxygen atoms of the amide group and of phthalimide fragment can participate in the coordination with metal ions

Co(II), Ni(II), and Cu(II) complexes were synthesized by reactions of $Co(CH_3COO)_2·4H_2O$, $Ni(CH_3COO)_2·4H_2O$, and $Cu(CH_3COO)_2·H_2O$, respectively, with *N*-(2-hydroxybenzamido)phthalimide in methanol at 50–60°C. Composition and structure of the resulting compounds were confirmed by the data of elemental analysis, IR, UV, and EPR spectroscopy, and thermogravimetry. According to the elemental analysis (Table 1), Co(II) and Ni(II) ions form $M(LH)_2$ complexes, whereas in the case of Cu(II) Cu_2L_2 complexes are formed (Scheme 2).

Scheme 1.



Scheme 2.



M = Co(II), Ni(II).

The IR spectra of the Co(II) and Ni(II) complexes in the regions of amide group vibrations and symmetric stretching vibrations of the C=O bond are characterized by a noticeable shift to the low-frequency region as compared with the free ligand. At the same time the vibrational band of the phenol OH group, which is observed in the original ligand spectrum at 3400 cm^{-1}, is absent from these spectra (Table 2). In the IR spectra of the Cu(II) complex the following changes are observed: a weak band at 1795 cm^{-1} almost disappears, the band at 1725 cm^{-1} is slightly shifted in the low-energy region (1721 cm^{-1}), and the amide band at 1653 cm^{-1} disappears completely. The band of the N-H stretching vibrations of amide group, which is present in the free ligand spectrum at 3272 cm^{-1}, is also absent. These data point to the participation of phenol oxygen, enol oxygen, and phthalimide fragment oxygen in the coordination with Cu(II) ions.

In the electronic spectra of the solution of the Cu(II) complex in a mixture of DMF and alcohol (1 : 10), absorption bands at 347 nm (a charge transfer band) and a very wide band at ~667 nm are observed in addition to the ligand bands [λ_{max} = 218 ($\varepsilon = 3\times10^4$ M^{-1} cm^{-1}), 228 ($\varepsilon = 2.7\times10^4$ M^{-1} cm^{-1}), and 300 nm ($\varepsilon = 8.1\times10^2$ M^{-1} cm^{-1}). The ESR spectrum of this complex in the polycrystalline state appears as an almost symmetric singlet with a line width of 450 Hz (between maximal slope points) and *g*-factor of 2.03.

In the spectrum of the cobalt(II) complex along with ligand absorption bands there are a charge transfer band at 365 nm ($\varepsilon = 1.3\times10^2$ M^{-1} cm^{-1}) and two low-intensity bands in the visible region: at 540 nm (ε = 27 M^{-1} cm^{-1}) and 649 nm (ε = 6 M^{-1} cm^{-1}). Spectrum of the nickel(II) complex contains three absorption bands in the visible region: 485 nm (ε = 85 M^{-1} cm^{-1}), 649 nm (ε = 8 M^{-1} cm^{-1}), and 740 cm^{-1} (ε = 7 M^{-1} cm^{-1}).

According to the thermogravimetric analysis, the decomposition of the synthesized Co(II), Ni(II), and Cu(II) complexes with *N*-(2-hydroxybenzamido)-phthalimide proceeds in two stages. The main weight

Table 1. Melting points and elemental analysis data for Co(II), Ni(II), and Cu(II) complexes with *N*-(2-hydroxybenzamido)-phthalimide

Complex	mp, °C	Found, %					Formula	Calculated, %					*M*, g/mol
		C	H	N	O	M		C	H	N	O	M	
Cu_2L_2	>255	52.40	2.33	8.15	18.62	18.50	$C_{30}H_{16}N_4O_8Cu_2$	51.70	2.47	8.19	18.44	19.20	688.0
$Ni(LH)_2$	>255	58.19	2.58	9.05	20.07	9.48	$C_{30}H_{16}N_4O_8Ni$	57.72	2.44	9.49	20.23	10.12	618.7
$Co(LH)_2$	>255	58.16	2.58	9.04	20.70	9.52	$C_{30}H_{16}N_4O_8Co$	57.74	2.81	8.82	21.06	9.57	618.9

Table 2. Data of the IR spectra of Co(II), Ni(II), and Cu(II) complexes with *N*-(2-hydroxybenzamido)phthalimide

Compound	ν, cm^{-1}					
	OH_{phenol}	NH_{amide}	$\nu_{as}(CO_{phtal})$	$\nu_s(CO_{phtal})$	CO_{amide}	CO_{phenol}
LH_2	3400 br	3272 m	1795 w	1734 s	1654 s	1212
$Co(LH)_2$	3377 br	3274 w	1794 w	1725	1651 s	1210
$Ni(LH)_2$	3377	3274 w	1795	1725	1648 s	1210
Cu_2L_2	3416	–	1721	1626	–	1156

loss occurs in the first stage in the temperature range 300–400°C (55–75%, depending on the metal nature). In the second stage at 400–600°C the final decomposition takes place to form corresponding oxides. Amounts of NiO and CuO remaining after decomposition of the Ni(II) and Cu(II) complexes correspond to the metal contents in the complexes (Table 2).

Thus**,** new complexes of Co(II), Ni(II), and Cu(II) complexes with *N*-(2-hydroxybenzamido)phthalimide were obtained, in which it acts as a monoanion bidentate or a dianion tridentate ligand depending on the metal nature. It was found that Co^{2+} and Ni^{2+} ions form $M(LH)_2$ complexes, whereas Cu^{2+} ions form Cu_2L_2 complexes.

Synthesis of the Cu_2L_2 complex. A mixture of 0.04 mol of *N*-(2-hydroxybenzamido)phthalimide and 35 mL of methanol was intensely stirred at 50–60°C for 30 min. The crystalline precipitate was filtered off, multiply washed with water and methanol, and dried.

The $Ni(LH)_2$ and $Co(LH)_2$ complexes were synthesized similarly using the mole ratio ligand : metal = 2 : 1.

The IR spectra were taken on a Nicolet IS10 spectrophotometer in KBr tablets. The electronic absorption spectra were obtained on a UV-vis Evolution 60S spectrophotometer. The ESR spectra were recorded on a Bruker BioSpin GmbH spectrophotometer. The thermogravimetric analysis was carried out using a NETZSCH STA 449 Fc derivatograph.

CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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