Synthesis, structure, and magnetic properties of iron—yttrium complexes containing acetylacetonate ligands

M. V. Tsodikov, O. V. Bukhtenko, O. G. Ellert, I. A. Petrunenko, A. S. Antsyshkina, G. G. Sadikov, Yu. V. Maksimov, Yu. V. Titov, and V. M. Novotortsev*

A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, 29 Leninsky prosp., 117912 Moscow, Russian Federation. Fax: +7 (095) 230 2224

Two new compounds have been obtained by the synthesis of heteronuclear iron—yttrium acetylacetonate, using the modified electrochemical dissolution of the [YFe_2] alloy. One of these compounds, with the $Fe(acac)_2 \cdot 2H_2O$ composition, has been studied by X-ray diffraction analysis. X-ray diffraction data: $a = 11.002(5)$, $b = 5.412(2)$, $c = 11.179(5)$ Å; $\beta = 106.39(4)°$; $V = 638.6$ Å^3, space group $P2_1/c$, $Z = 2$. According to the data on magnetic susceptibility, Mössbauer spectroscopy, and X-ray electron microanalysis, single crystals of this complex are covered with an amorphous film containing finely dispersed $[Y_{1-a}Fe_a]_n$ clusters and, probably, superparamagnetic γ-Fe_2O_3 species. The second oligomeric acetylacetonate complex contains ions of high-spin two-valence iron, yttrium, and finely dispersed ferromagnetic $[Y_{1-a}Fe_a]_n$ intermetallide clusters.

Key words: anodic electrochemical dissolution, diaqua(bisacetylacetonato)iron(II), heteronuclear iron—yttrium acetylacetonate, finely dispersed ferromagnetic $[Y_{1-a}Fe_a]_n$ clusters, X-ray diffraction analysis, magnetic susceptibility, Mössbauer spectroscopy, X-ray electron microanalysis.

Special attention has been paid recently to acetylacetonate metal complexes, along with alcoholates, since they are used as precursors of phases in alkoxosyntheses of complex oxides.[1—3] We (Refs. 4 and 5) and foreign authors (Refs. 6 and 7) have shown previously that low-temperature synthesis of intermediates of multicomponent and, in several cases, monophase oxides, which are of interest as materials for the electronic industry and as catalysts of a new generation, can be performed on the basis of these complexes.

It is also known that in order to form intermediates of several complex and monophase metal-containing oxides, in several cases it is most expedient to use bimetallic precursors and, in particular, bimetallic alkoxides, whose syntheses are well developed presently.

The preparation of mononuclear metal acetylacetonates is also described. Several acetylacetonate complexes were synthesized by the anodic electrochemical dissolution of metals in a medium of acetylacetone, a supporting electrolyte, and a small amount of conducting addition.[8] The method suggested allows one to prepare rather simply highly purified acetylacetonate complexes.

At the same time, only few works devoted to preparing heteronuclear acetylacetonates are known.[9]

In this work, the synthesis of the [YFe_2] iron—yttrium alloy by the modified electrochemical dissolution in acetylacetone, structures and magnetic properties of heteronuclear iron—yttrium acetylacetonates are studied with the purpose of using them in preparation of complex oxides.

Experimental

Iron—yttrium complexes were synthesized in an electrolyzer equipped with a reflux condenser with a calcium chloride tube.

Cylindrical rods, ~10 mm in diameter of YFe_2 intermetallide (so-called "Laves phase") were used as electrodes. The electrochemical dissolution of the intermetallide in acetylacetone was carried out with an alternating current for 15 h, V = 120 V and I = 0.1 mA.

An organic electrolyte consisted of anhydrous acetylacetone (Hacac) and a supporting solvent acetonitrile (AcN) taken in the volume ratio Hacac : AcN = 1 : 1. A small amount of Et_4NBr was used as a conducting additive.

After voltage feeding was ceased, the organic solution was stored at 0 to 4 °C for 48 h. Rather large yellow crystals precipitated during this time. The crystals precipitated were separated from the mother liquor on a Büchner funnel and recrystallized from a hexane—acetone (8 : 1) mixture. After recrystallization the product (complex **1**) was washed on a Büchner funnel with warm hexane to remove an admixture of iron(III) acetylacetonate formed.

The mother liquor was evaporated on a rotary evaporator. A solid residue was dissolved in acetone, and six volumes of hexane were added to the solution. The solid residue formed was separated on a Büchner funnel, and the product (complex **2**) was washed with warm hexane.

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Solid complexes **1** and **2** were dried in a vacuum drier at the residual pressure of 1 Torr and temperature of 50 to 60 °C and then in a Fischer drying apparatus over P_2O_5.

For complex **1** found (%): C, 42.3; H, 5.3; Fe, 18.4; Y, 8.4; O, 25.6. $Fe_{0.32}Y_{0.10}C_{3.52}H_{5.30}O_{1.60}$. For complex **2** found (%): C, 35.0; H, 4.4; Fe, 2.4; Y, 31.0; O, 26.6. $Fe_{0.04}Y_{0.35}C_{2.91}H_{4.40}O_{1.66}$.

Complex **1** was studied on a Syntex $P2_1$ automated X-ray diffractometer (Mo-Kα irradiation, a graphite monochromator, θ/2θ-scanning to $\theta_{max} = 28°$). 2658 reflections were measured, and 930 independent reflections with $I > 2\sigma(I)$ were used for refinement. Parameters of the monoclinic unit cell: a = 11.002(5), b = 5.412(2), c = 11.179(5) Å, β=106.39(4)°, V = 638.6(1) Å^3, d_{calc} = 1.51 g cm^{-3}, space symmetry group $P2_1/c$, $Z = 2$.

