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LETTERS TO THE EDITOR

Complexes of Fe(II) and Mn(II) with *N*-(2-Hydroxybenzamido)phthalimide

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Abstract—Complexes of Fe(II) and Mn(II) with N-(2-hydroxybenzamido)phthalimide of the general formula $[M(LH)_2]$ were synthesized and studied by IR, electronic absorption, and ESR spectroscopy and thermogravimetry. The ligand coordinates to Fe(II) and Mn(II) through the oxygen atom of the amido group which is present in the enolic form.

Keywords: *N*-(2-hydroxybenzamido)phthalimide, iron complexes, manganese complexes **DOI:** 10.1134/S1070363218030362

Carboxylic acid hydrazide derivatives and their metal complexes exhibit biological activity and are used in medicine and technics. Hydrazides that act as antitubercular [1, 2], anticancer [3–5], antimalarial [6], and antimicrobial agents are known [7, 8]. The antimicrobial activity is characteristic of such phthalimide derivatives of hydrazides as N-(arylcarboxamido)phthalimides [9, 10]. The structure of one of the specimens of this class of compounds was studied in [11]. Carboxylic acid hydrazides show nootropic and antidepressant properties and improve brain function [12]. Metal complexes of hydrazides are environmentally friendly compounds, and they have found application in agriculture as efficient plant growth regulators. Many hydrazides are applied for metal extraction from industrial wastewater [13].

Literature search showed that the publications of the synthesis of carboxylic acid hydrazide derivatives are few in number; in particular, the synthesis of derivatives of salicylhydrazide and phthalic anhydride and their metal complexes has never been reported.

We synthesized *N*-(2-hydroxybenzamido)phthalimide [*N*-(1,3-dioxo-1,3-dihydro-2*H*-isoindol-2-yl)-2-hydroxybenzamide] **1** (LH₂) and its Fe(II) and Mn(II) complexes and studied their structure by physicochemical methods.

N-(2-Hydroxybenzamido)phthalimide **1** was synthesized by the reaction of salicylhydrazide with phthalic anhydride in DMF at 85°C for 3.5 h (Scheme 1).

The IR spectrum of ligand 1 displays bands at 3378 and 2200–3500 cm⁻¹, which are assignable to the amide NH and phenol OH groups. The absorption bands at 1794 and 1725 cm⁻¹ correspond to symmetrical and antisymmetrical vibrations of the phthalimide carbonyls and the band at 1654 cm⁻¹ is associated with the amide C=O group.





Due to the enolization of the amide group (Scheme 2), ligand 1 can be present both as a monoanion (LH^{1-}) and a dianion (L^{2-}) . Metal ions can coordinate to the phenolic, amide, and phthalimide oxygen atoms.

Complexes 2 and 3 were prepared by the reaction of *N*-(2-hydroxybenzamido)phthalimide 1 with FeSO₄ (NH₄)₂SO₄·6H₂O or Mn(OAc)₂ in methanol at 50–60°C for 30 min. According to the elemental analyses (Table 1), Fe(II) and Mn(II) form complexes of the composition M(LH)₂.

The carbonyl and amide groups in the IR spectrum of the Fe(II) complex are slightly shifted red (1723 and 1651 cm⁻¹, respectively). The stretching vibration band of the amide N–H group at 3272 cm⁻¹ completely disappears. In view of the large shift of the phenolic v_{C-O} band (Table 2) we can suggest the involvement of phenolic oxygen in bridging to the metal atom.



The electron absorption spectrum of a solution of Fe(II) complex **2** in ethanol shows, along the ligand bands at 218 ($\varepsilon 3 \times 10^4$ mol L⁻¹ cm⁻¹), 228 ($\varepsilon 2.7 \times 10^4$ mol L⁻¹ cm⁻¹), and 300 nm ($\varepsilon 8.1 \times 10^2$ mol L⁻¹ cm⁻¹), a charge-transfer band at 370 nm and a broad band at ~469 nm corresponding to the *d*'-*d* transition [14].

