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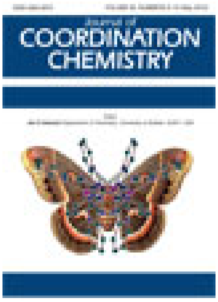

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Bis-chelate Fe(III) complex of an azomethine at the focal point of a branched ester functionalized with cyclohexylbenzoic acid

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Bis-chelate Fe(III) complex of an azomethine at the focal point of a branched ester functionalized with cyclohexylbenzoic acid

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A Fe(III) complex with Cl counter ion based on a branched Schiff base has been synthesized and studied. The compound was produced by the reaction of the Schiff base with $FeCl_3$ at room temperature in benzene–ethanol. The complex is symmetric, i.e., bis-chelate, with an octahedral coordination of Fe. The compound revealed phase transitions of the "solid–solid" type. The complex displayed a temperature-induced spin transition ($S = 1/2 \leftrightarrow 5/2$) which was detected by EPR.

Keywords: Iron(III) complex; Schiff base; EPR spectroscopy; Electronic structure; Bis-chelate; Phase transition; Infrared spectroscopy

1. Introduction

Metal complexes in a dendrimeric (branched) environment have attracted attention [1, 2], finding wide application due to their catalytic activity and as redox sensors [3, 4]. These materials can be employed as components in molecular electronics and photochemical molecular devices for solar energy conversion and information storage [5–7]. Some communications reporting investigations of complexes containing Fe ions with azomethine ligands are of particular interest [8–12]. Such systems with controlled magnetic moment and changeable magnetic and paramagnetic spin find their application as model systems when investigating processes occurring in nature and analyzing intermolecular interactions in artificial environments [13]. The purpose of this work is to obtain an ionic complex with a mixed azomethine ligand (containing cyclohexyl and aromatic fragments), to determine its structure, to confirm its purity, and to study its phase behavior and structural characteristics.

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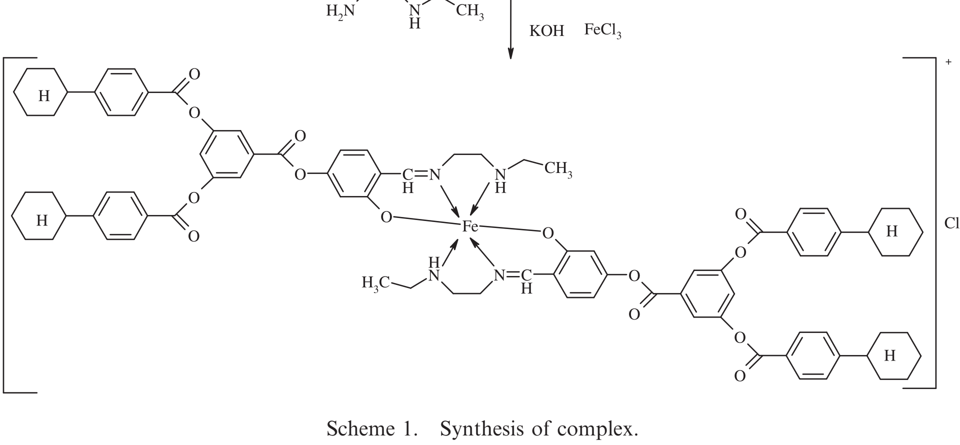
2. Experimental

The reactants and solvents used in the research were chemically pure. 3,5-Di(4-cyclohexylbenzoyloxy)benzoyl-4-oxy-2-hydroxybenzaldehyde was synthesized according to the proposed technique [14] (scheme 1). Infrared (IR)-spectra were recorded using a Bruker Vertex 80 V device from 7500 to 370 cm^{-1} and 670 to 190 cm^{-1} in KBr and CsBr pellets. C, H, N, and O elemental analyses were performed using a FlashEA 1112 analyzer. ^{1}H NMR spectra (500.17 MHz) were obtained using a Bruker Avance-500. Mass-spectra were recorded by an MALDI-ToF mass spectrometer Bruker Daltonics Ultraflex in the positive ion mode, target voltage 20 mV; 2,5-dihydroxybenzoic acid was used as a matrix and chloroform as a solvent. Differential scanning calorimetry (DSC) was performed by an NETZCH DSC 204 FI device, Al pellet, sample mass 10 mg, heating rate 10°C min^{-1} in N_2. The electron paramagnetic resonance (EPR) spectra were obtained using a CW-EPR EMXplus Bruker spectrometer operating at 9.41 GHz (X-band); the modulation frequency was 100 kHz. Commercial cryostats were used to vary the temperature of sample from 4.2 to 300 K.

