

Template Synthesis of the Iron(III) Complex with the Ligands Based on Acylpyrazolonepyridines

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Abstract—The reaction of new bidentate ligand, 1-(5-hydroxy-1-methyl-3-(pyridin-2-yl)-1*H*-pyrazol-4-yl)ethan-1-one (L), with iron(III) chloride affords the mononuclear iron(III) complex FeL₂Cl₃, which is characterized by XRD (CIF file CCDC no. 2309481). The intramolecular hydrogen bond between the protonated pyridyl and acetyl groups in ligand L, which exists in the crystal as a zwitterion, provides the formation of rarely met iron complexes in which the β-diketonate fragment coordinates via the η¹ mode. A similar coordination mode along with a possibility of a more favorable η² coordination provides new possibilities for the design of heteropolynuclear compounds of various structures used in the fabrication of molecular devices of data storage and processing.

Keywords: pyrazolylpyridines, iron complexes, XRD, polynuclear complexes, oxophilic and nitrophilic ions

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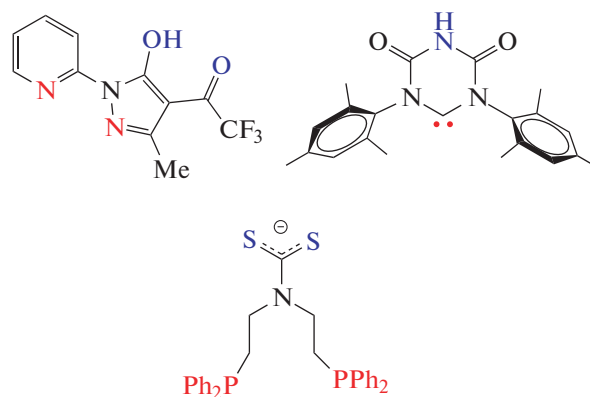
INTRODUCTION

The development of new technological solutions aimed at enhancing the productivity of computation technology is one of the most important tasks of modern microelectronics [1]. Although many devices for data storage and processing are built of inorganic materials [2, 3], recent interest of researchers shifts to molecular compounds capable of intramolecular transferring of an electron due to the simplicity of their chemical modification and diverse properties [4, 5]. Among these compounds are metal complexes with organic polyfunctional ligands, which can coordinate the second metal ion thus providing a possibility of the intramolecular electron transfer in the complex [4, 5]. The presence or absence of this transfer makes it possible to use such complexes in molecular spintronics devices for the storage and processing (in the form of spin cubits) of information [6, 7].

The corresponding complexes are synthesized, as a rule, by template self-assembling as the most efficient method for the synthesis of polyheteronuclear compounds [8]. However, it is not always possible to predict beforehand their structural features (geometry, number of nuclei, and type of the latter) and the more so the properties [9]. Ligands of the “two-face” type are used sometimes for their selective synthesis (Scheme 1) [10–13]. They contain two and more coordination sites capable of selectively binding *d*- and *f*-metal ions of different types, which allows one to

synthesize heteropolynuclear complexes with beforehand specified structures.

These ligands can be substituted acylpyrazolonepyridines [14], carbenoimidates [12], and diphosphin-edithiocarbamates [15] containing coordination sites of different natures (for example, nitrophilic and oxophilic). Structural similarity and different rigidity/softness of two chelating fragments toward various transition metal ions make it possible to selectively prepare mononuclear complexes: precursors for heteropolynuclear complexes [13].

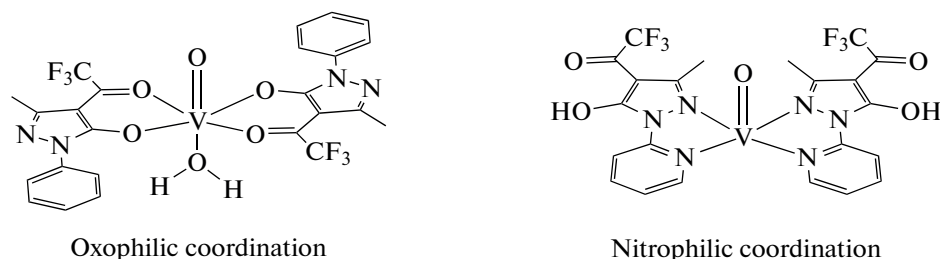


Scheme 1.

