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SOLVENT EFFECT IN THE PREPARATION OF IRON(III) AZOMETHINE COMPLEXES BASED ON 4,4′-DODECYLOXYBENZOYLOXYBENZOYL-4-SALICYLIDENE-N′-ETHYL-N-ETHYLENEDIAMINE

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Mono- and bis-chelate iron(III)-containing complexes with a tridentate azomethine ligand based on *n*-dodecyloxybenzoic acid ester derivatives with oxybenzoyl-4-salidene-N′-ethyl-N-ethylenediamine with NO_3^- counterions are obtained. The structure of the compounds is determined by IR spectroscopy, elemental analysis, and mass spectrometry (MALDI-ToF MS). It is found that the complexation of iron salts with tridentate ligands in a mixture of solvents (alcohol:benzene) results in the formation of bis-chelate compounds of the composition 1:2 with octahedral packing of iron in the complex, while in pure alcohol solutions, asymmetric mono-chelate complexes are obtained.

Keywords: azomethines, structure, solvent effect, iron(III) complexes, mass spectrometry, IR spectroscopy.

INTRODUCTION

Azomethine metal complexes currently attract the attention of researchers [1, 2]. These compounds are widely used due to the catalytic activity and redox properties of the chelating metal [3, 4]. These substances can be used as components in molecular electronics and photochemical molecular devices for solar energy conversion and storage [5-7]. Some communications reporting the investigations of complexes containing Fe ions with azomethine ligands are of particular interest [8-11]. One of their most important features is the ability of small modifications in the structure to significantly alter the key properties of the corresponding complexes [12-14]. Therefore, the determination of the spatial environment of iron and the structure of the complex is currently an important problem. The effect of solvents as reaction medium on complexation is one of the key factors governing both the yield [15, 16] and the structure [17] of the product. Moreover, the solvent can also trigger certain properties of target products. For example, the work [18] showed the induction of the liquid crystalline state by microsegregation processes occurring between the solvent (decanol, benzene, or chloroform) and dendrimers (polypropylenimine derivatives) with the nonmesomorphic nucleus and the periphery.

This paper presents the results of studies on the structure of two iron(III)-containing complexes that are of interest as model systems for the study of magnetic properties of organometallic compounds. The aim of this work is to determine the structure of the complexes obtained by the reaction between the Schiff base and an iron salt at room temperature, depending on the solvent.

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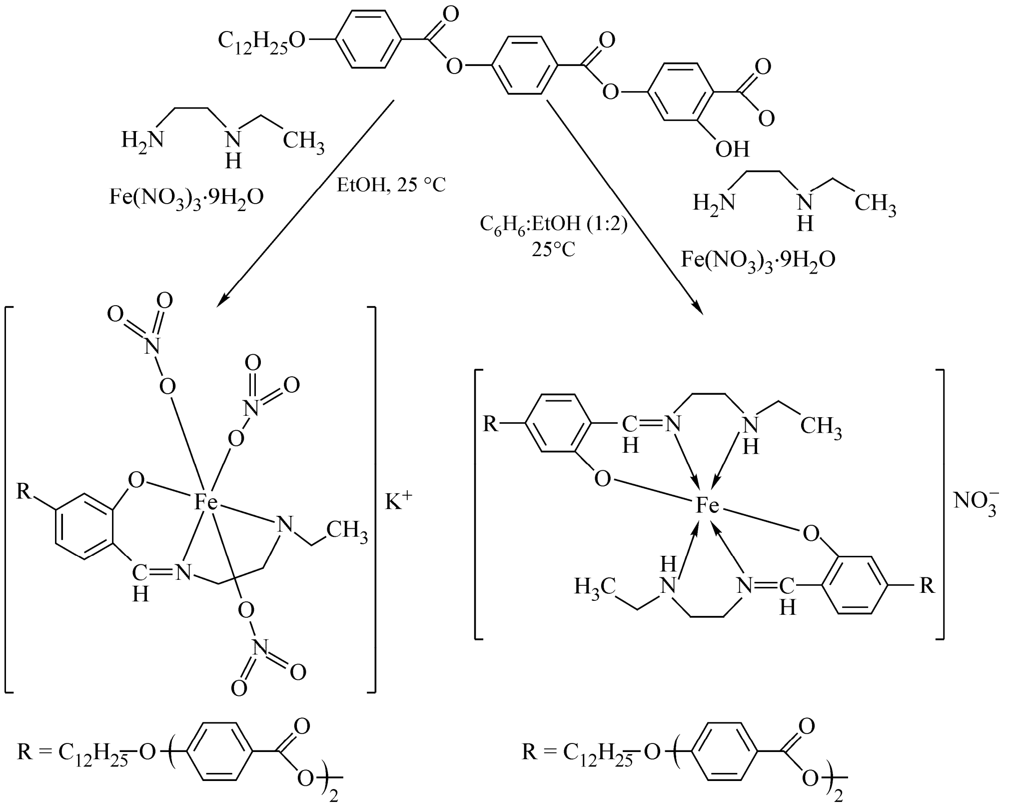
EXPERIMENTAL