2.1. *Bis-chelate Fe(III) complex based on 3,5-di(4-cyclohexylbenzoyloxy) benzoyl-4-oxysalicylidene-N′-ethyl-N-ethylenediamine with Cl^-*

3,5-Di(4-cyclohexylbenzoyloxy)benzoyl-4-oxy-2-hydroxybenzaldehyde [14] (0.767 g) was dissolved in a mixture of ethanol and benzene (1 : 1) (scheme 1). *N*-ethylethylenediamine (0.104 g) and KOH (0.152 g) dissolved in EtOH were added. After 30 min of continuous stirring, $FeCl_3$ (0.096 g) in ethanol was added slowly. The reaction



Scheme 1. Synthesis of complex.

continued for another 4 h. The resulting dark brown solution was filtered on a glass filter to separate the precipitate formed. The product is a finely dispersed brown powder. Yield: 0.214 g. Found for $C_{88}H_{94}N_4O_{14}Fe \cdot Cl \cdot H_2O$ (%): C 67.94, H 6.78, N 3.15, O 15.92. Calcd (%): C 68.49, H 6.40, N 3.63, O 15.55.

FT-IR of complex (cm^{-1}): 3426, 3263 (m, stretching vibrations of OH), 3060 (w, aromatic vibrations of C–H), 2928–2853 (s, $-(CH_2)_n-CH_3$), 1737 (s, C=O), 1609 (s, C=N), 1447–1387 (m, $-(CH_2)_n-CH_3$), 1258 (s, Alk–C–O–C(Ph)), 1180 (m, deformation vibrations of the NH aliphatic amine), 1067 (m, NH), 841 (s, flat deformation vibrations –CH of the 1,4-disubstituted aromatic ring), 763 (m, $-CH_2$-vibrations in cyclohexane), 704 (m, non-flat deformation vibrations −CH of 1,3,5-substituted aromatic ring).

^1H NMR of complex ($CDCl_3$, TMS) δ: 0.88 (t, 6H, CH_3–); 1.26 (m, 20H, $-CH_2$-cyclohexyl); 1.38 (m, 8H, $-CH_2$-cyclohexyl); 1.87 (m, 16H, $-CH_2$-cyclohexyl); 2.56 (m, 4H, H-cyclohexyl); 2.95–2.88 (d, 4H, N–CH_2–CH_2–NH); 3.65 (d, 4H, N–CH_2–CH_2–NH); 4.35 (d, 2H, NH); 5.33 (s, 2H, –CH=N); 7.15 (s, 2H, Ph-H); 7.35 (d, 4H, Ph-H); 7.73 (s, 2H, Ph-H); 7.82 (s, 4H, Ph-H); 7.95 (d, 8H, Ph-H); 8.11 (d, 8H, Ph-H).

3. Results and discussion

3,5-Di(4-cyclohexylbenzoyloxy)benzoyl-4-oxy-2-hydroxybenzaldehyde [14] was prepared by system protection block–generation–deprotection functional group. Benzyl ester of 3,5-dihydroxybenzoic acid was used as a building block [15]. The esterification reaction was carried out using OH-group and deprotection of the benzyl group was achieved by hydrogenolysis using 5% Pd/C as a catalyst. The target aldehyde was synthesized from 3,5-di(5-cyclohexylbenzoyloxy)benzoic acid by the formation of ester bond with 2,4-dihydroxybenzaldehyde. Synthesis of the target product was carried out directly through the formation of Schiff base without the isolation of the ligand from the alcoholic solution and the subsequent complex formation with the salt of iron(III).

It was necessary to use a number of physicochemical methods of analysis to determine the structure of the compound obtained. Spectral characteristics of the complex and their interpretation are given below.