Sufficiently many complexes with pyridylpyrazolones in which the metal ion coordinates either the oxophilic (β-diketonate), or nitrophilic (pyridinepyra-

zole) fragment (Scheme 1) have been synthesized to date. However, general recommendations on the chemical modification of the ligand and synthesis conditions for the corresponding complexes with transition metal ions for controlling the coordination

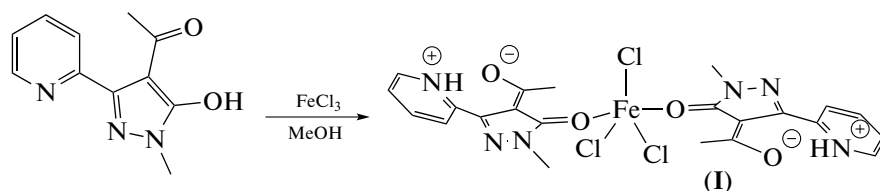
mode are still lacking [16–18]. For instance, the introduction of the pyridine substituent into the first position of the pyrazole ring changes the coordination mode of vanadyl sulfate from oxophilic to nitrophilic (Scheme 2) [18].



Scheme 2.

Acylpyrazolones are known to react with iron(II/III) salts with the η^2 coordination of the β -diketonate fragment [19]. We assumed that the introduction of the pyridine substituent into the acylpyrazolone ligand upon complex formation with iron(III) chloride in the absence of a base would make it possible to coordinate to the nitrogen atom for even such transition metal ion as iron(III) that predominantly binds to oxygen-containing

ligands. The design proposed for the acylpyrazolone ligand allowed us to synthesize the first example of the iron(III) complex FeL_2Cl_3 (**I**) in which this ligand, namely, 1-(5-hydroxy-1-methyl-3-(pyridin-2-yl)-1*H*-pyrazol-4-yl)ethan-1-one (**L**), is coordinated by the metal ion to the β -diketonate fragment via the rarely met η^1 mode (Scheme 3).



Scheme 3.

EXPERIMENTAL

All procedures related to the synthesis of ligand **L** and its complex were conducted in air using commercially available organic solvents. Tetrahydrofuran (THF) was purified by distillation over sodium with benzophenone or sodium hydride. Analyses to carbon, nitrogen, and hydrogen were carried out on a Carlo Erba (model 1106) microanalyzer. NMR spectra were recorded on a Varian INOVA 400 spectrometer (frequency 400.1 MHz for ^1H and 100.6 MHz for ^{13}C) at 25°C.

Synthesis of ethyl picolinate. Concentrated sulfuric acid (10 mL) was added with stirring to a solution of picolinic acid (20 g, 16.2 mmol) in ethanol (400 mL). The reaction mixture was refluxed at 85°C (oil bath) for 8 h. The resulting mixture was evaporated on a rotary evaporator, distilled water (50 mL) was added, and the mixture was neutralized with Na_2CO_3 to reach the neutral pH. The aqueous solution was three times

extracted with dichloromethane (20 mL). The extract was evaporated on a rotary evaporator, and the formed light yellow solution was distilled. The prepared product was a transparent liquid. The yield was 14.3 g (58%).