All reagents and solvents were chemically pure and not further purified. 4,4′-Dodecyloxybenzoyloxybenzoyl-4-oxy-2-hydroxybenzaldehyde was obtained by the procedures described in [19-21]. Target compounds **I** and **II** were synthesized according to the scheme below directly via the formation of a Schiff base without isolating the ligand from the solution, followed by complexation with iron(III) salts. The purity and identity of the compound was assessed by elemental analysis and IR and NMR spectroscopic studies. The spectral characteristics of the compounds are listed below.



(I) **(II)**

Target compound synthesis scheme

Mono-chelate Fe(III)-containing complex based on 4,4′-dodecyloxybenzoyloxybenzoyl-4-salicylidene-N′-ethyl-N-ethylenediamine with an NO_3^- counterion (I). Weighed portions of 4,4′-dodecyloxybenzoyloxybenzoyl-4-oxy-2-hydroxybenzaldehyde (1.28 g), N-ethylenediamine (0.21 g), and KOH (0.18 g) were dissolved in ethanol (40 ml, 10 ml, and 10 ml respectively) and stirred for 30 min. Then an alcohol solution of $Fe(NO_3)_3·9H_2O$ (0.47 g) was gradually poured into the mixture. The dark brown reaction mixture was stirred for 2 h; the precipitate was filtered using a glass filter and washed with diethyl ether. The product was recrystallized from a mixture of dried solvents: benzene–ethanol (1:4). The product is a fine brown powder [22]. Yield: 0.46 g. Found, %: C 46.79, H 6.12, N 7.24, and O 26.91. $C_{37}H_{47}N_5O_{15}Fe·NO_3·5H_2O$. Calculated, %: C 46.84, H 6.16, N 7.38, and O 33.72. A large distortion of the elemental analysis data for the oxygen atom is likely to be caused by the presence of a large number of heteroatoms (N, P, and F) in the samples. During the analysis, the absorption column for the determination of oxygen partially captures the traces of other heteroatoms, which affects the data on the content of the element being analyzed.

IR spectrum (**I**), *v*, cm^{-1}: 3412.82 (s, OH stretching vibrations); 3075 (s, aromatic C–H vibrations); 2921.97 and 2852.52 (s, $–(CH_2)_n–CH_3$ vibrations); 1738.71 (s, C=O vibrations); 1639.46 (s, C=N); 1602.75, 1514.47, and 1507.67 (s, aromatic C–H vibrations); 1472.81 (s, $–(CH_2)_n–CH_3$ vibrations); 1383.83 (s, NO_3^- vibrations); 1312.11 (s, $–(CH_2)_n–CH_3$ vibrations); 1250.75, 1203.27, and 1162.03 (s, Alk–C–O–C(Ph)); 1058.72 (m, NH vibrations); 845.73 and 824.91 (s, symmetric vibrations of 1,4-disubstituted aromatic ring); and 721.33 and 762.79 (s, $–(CH_2)_n–CH_3$ vibrations).

^{1}H NMR spectrum ($CDCl_3$, TMS): δ, ppm 0.91 m (6H, $–CH_3$); 1.29 m (16H, $–C\underline{H}_2–$Alk); 1.48 t (2H, $–O–CH_2–C\underline{H}_2–$Alk); 1.85 s (2H, $–CH_2–$); 2.09 d (2H, $–C\underline{H}_2–$Alk); 3.01 t (2H, $N–C\underline{H}_2–$); 3.83 t (2H, $N–CH_2–C\underline{H}_2–NH$); 4.07 s (2H, $–O–C\underline{H}_2–$Alk); 5.16 s (1H, $–\underline{NH}–CH_2–$); 5.89 qu (1H, $–CH{=}N–$); 7.02 m (4H, H–Ph); 7.48 m (2H, H–Ph); 7.78 d (2H, H–Ph); 8.18 d (1H, H–Ph); and 8.26 d (2H, H–Ph).