The IR spectra of complex exhibited a strong absorption band at 1609 cm^{-1} characteristic of the azomethine bond HC=N [16], close to the band of vibrations of the carboxyl C=O (1737 cm^{-1}). Comparison of the spectroscopic data of the complex obtained and the free Schiff base reveals that $\nu(C{=}N)_{imine}$ at 1609 cm^{-1} in the complex shifts to lower frequency at 1584 cm^{-1}; this indicates that the metal is coordinated with the ligand through nitrogen of the azomethine [17]. A new band at 1568 cm^{-1} is attributed to coordination of the Fe with two ligands. Bands at 1617 cm^{-1} due to ν(O–H) were absent in the complex, indicating coordination to the metal as O^- through deprotonated ligand. A broad absorption band with maximum at 3263 cm^{-1} indicates the presence of OH– of water, confirmed by weak bands at 650 and 930 cm^{-1} attributable to wagging and rocking modes of coordinated water, respectively [18]. Analogous bands attest to the presence of H_2O on external and internal to the coordination sphere of complex [17, 19]. Far FT-IR spectra of the complex (figure 1) show the participation of phenolic oxygen and azomethine nitrogen in the complex by strong IR peaks for stretching vibrations of Fe–O (446 cm^{-1}) and Fe–N (526–518 cm^{-1})

[20–23]. Elemental analysis of the complex shows the presence of one mole of water giving formula as $C_{88}H_{94}N_4O_{14}Fe \cdot Cl \cdot H_2O$.

Table 1 shows the values of molecular and fragmentary ionic mass, both calculated and observed by the MALDI-ToF-MS method on 2,5-dihydroxybenzoic acid used as a matrix. The experimental results show that there are two ligands per Fe ion, in agreement with a symmetric complex of composition $[2L \cdot Fe \cdot Cl \cdot H_2O]^+$ and molecular mass ~1542 (figure 2). This confirms the octahedral environment of the iron due to the metal ion interacting with nitrogen atoms from the *N*-ethylenediamide fragments and hydroxyl groups from the salicylic aldehyde. The molecular ion is also stabilized by sodium ion to form a particle of composition $[2L \cdot Fe \cdot Cl \cdot H_2O \cdot Na]^{+,}$ clearly indicating the formation of a bis-chelate Fe(III) complex on the basis of the branched azomethine.

The phase behavior of the bis-chelate formed was studied by DSC. The complex exhibited several irreversible endothermic phase transitions of the ''solid–solid'' type at 81°C and 170°C, with decomposition occurring at 250°C (figure 3).

In order to detect the spin-crossover behavior (the transition of Fe(III) ions from low-spin ($S = 1/2$) to high-spin ($S = 5/2$) states), the powder complex was investigated

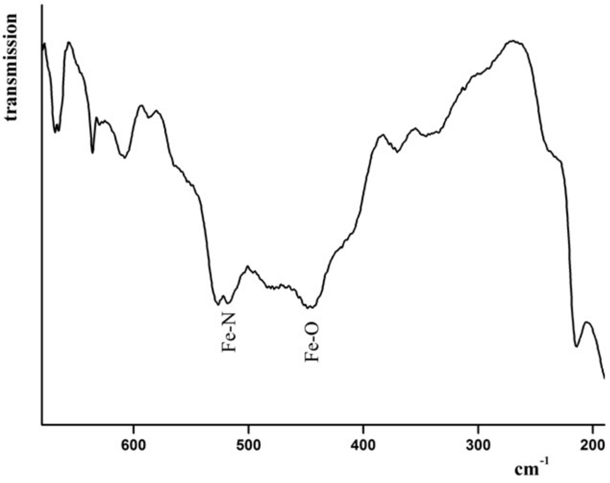


Figure 1. The IR spectrum of $C_{88}H_{94}N_4O_{14}FeCl \cdot H_2O$ from 690 to 170 cm^{-1}.

Table 1. The values of *m*/*z* of the complex.