^1H NMR (CDCl_3 ; 400 MHz; δ , ppm): 8.69 (dd, $^3J_{\text{H,H}} = 4.7$ Hz, $^4J_{\text{H,H}} = 1.2$ Hz, 1H, 6-Py), 8.07 (d, $^3J_{\text{H,H}} = 7.8$ Hz, 1H, 3-Py), 7.77 (td, $^3J_{\text{H,H}} = 7.8$, $^4J_{\text{H,H}} = 1.2$ Hz, 1H, 4-Py), 7.40 (dd, $^3J_{\text{H,H}} = 7.8$ Hz, $^3J_{\text{H,H}} = 4.7$ Hz, 1H, 5-Py), 4.41 (q, $^3J_{\text{H,H}} = 7.1$ Hz, 2H, CH_2), 1.37 (t, $^3J_{\text{H,H}} = 7.1$ Hz, 3H, CH_3). ^{13}C NMR (CDCl_3 ; 101 MHz; δ , ppm) 165.18, 149.79, 148.15, 136.97, 126.81, 125.05, 61.91, 14.28.

Synthesis of ethyl 3-oxo-3-(pyridin-2-yl)propanoate. Potassium *tert*-butoxide (7.4 g, 66 mmol) was added with stirring to a solution of ethyl picolinate (5.0 g, 33.1 mmol) in THF (100 mL), and ethyl acetate (6.5 mL, 66 mmol) was added dropwise slowly. The

reaction mixture was stored at room temperature for 3 h. The formed mixture was evaporated on a rotary evaporator, distilled water (30 mL) was added, and the mixture was neutralized with HCl to the neutral pH. The aqueous solution was three times extracted with dichloromethane (20 mL), MgSO_4 was added to remove moisture traces, and the mixture was carefully decanted and evaporated on a rotary evaporator. The product formed as a yellow oil was dried in vacuo and used without further purification. The yield was 4.1 g (64%).

^1H NMR (CDCl_3 ; 400 MHz; δ , ppm): 8.59 (d, $^3J_{\text{H,H}} = 4.8$ Hz, 1H, 6-Py), 7.99 (d, $^3J_{\text{H,H}} = 7.8$ Hz, 1H, 3-Py), 7.80 (t, $^3J_{\text{H,H}} = 7.8$ Hz, 1H, 4-Py), 7.42 (dd, $^3J_{\text{H,H}} = 7.8$ Hz, $^3J_{\text{H,H}} = 4.8$ Hz, 1H, 5-Py), 4.13 (q, $^3J_{\text{H,H}} = 7.1$ Hz, 2H, OCH_2), 3.38 (s, 2H, CH_2), 1.17 (t, $^3J_{\text{H,H}} = 7.1$ Hz, 3H, CH_3). ^{13}C NMR (CDCl_3 ; 101 MHz; δ , ppm): 194.57, 148.97, 136.98, 127.54, 121.98, 61.28, 50.03, 44.76, 30.07, 13.99.

Synthesis of 1-methyl-5-(pyridin-2-yl)-1H-pyrazol-3-ol. Potassium carbonate (1.66 g, 12.0 mmol) was added with stirring to a solution of ethyl 3-oxo-3-(pyridin-2-yl)propanoate (2.1 g, 10.9 mmol) in ethanol (100 mL), and methyl hydrazinium sulfate (0.986 g, 12.0 mmol) was added. The reaction mixture was stored at room temperature for 12 h. The solution was separated from a precipitate, washed with a small amount of ethanol, and evaporated on a rotary evaporator. The formed dry residue was washed with a small amount of acetone and dried in vacuo. The yield was 1.56 g (82%).

For $\text{C}_9\text{H}_9\text{N}_3\text{O}$

Anal. calcd., %	C, 61.70	H, 5.19	N, 23.99
Found, %	C, 61.59	H, 5.10	N, 24.10

^1H NMR (CDCl_3 ; 400 MHz; δ , ppm): 14.35 (s, 1H, OH), 8.64 (d, $^3J_{\text{H,H}} = 5.1$ Hz, 1H, 6-Py), 8.07 (d, $^3J_{\text{H,H}} = 7.8$ Hz, 1H, 3-Py), 7.91 (t, $^3J_{\text{H,H}} = 7.8$ Hz, 1H, 4-Py), 7.55 (dd, $^3J_{\text{H,H}} = 7.8$ Hz, $^3J_{\text{H,H}} = 5.1$ Hz, 1H, 5-Py), 3.67 (s, 1H), 3.61 (s, 3H, CH_3). ^{13}C NMR (CDCl_3 ; 101 MHz; δ , ppm): 153.22, 146.34, 144.20, 138.65, 123.26, 122.48, 97.66, 33.72, 16.78.