Bis-chelate Fe(III)-containing complex based on 4,4′-dodecyloxybenzoyloxybenzoyl-4-salicylidene-N′-ethyl-N-ethylenediamine with an NO_3^- counterion (II). 4,4′-Dodecyloxybenzoyloxybenzoyl-4-oxy-2-hydroxybenzaldehyde [19, 20] (0.45 g) was dissolved in a mixture of ethyl alcohol with benzene (40 ml:20 ml). Weighed portions of N-ethylethylenediamine (0.07 g) and KOH (0.102 g) dissolved in ethyl alcohol (10 ml and 10 ml respectively) were added to the aldehyde solution and stirred for 30 min. Then an alcohol solution of $Fe(NO_3)_3·9H_2O$ (0.166 g) was gradually poured into the mixture. The dark brown reaction mixture was stirred for 3 h and then cooled; the precipitate was filtered using a glass filter. The product was recrystallized from a mixture of dried solvents: benzene–ethanol (1:4). The product is a fine brown powder. Yield: 0.204 g. Found, %: C 64.51, H 6.97, N 5.83, and O 17.74; $C_{74}H_{94}N_5O_{15}Fe·H_2O$. Calculated, %: C 64.89, H 7.21, N 5.11, and O 18.69.

IR spectrum (**II**), *ν*, cm^{-1}: 3408 and 3226 (m, OH stretching vibrations); 3061 (w, aromatic C–H vibrations); 2971-2870 (s, $–(CH_2)_n–CH_3$ vibrations); 1717 (s, C=O vibrations); 1583 (s, –C=N–); 1478 (m, $–(CH_2)_n–CH_3$ vibrations); 1382 (s, NO_3^- vibrations); 1306 (s, $–(CH_2)_n–CH_3$ vibrations); 1258 (s, Alk–C–O–C(Ph)); 1146–1117 (s, symmetric vibrations of the 1,2,4-substituted aromatic ring); 1057 (m, NH vibrations); and 826 (s, symmetric vibrations of the 1,4-disubstituted aromatic ring).

We were unable to record the NMR spectrum because the substance is not soluble in deuterium solvents.

The attempts to obtain single crystals from concentrated solutions of the synthesized compounds were unsuccessful.

The IR spectra were recorded with a Bruker Vertex 80V device in the 7500-370 cm^{-1} and 670-190 cm^{-1} ranges in KBr and CsBr pellets. The elemental analysis (C, H, N, and O) was carried out using a FlashEA 1112 analyzer. The mass spectra were recorded with a MALDI-ToF Bruker Daltonics Ultraflex mass spectrometer in the positive ion mode; the target voltage was 20 mV; with 2,5-dihydroxybenzoic acid as matrix and chloroform as solvent.

The thermogravimetric analysis was carried out using a NETZCH TG 209 F1 analyzer in a 20 ml/min stream of argon at a rate of temperature elevation of 10°C/min. The differential scanning calorimetry was performed using a NETZCH DSC 204 F1 instrument with the Al capsule material and a sample mass of ≈10 mg at a heating rate of 10°C/min under N_2 atmosphere.

RESULTS AND DISCUSSION

The target compounds were synthesized without isolating the ligand from the solution; therefore, it was important to establish the presence of the Schiff base in the structure of the complexes.

The analysis of the spectra of the complexes in the near-infrared region indicates the presence of the Schiff base formed by N-ethylenediamine. The bands in the ranges 5850-5839 cm^{-1} and 5709-5703 cm^{-1} correspond to two amines: tertiary and secondary respectively [23]. The range 3800-2600 cm^{-1} is dominated by 2921-2851 cm^{-1} bands of the stretching vibrations of $–CH_2–$ alkyl fragments. The 3071 cm^{-1}vibrational bands of aromatic ring protons $\nu_{H–Ph}$ are significantly less intense. The strong absorption bands at 1639 (**I**) cm^{-1} and 1583 (**II**) cm^{-1} in the infrared spectra of the compounds are typical of the azomethine HC=N bond and are located near the vibrational band of the C=O carboxyl group (1733 (**I**) cm^{-1} and 1719 (**II**) cm^{-1}). The two new bands at 1600 (**I**) cm^{-1} and 1540 (**II**) cm^{-1} show a symmetrical coordination of the iron ion with two ligand molecules, indicating that the metal coordinates to the ligand via the nitrogen atom of the azomethine group