Ion	*m*/*z*	
	Found	Calcd
$C_{88}H_{94}N_4O_{14}FeCl \cdot H_2O$		
$[L^+]$	715.29	715.85
$[2L \cdot Fe]^+$	1485.2	1487.55
$[2L \cdot Fe \cdot Cl \cdot H_2O]^+$	1542.4	1542.53
$[2L \cdot Fe \cdot Cl \cdot H_2O \cdot Na]^+$	1565.5	1565.53

by EPR spectroscopy from 4.2 K to 297 K. EPR (X-band, $h\nu = 0.3\,\mathrm{cm}^{-1}$) spectra of $C_{88}H_{94}N_4O_{14}FeCl \cdot H_2O$ demonstrated the presence of three types of Fe(III) centers in the system: two types of high-spin Fe ions and one of low-spin. The high-spin

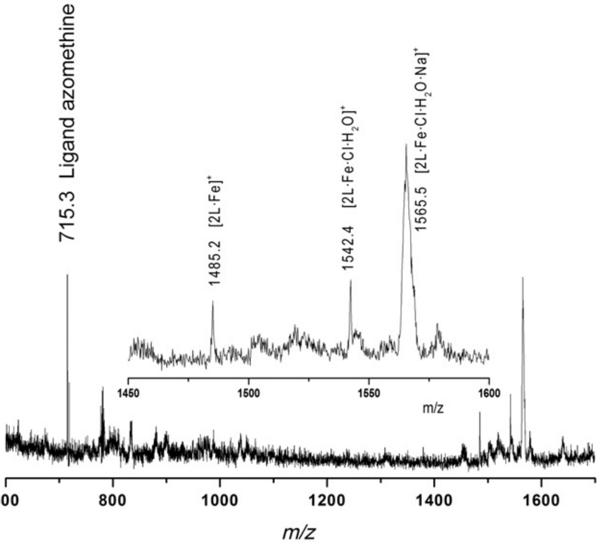


Figure 2. Mass spectrum of $C_{88}H_{94}N_4O_{14}FeCl \cdot H_2O$.

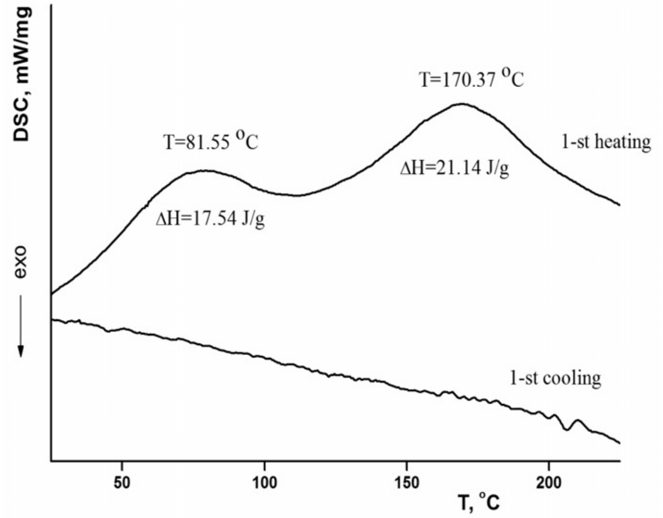


Figure 3. The DSC curves of $C_{88}H_{94}N_4O_{14}FeCl \cdot H_2O$ on heating and cooling.

(HS, ground state $^6S_{5/2}$) Fe(III) centers have been described by the Spin-Hamiltonian [24, 25]:

$$\hat{H} = g\beta BS + D\left[\hat{S}_z^2 - \frac{1}{3}S(S+1)\right] + E\left(\hat{S}_x^2 - \hat{S}_y^2\right), \tag{1}$$

with $g = 2$ and $S = 5/2$, where D and E are zero-field splitting parameters characterizing, respectively, the axial and the rhombic distortions of the crystal field on Fe ion from the octahedral symmetry; the relation $0 < E/D \leq 1/3$ holds. The first (I) type of HS centers (signal with $g_{\text{eff}} = 4.3$) corresponds to Fe ions having a strong ($D \gg 0.3\,\text{cm}^{-1}$) low-symmetry ($E/D = 1/3$) crystal field (figure 4). The second (II) type of HS centers (signal with $g_{\text{eff}} = 2$) belongs to Fe ions in an octahedral environment with weak ($D \ll 0.3\,\text{cm}^{-1}$, $E = 0$) distorted axial crystal field. The low-spin (LS, ground state $^2T_2$) Fe(III) centers have been characterized by the following magnetic resonance parameters: $g_x = g_y = 2.20$, $g_z = 1.935$.