Synthesis of 1-methyl-5-(pyridin-2-yl)-1H-pyrazol-3-yl acetate. Triethylamine (1.923 mL, 13.8 mmol) was added to a solution of 1-methyl-5-(pyridin-2-yl)-1H-pyrazol-3-ol in THF (100 mL), and the mixture was stirred for 5 min. Then acetyl chloride (0.6 mL, 5.06 mmol) was added to the resulting solution, and the reaction mixture was stored at room temperature for 30 min. A formed white precipitate was separated from the solution using the Schott filter, evaporated, and dried in vacuo. The yield was 1.15 g (90%).

^1H NMR (CDCl_3 ; 300 MHz; δ , ppm): 8.55 (dd, $^3J_{\text{H,H}} = 4.7$ Hz, $^4J_{\text{H,H}} = 1.5$ Hz, 1H, 6-Py), 7.84 (d, $^3J_{\text{H,H}} = 7.8$ Hz, 1H, 3-Py), 7.65 (td, $^3J_{\text{H,H}} = 7.8$ Hz,

$^4J_{\text{H,H}} = 1.5$ Hz, 1H, 4-Py), 7.15 (dd, $^3J_{\text{H,H}} = 7.8$, 4.7 Hz, 1H, 5-Py), 4.52 (s, 1H), 3.63 (s, 3H, NCH_3), 1.94 (s, 3H, $\text{C}(\text{O})\text{CH}_3$).

Synthesis of 1-(5-hydroxy-1-methyl-3-(pyridin-2-yl)-1H-pyrazol-4-yl)ethan-1-one (L). Titanium(IV) chloride (2 mL, 18.6 mmol) was added to a solution of 1-methyl-5-(pyridin-2-yl)-1H-pyrazol-3-yl acetate (1.15 g, 4.11 mmol) in dichloromethane (100 mL). The reaction mixture was stored at room temperature for 12 h. At the end of the reaction, distilled water was added with stirring to the solution, and the mixture was stored until the red color of the solution changed to yellow. The formed emulsion was three times extracted with dichloromethane (20 mL), which was evaporated on a rotary evaporator. The formed yellow powder was dried in vacuo. The yield was 0.69 g (60%).

For $\text{C}_{11}\text{H}_{11}\text{N}_3\text{O}_2$

Anal. calcd., %	C, 60.82	H, 5.11	N, 19.35
Found, %	C, 60.91	H, 5.25	N, 19.48

^1H NMR (CDCl_3 ; 300 MHz; δ , ppm): 8.40–8.29 (m, 2H, 6-Py, 3-Py), 7.99 (t, $^3J_{\text{H,H}} = 7.8$ Hz, 1H, 4-Py), 7.42 (d, $^3J_{\text{H,H}} = 7.8$ Hz, 1H, 5-Py), 3.52 (s, 3H, NCH_3), 2.69 (s, 3H, $\text{C}(\text{O})\text{CH}_3$). ^{13}C NMR (CDCl_3 ; 101 MHz; δ , ppm): 187.34, 166.77, 149.60, 141.64, 140.59, 123.43, 121.52, 102.17, 31.93, 22.50.

Synthesis of FeL_2Cl_3 (I). A solution of 1-methyl-5-(pyridin-2-yl)-1H-pyrazol-3-yl acetate (100 mg, 0.46 mmol) in methanol (10 mL) was prepared in a 25-mL round-bottom flask, and iron(III) chloride (37 mg, 0.00023 mol) was added to the solution. The mixture was stirred at room temperature for 4 h. Diethyl ether was slowly added to the resulting solution to form a methanol–diethyl ether interface. Then the solution was stored at room temperature for 3 days until dark red crystals of the target iron(III) complex began to form. The yield was 92 mg (67%).