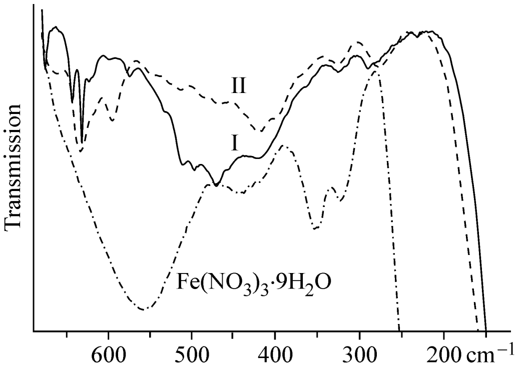


Fig. 1. Comparison of the far IR spectra of complexes **I** and **II** with the source iron salt $Fe(NO_3)_3·9H_2O$ (CsBr pellets).

TABLE 1. *m*/*z* Values for Complexes **I** and **II**

Ion	I_{rel}, %	*m*/*z*		Ion	I_{rel}, %	*m*/*z*	
		exp.**	theor.*			exp.**	theor.*
$C_{37}H_{47}N_5O_{15}Fe·5H_2O$				$C_{74}H_{94}N_5O_{15}Fe·H_2O$			
$[L^+]$	7.67	618.73	616.78	$[L^+]$	7.55	617.42	616.78
$[L·Fe·NH_4]^+$	6.51	688.79	690.63	$[2L–C_2H_5]^+$	5.71	1201.6	1204.5
$[L·Fe·K]^+$	2.55	707.42	711.71	$[2L–C_2H_5·Na]^+$	6.62	1224.9	1227.5
$[L·Fe·NO_3]^+$	1.85	738.34	734.62	$[2L·Na]^+$	4.58	1257.5	1256.5
$[L·Fe·NO_3·K]^+$	1.88	777.65	773.62	$[2L·Ca]^+$	2.18	1272.8	1273.5
$[L·Fe·2NO_3·Na]^+$	1.70	825.10	819.63	$[2L·Fe]^+$	1.87	1285.5	1289.4
$[L·Fe·3NO_3·3H_2O]^+$	3.75	912.46	912.62	$[2L·NO_3]^+$	2.56	1293.1	1295.5
$[L·Fe·3NO_3·K·5H_2O]^+$	1.70	984.14	988.62	$[2L·Fe·H_2O]^+$	1.52	1307.3	1308.4
				$[2L·Fe·NO_3·H_2O]^+$	1.51	1370.4	1370.4
				$[2L·Fe·NO_3·H_2O·Na]^+$	1.53	1395.3	1393.4

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*The value for the hypothetical composition of the molecular ligand $[L^+]$ ion with the inclusion of metal ions.

**The composition of the experimental molecular ion.

[24, 25]. A broad absorption band with the maximum at 3423 (**I**) cm^{-1} and 3411 (**II**) cm^{-1} indicates the presence of OH groups of the water molecule in the structure of the complex, which is confirmed by the MALDI-ToF, elemental analysis (Table 1), and the thermogravimetric experiment. The IR spectra are also observed to contain the absorption bands of the nitrate counterion: a strong narrow band of NO_3^- vibrations at 1383 cm^{-1} [26-28] and a moderate-intensity band at 849 (**I**) cm^{-1} and 823 (**II**) cm^{-1}.

The far IR spectra of compounds **I** and **II** (Fig. 1) were compared with the spectra obtained for nonahydrated iron(III) nitrate. The positions of the $M–NO_3^-$ characteristic bands for **I** (291 cm^{-1} and 323 cm^{-1}), the Fe–O stretching vibrations (471 cm^{-1} (**I**) and 422 cm^{-1} (**II**)), and the Fe–N stretching vibrations (513 cm^{-1} and 512 cm^{-1}) were determined [28].