Heating of the sample from 4.2 to 100 K is accompanied by a reversible structural phase transition at which the symmetry of the nearest environment of Fe ions is changed sharply and type I of HS centers are transformed to II. Further heating of the sample is accompanied by decrease of the number of LS centers and increase of the number of HS centers of type II. Such behavior testifies to the existence of the spin ($S = 1/2 \leftrightarrow 5/2$) transition in the system.

The complex shows multiplet NMR spectrum, but of paramagnetic character (figure 5). We find that explanation of this fact is difficult, but several samples of paramagnetic complexes which demonstrate multiplet proton signals as for mono-chelate [12, 26] and bischelate Fe (III) complexes [27] and for Cu symmetrical phthalocyanines complexes [28] were described. In our case, there are two main reasons to explain the multiplicity in NMR spectrum of the complex. In the first place, low concentration of sample in $CDCl_3$ (10^{-3} mol L^{-1}) can lead to a weak dipole interaction between molecules, detected by weak broadening of signal. Second, it is known that the spin state of coordinating compound can change under the influence of solvent by solvation [29, 30] for complexes with counterion in coordination core and out of coordination sphere. If spin equilibrium exists in the powder of sample, the low spin state of Fe^{3+} can appear in solution. Consequently, this gives the observed spectrum of complex.

4. Conclusions

Octahedral complexes of Fe(III) with an N_4O_2 coordination core were prepared previously employing the Schiff-base as a ligand by the condensation of some aldehydes with *N*-ethylethylenediamine [31, 32]. In some cases, they were nonmesogenic [31] or liquid crystalline complexes [32] with spin-crossover behavior for some anions. A bis-chelate Fe (III) complex based on branched esters with a Schiff base functionality has been synthesized for the first time. Fe^{3+} has octahedral coordination. The phase behavior of the complex has also been established. The presence of cyclohexyl as functional groups at the periphery of the branched ligand and their spatial configuration (*cis*-, *trans*-) cause steric hindrance in the complex due to the repulsion of $-CH_2$-