For $\text{C}_{22}\text{H}_{22}\text{N}_6\text{O}_4\text{Cl}_3\text{Fe}$

Anal. calcd., %	C, 44.29	H, 3.72	N, 14.09
Found, %	C, 44.47	H, 3.77	N, 14.22

XRD of single crystals of complex **I** was conducted on a Bruker Quest D8 diffractometer (MoK_α radiation, graphite monochromator, ω scan mode) at 100 K. The structure was solved using the ShelXT program [20] and refined by full-matrix least squares using the Olex2 program [21] in the anisotropic approximation for F_{hkl}^2 . The hydrogen atoms of the NH group were localized in the difference Fourier synthesis, and positions of other hydrogen atoms were calculated geometrically and refined in the isotropic approximation by the riding model. The main crystal-

Table 1. Crystallographic data and refinement parameters for FeL₂Cl₃

Parameter	Value
Empirical formula	C ₂₂ H ₂₂ N ₆ O ₄ Cl ₃ Fe
<i>FW</i>	597.72
<i>T</i> , K	100
Crystal system	Monoclinic
Space group	<i>P2/c</i>
<i>Z</i>	2
<i>a</i> , Å	11.4449(6)
<i>b</i> , Å	8.2541(4)
<i>c</i> , Å	13.3040(7)
α , deg	90
β , deg	105.245(3)
γ , deg	90
<i>V</i> , Å ³	1212.57(11)
ρ_{calc} , g cm ⁻³	1.637
μ , cm ⁻¹	9.99
<i>F</i> (000)	611
2 θ_{max} , deg	56
Number of measured reflections	13826
Number of independent reflections	2878
Number of reflections with <i>I</i> > 2 σ (<i>I</i>)	2245
Number of refined parameters	207
<i>R</i> ₁	0.0503
<i>wR</i> ₂	0.1266
GOOF	1.081
Residual electron density (min/max), e Å ⁻³	−0.624/0.908

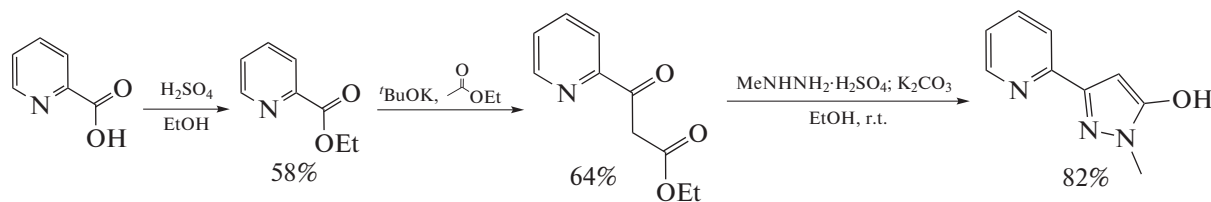
lographic data and refinement parameters are given in Table 1.

The structural parameters for complex **I** were deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC no. 2309481; <http://www.ccdc.cam.ac.uk/>).

RESULTS AND DISCUSSION

The precursor of ligand **L**, 1-methyl-3-(pyridin-2-yl)-1*H*-pyrazol-5-ol, was synthesized in five

stages from picolinic acid. The first three stages included the esterification of picolinic acid with ethanol in an acidic medium, the Claisen condensation between the formed ethyl picolinate and ethyl acetate under the action of potassium *tert*-butoxide in THF, and the condensation of the formed diketone and methyl hydrazinium sulfate followed by one-stage cyclization in ethanol in the presence of potassium carbonate (Scheme 4) to form pyrazolypyridine.