The structure and purity of the complexes were determined using mass spectrometry (MALDI-ToF MS). Table 1 shows the calculated and measured masses of molecular and fragmentary ions, which indicate the existence of a number of stable particles characterizing ferric ions in their immediate environment. The disagreement between the theoretically calculated molecular weights and the experimental weights was 2 au to 6 au. This is likely to be due to experimental error and the matrix used in the MALDI experiment. Azomethine with a molecular weight of ~618, which acts as a ligand, is observed in the mass spectra of all the complexes (Table 1). Since iron ions were found in the coordination sphere of the complex,

TABLE 2. Phase Transition Temperatures from the Differential Scanning Calorimetry Data in the Heating Cycle

Compound	T_{ph1}, °C	ΔH_1, J/g	T_{ph2}, °C	ΔH_2, J/g	*m.p.*, °C	ΔH_m, J/g
$C_{37}H_{47}N_5O_{15}Fe\cdot 5H_2O$	98.11	3.29	114.11	3.92	141.75	19.04
$C_{74}H_{94}N_5O_{15}Fe\cdot H_2O$	84.46	73.12	—	—	137.55	15.39

an increase in the molecular weight due to the addition of iron and counterions was calculated using the foregoing results of the IR and EA measurements.

The recorded mass spectra indicate the presence of three nitrate ions in compound **I** and their interaction with the iron ion, with the intensity of the molecular $[L\cdot Fe\cdot 3xNO_3\cdot 3H_2O]^+$ ion being high and comparable to that of the azomethine molecular $[L^+]$ ion. However, molecular ions of the composition organic environment–Fe^{3+} ion as 2:1 are not observed in the mass spectrum of compound **I**, thus it being the mono-chelate coordination compound [29]. It can be concluded that the complex has an octahedral structure, and, most likely, one of the nitrate ion is in the same plane as the organic molecule and the second and third nitrate ions are above and below the iron ion. It follows from the experimental results that in complex **II** there are two ligand molecules per iron ion, which form a symmetric bis-chelate complex with the octahedral environment of the iron ion, one NO_3^- counterion, and a water molecule in the outer sphere of the complex.

The phase behavior of the synthesized complexes was studied by differential scanning calorimetry. The temperatures and enthalpies of phase transitions are listed in Table 2. Given that the organic part of the complex molecule, as well as the anion, remains unchanged in all cases, except for its ratio to the chelating metal, we can assume that the predominant contribution to the phase behavior of the compounds is made by the structure of the coordination compound and the differences in the ligand environment of the iron(III) ion. It was found for nitrate complex **I** that m.p. is 141°C with exothermic decomposition at about 180°C. In the heating cycle, complex **II** melts at *T* 137°C, passing to an amorphous melt to crystallize at about 115°C during cooling. The thermal decomposition of the complex occurs at 304-306°C in one step.

During the work two complexes containing the Schiff base were obtained with different ligand-to-metal-ion ratios: mono-chelate and bis-chelate coordination compounds. Both samples were found to have an octahedral structure. During the formation of the Schiff base, when 1 mole of the ligand is obtained, 1 mole of water forms. In the subsequent complexation with iron(III) salts, without isolating the ligand from the solution, water molecules may locate both in the inner and outer coordination spheres of the compound [30, 31]. The synthesis of the mono- or bis-chelate coordination compound is significantly affected by the complexation reaction medium. Thus, in the case of the alcohol medium, the dominant reaction is the formation of the linear monocationic monoligand compound $K[Fe(L)(NO_3)_3](H_2O)_5$, in which the Fe(III) ion has the octahedral environment formed by three (ONN) atoms of the tridentate ligand, three nitrate anions, and also a potassium ion and five water molecules in the outer coordination sphere.

The use of the binary solvent (benzene/ethanol) leads to the formation of the bis-chelate bicationic complex $[Fe(L)_2]^+\cdot X^-\cdot H_2O$, ($X = NO_3^-$), whose solubility in organic solvents and other physical and chemical characteristics differ from those of the former compound. The molecules of water and ethanol appear to be partially embedded in the inner sphere of complex **I** during its formation due to hydrogen bonds and block the formation of the bis-chelate compound, thus reducing its solubility and causing a rapid sedimentation process. This does not happen in the case of the mixed solvent because benzene prevents the interaction of water molecules with ligand molecules, forming a ternary azeotrope (benzene–ethanol–water) and shifting the equilibrium to the right. The sedimentation process for compound **II** takes more time, which indirectly confirms our assumption.

In the work we also determined the phase behavior of complexes **I** and **II**. The use of a long linear alkyl (dodecyl) in the periphery of the ligand facilitated the ordering of the complex structure, as indicated by the reversible phase transitions in the crystal–crystal heating/cooling cycles and the high temperature thermal decomposition.

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