The electron absorption spectrum of Mn(II) complex contains, along with the absorption bands on the ligand, a charge-transfer band at 370 nm and a lowintensity visible band at 454 nm assignable to a transition to ⁴G term components [14]. The ESR spectrum of this complex in the polycrystalline state displays a nearly symmetrical singlet with the line width (between the steepest slope points) 320 Hz and g factor 2.125.

According to the thermogravimetry (TG) data, complexes 2 and 3 decompose in 2 stages. The major weight loss takes place in the first stage in the temperature range 250–350°C (55–75%). Complete decomposition to form oxides takes place in the second stage at 400–600°C. The oxide residue after decomposition corresponds to the metal content of the complexes (Table 1).

Thus, we prepared a new ligand, *N*-(2-hyd-roxybenzamido)phthalimide, which can behave as a monoanion bidentate or dianion tridentate ligands depending of the nature of the metal ion. As shown by IR and electron absorption spectroscopy, Fe^{2+} and Mn^{2+} ions form complexes M(LH)₂, where the LH

Comp. no.	Elemental formula	mp, °C	Calculated/found, %					м
			С	Н	Ν	0	М	IVI
1	$C_{15}H_{10}N_2O_4$	251	63.83	3.57	9.93	22.67	-	282.00
			63.77	3.64	9.96	22.63	-	
2	$C_{30}H_{16}N_4O_8Fe$	>255	58.46	2.60	9.09	20.78	9.07	615.85
			59.38	2.47	8.19	19.44	10.52	
3	$C_{30}H_{16}N_4O_8Mn$	>255	58.19	2.58	9.05	20.07	9.48	618.70
			57.72	2.44	9.49	20.23	10.12	

Table 1. Melting points and elemental analyses of compounds 1-3

Comp. no.	v, cm^{-1}								
	O-H (phenol)	N–H (amide)	v _{as} (C=O) (phthalimide)	v _s (C=O) (phthalimide)	C=O (amide)	C–O (phenol)			
1	3400 br	3272 m	1795 sh	1734 s	1654 cs	1212			
2	3378 br	_	1794 sh	1723	1651 s	1206			
3	3416 br	_	1794 sh	1722	1651 s	1153			

Table 2. IR spectral data for compounds 1–3

ligand is present in the enol form and coordinates to the metal ions via the phenolic oxygen and amide nitrogen atoms.

N-(1,3-Dioxo-1,3-dihydro-2*H*-isoindol-2-yl)-2hydroxybenzamide (1). A mixture of 50 mL of DMF, salicylhydrazide (0.02 mol), and phthalic anhydride (0.02 mol) was stirred for 3.5 h at 85°C. After cooling to room temperature the reaction mixture was diluted with 2 L of distilled water and left to stand for 1 day. The colorless crystals that formed were separated, washed with ethanol, and dried in a vacuum.

Complex Fe(LH)₂ (2). A mixture of 0.04 mol of *N*-(2-hydroxybenzamido)phthalimide 1, 0.04 mol of FeSO₄ (NH₄)₂SO₄·6H₂O, and 35 mL of methanol was vigorously stirred at 50–60°C for 30 min and then left to stand overnight. The dark violet crystals that formed were separated, washed with water and methanol, and dried at room temperature.

Complex Mn(LH)₂ (3) was synthesized in a similar way from manganese acetate.

The melting points, IR spectral data, elemental analyses of the synthesized compounds are listed in Tables 1 and 2.

The IR spectra were measured on a Nicolet IS10 spectrometer. The electron absorption spectra were obtained on an Evolution 60S UV-VIS spectrophotometer. The thermogravimetric analysis was performed on a NETZSCH STA 449 Fc derivatograph. The EPR spectra were run on a Bruker BioSpin spectrophotometer.

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