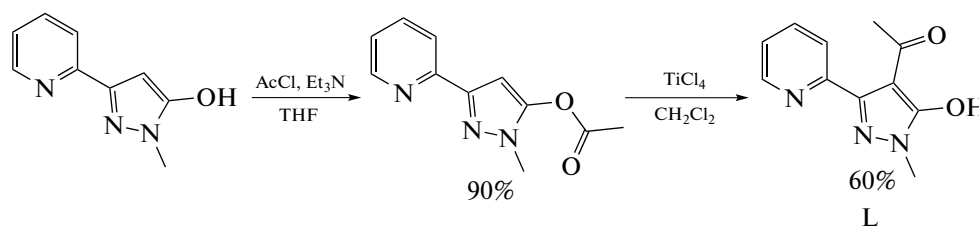

Scheme 4.

In the presence of calcium hydroxide or triethylamine, the subsequent C-acylation of pyrazolypyri-

dine unexpectedly [22] afforded a mixture of C- and O-acylation products or selective O-acylation prod-

uct, respectively. This can be due to the chelating ability of the pyridine ring owing to which the calcium(II) ion coordinates at the nitrophilic position rather than oxophilic position thus promoting O-acylation.

To synthesize the C-acylation products, the corresponding reaction was conducted in two consecutive stages: reacting with acetyl chloride in the presence of triethylamine followed by the rearrangement of the product under the action of titanium(IV) chloride (Fries rearrangement [23], Scheme 5). Target ligand L



Scheme 5.

For the presumable coordination of the oxophilic metal ion at the nitrophilic position of ligand L, we chose the iron(III) ion, whose oxophilicity is intermediate [24]. For this purpose, the ligand was introduced into the reaction with iron(III) chloride in a ratio of 2 : 1 in methanol (Scheme 2). According to the XRD data (Fig. 1, Table 2), the reaction product turned out to be the iron(III) complex FeL_2Cl_3 in which the iron(III) ion in the high-spin state [25] coordinated three chloride anions ($\text{Fe}-\text{Cl}$ 2.2277(15)–2.3041(9) Å) and two symmetrically equivalent ligands L, and only one carbonyl group of the β -diketonate fragment was involved in the coordination ($\text{Fe}(1)-\text{O}(1)$ 1.979(3) Å). The C–O bond lengths (1.274(4) and 1.258(5) Å) appreciably exceeded the values characteristic of the C=O double bonds (1.24 Å [26]). In addition, the C–C bond between the pyrazole ring and acetyl group (1.431(4) Å) was intermediate between the ordinary and double bonds (1.54 and 1.34 Å [27]), which is due to the tautomeric distribution of the negative charge over the β -diketonate fragment. The positive charge in the ligand, which was the zwitterion, is localized on the protonated pyridyl fragment that formed a strong intramolecular hydrogen bond ($\text{N}\cdots\text{O}$ 2.573(4) Å, NHO 162.56(18)°) with the carbonyl group of the acetyl substituent of ligand L. It is most likely that the latter additionally stabilized its planar (within 0.05 Å for non-hydrogen atoms) conformation. For instance, the angle between the planes of the pyrazole and pyridine rings was only 0.51(13)°.

The coordination environment of the iron(III) ion in complex I is a distorted octahedron with one vacant vertex, which was indicated by the so-called “symmetry measures” [28]. The lower these “measures,” the better the polyhedron shape is described by the corresponding polygon, such as an ideal octahedron with one vacant vertex (vOC-5) (Table 2). For the iron(III)

exists in the β -diketonate form, since the ^1H NMR spectrum exhibits no signal from the OH group and contains two different binding positions (nitrophilic and oxophilic), which can be used for the selective preparation of hetero- and bimetallic complexes when coordinating such transition metal ions as iron(II/III), cobalt(II), or manganese(II) to the oxophilic position and nickel(II) and copper(II) to the nitrophilic position.

ion, the “symmetry measure” $S(\text{vOC-5})$ estimated from the XRD data using the Shape 2.1 program [28] was only 2.496. For comparison, the “symmetry measure” characterizing the deviation of the polyhedron shape from one more ideal polyhedron with five vertices, spherical square pyramid (SPY-5), adopted a higher value of 4.168.