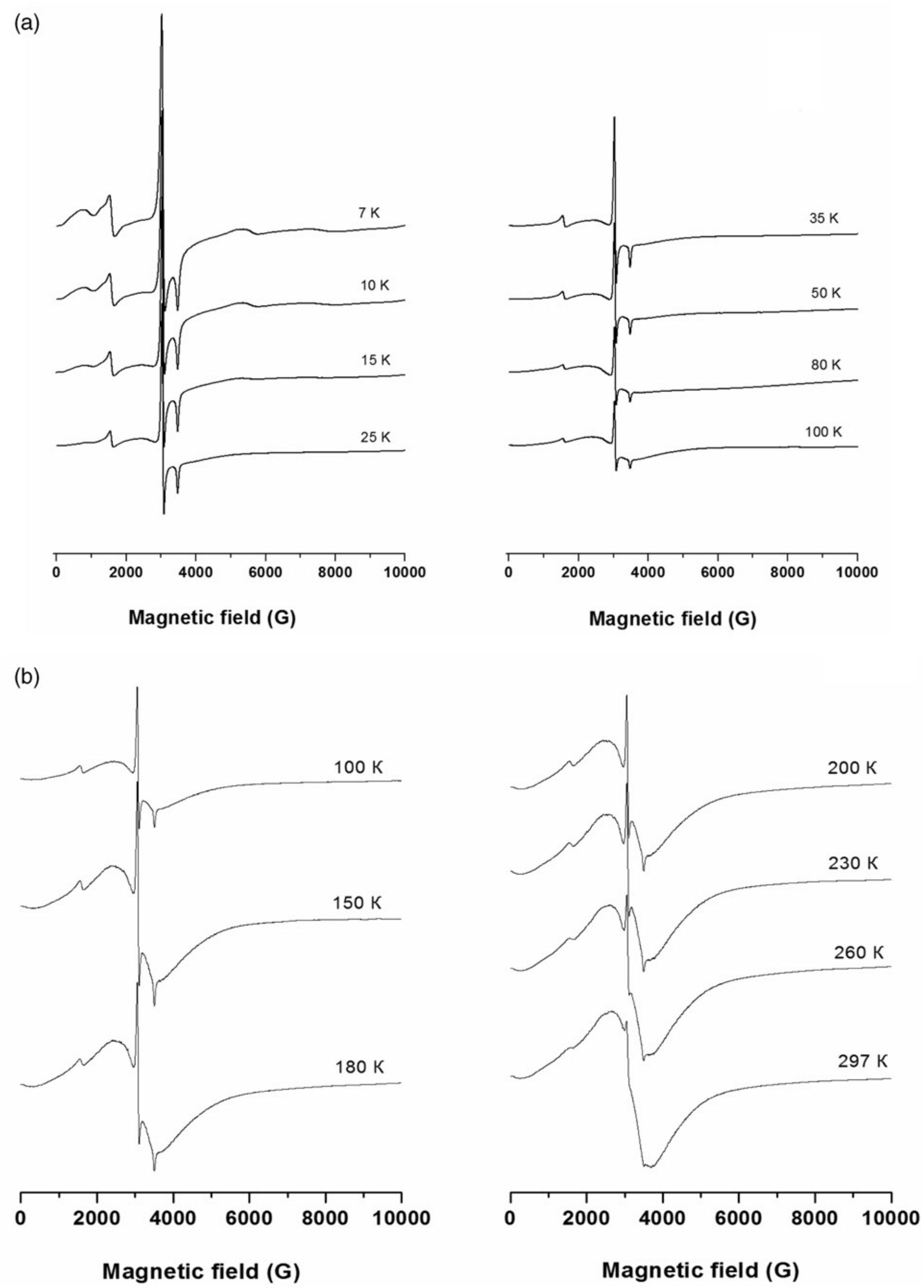


Figure 4. The temperature dependence of the EPR spectra of the compound from (a) 7 K to 100 K; (b) 100 K to 297 K.

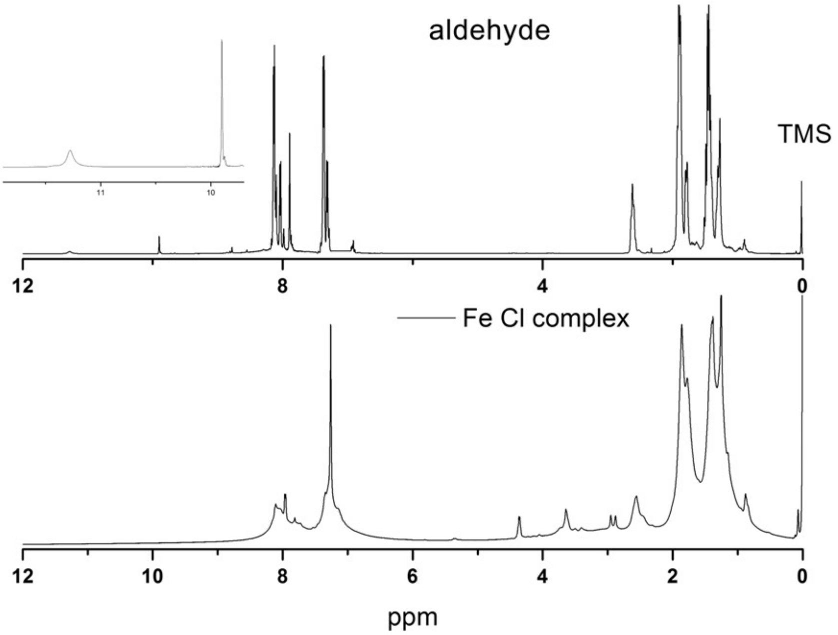


Figure 5. NMR spectra of azomethine and $C_{88}H_{94}N_4O_{14}FeCl \cdot H_2O$ in $CDCl_3$.

groups of the cyclohexane rings, resulting in an earlier temperature decomposition and irreversible endothermic phase transitions of the ‘‘solid–solid’’ type. This iron complex exhibits a temperature induced spin-crossover ($1/2 \leftrightarrow 5/2$) behavior.

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