Note that the change in the complex formation stoichiometry did not result in other products differed from complex I. Thus, using the design proposed by us for acylpyrazolone ligand L in the third position of the pyrazole ring, we synthesized the first iron(III) complex in which this ligand coordinates the metal ion by only one carbonyl group of the β -diketonate fragment. The complex formation occurred with the formation of a strong intramolecular hydrogen bond between the second carbonyl group and protonated pyridyl fragment in the ligand. The presence of this bond pre-determines, most likely, the nature of the reaction product, since only one oxygen atom of the β -diketonate fragment remains accessible for coordination and, therefore, the complex with the coordination of the iron(III) ion only via the rarely met [29] η^1 mode instead of the traditional η^2 coordination mode. The formation of complex I with this coordination mode is also favored by the choice of the counterion: the coordinating chloride anion that builds up the coordination sphere of the metal ion to a distorted octahedron with one vacant vertex.

In spite of the earlier described vanadyl complexes with pyridylpyrazolones [18], the pyridyl substituent in the acylpyrazolone ligand could not promote the nitrophilic coordination of the iron(III) ions. However, its introduction into position 3 of the pyrazole ring makes it possible to accomplish the linear geometry of binding polydentate ligands, which can be used

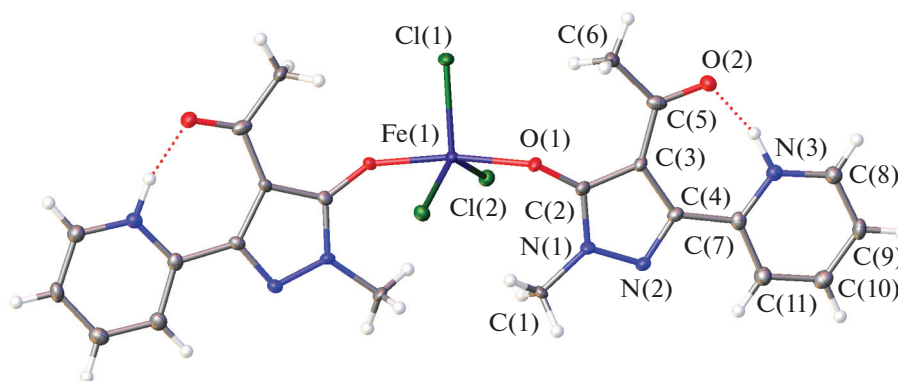


Fig. 1. General view of the FeL₂Cl₃ complex in the representation of atoms by thermal vibration ellipsoids ($p = 50\%$). The complex in the crystal occupies the partial position: the twofold axis passes through the iron(III) ion and coordinates to it chloride anion Cl(1). The minor disordering component with the population $<3\%$ is omitted, and the numeration is given only for symmetrically independent atoms.

for the synthesis (by the coordination of the free nitrophilic position) of heteropolynuclear complexes of different structures for the fabrication of molecular devices for data storage and processing. However, the intramolecular hydrogen bond in the FeL₂Cl₃ complex should preliminarily be decomposed, which can presumably be accomplished by the action of noncoordinating bases, for example, 1,8-diazobicyclo(5.4.0)undecen-7-ene.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

Table 2. Selected geometric parameters for the FeL₂Cl₃ complex according to the XRD data at $T = 100\text{ K}^*$

Parameter	FeL ₂ Cl ₃
Fe–O(1), Å	1.979(3)
Fe–Cl(1), Å	2.2277(15)
Fe–Cl(2), Å	2.3041(9)
S(PP-5)	24.548
S(vOC-5)	2.496
S(TBPY-5)	8.895
S(SPY-5)	4.168
S(JTBPY-5)	8.330

* The values are presented only for the major disordering component with the population $>97\%$. The parameters S(PP-5), S(vOC-5), S(TBPY-5), S(SPY-5), and S(JTBPY-5) describe the deviation of the shape of the metal ion polyhedron from ideal polyhedra with five vertices: pentagon (PP-5), octahedron with one vacant vertex (vOC-5), trigonal bipyramid (TBPY-5), spherical square pyramid (SPY-5), and Johnson trigonal bipyramid (JTBPY-5), respectively.

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