The structure was resolved by the heavy atom method in the series of the difference Fourier syntheses, and all atoms were localized. The refinement was performed by the full-matrix least-square method in the anisotropic-isotropic (for H atoms) approximation to $R = 0.041$, $R_w = 0.039$. Calculations were performed by a SHELX-90 program on an IBM AT-286 computer. Coordinates of atoms with equivalent temperature corrections for nonhydrogen atoms and with isotropic corrections for hydrogen atoms are presented in Table 1. Values of bond lengths and bond angles are presented in Table 2.

Phase compositions were studied on a Philips PW1700 X-ray installation, using copper filtered radiation. Parameters of the crystalline lattice were determined by the standard procedure.[10] Phases were identified by comparison between values of indicated interplanar distances and intensities of reflections with the corresponding known values.[11]

Magnetic properties of iron-containing complexes were studied by the Faraday method on the installation described previously.[12] The temperature dependence of the static magnetic susceptibility $\chi(T)$ was determined in the 77 to 300 K temperature range. The dependence of the susceptibility on the applied magnetic field was recorded at room temperature and at the temperature of liquid nitrogen. Values of the effective magnetic moments were calculated on the basis of the known dependence[12]

$$\mu_{eff} = 2.28\sqrt{\chi_{mol}T},$$

where χ_{mol} is the molar magnetic susceptibility with the correction for diamagnetism.

Mössbauer spectra of iron-containing complexes were obtained on an electrodynamic type installation with the ^{57}Co source in the chromium matrix at 300 K. Isomeric shifts (I.s.) and values of quadrupole splitting (Q.s.) were counted relative to the signal of α-Fe. The spectra were treated by standard programs of the least-squares method for the Mössbauer transition 3/2—1/2.

IR spectra of compounds **1** and **2** (pellets with KBr) were obtained on a Specord 8000 spectrophotometer.

Elemental composition was determined by atomic absorption spectroscopy on a Perkin-Elmer 400 spectrometer.

Microanalyses of complexes **1** and **2** were performed on a Camebax X-ray spectral microanalyzer with wave spectrometers. A working voltage was 15 kV at a current I = 2.10 to 8 A. Concentrations of Fe and Y were determined from intensities of characteristic X-ray lines of Fe-Kα and Y-Lα. Single crystals of complex **1** were 0.5 to 1.5 mm in size. Microcompositions of monocrystals were studied by the chip surface (110) (S). The composition of a powdered complex was analyzed by a defocused beam with the diameter of a probe of ~100 μm.

Table 1. Coordinates of atoms (×10^4, for H atoms ×10^3) and thermal corrections B_{iso}/B_{eq} for complex **1**

Atom	x	y	z	B_{iso}/B_{eq}
Fe	5000(0)	5000(0)	5000(0)	2.36(2)
O(1)	3796(3)	3334(6)	5835(3)	2.91(9)
O(2)	3518(3)	7111(6)	4013(3)	2.68(8)
O(w)	5479(5)	7929(8)	6438(4)	4.3(1)
C(1)	2607(5)	3293(9)	5440(4)	2.6(1)
C(2)	1878(4)	488(1)	4507(4)	2.8(1)
C(3)	2353(4)	6708(8)	3878(4)	2.4(1)
C(4)	1927(7)	1420(10)	5998(5)	3.5(2)
C(5)	1437(6)	8360(10)	2979(5)	3.2(1)
H(2)	104(4)	459(9)	433(4)	2(1)
H(41)	204(5)	170(10)	677(6)	5(2)
H(42)	101(7)	130(10)	559(6)	6(2)
H(43)	220(6)	0(10)	584(6)	6(2)
H(51)	66(7)	780(10)	287(6)	6(2)
H(52)	157(6)	820(10)	215(6)	6(2)
H(53)	147(6)	980(20)	326(6)	7(2)
H(1w)	550(7)	780(10)	719(7)	9(2)
H(2w)	557(5)	901(9)	636(4)	1(1)

Table 2. Bond lengths and bond angles in complex **1**

Bond	d/Å	Bond	d/Å
Fe—O(1)	2.034(3)	Fe—O(2)	2.041(3)
Fe—O(w)	2.212(4)	O(1)—C(1)	1.258(6)
O(2)—C(3)	1.266(6)	O(w)—H(1w)	0.84(7)
O(w)—H(2w)	0.61(5)	C(1)—C(2)	1.412(7)
C(1)—C(4)	1.496(8)	C(2)—C(3)	1.399(7)
C(2)—H(2)	0.90(5)	C(3)—C(5)	1.501(7)
C(4)—H(41)	0.85(6)	C(4)—H(42)	0.99(8)
C(4)—H(43)	0.86(8)	C(5)—H(51)	0.88(8)
C(5)—H(52)	0.98(7)	C(5)—H(53)	0.86(9)

Angle	ω/deg	Angle	ω/deg
O(1)—Fe—O(2)	88.4(1)	O(1)—Fe—O(w)	92.1(2)
O(2)—Fe—O(w)	89.0(2)	Fe—O(1)—C(1)	126.5(3)
Fe—O(2)—C(3)	126.6(3)	Fe—O(w)—H(1w)	128(5)
Fe—O(w)—H(2w)	127(5)	H(1w)—O(w)—H(2w)	104(7)
O(1)—C(1)—C(2)	124.5(4)	O(1)—C(1)—C(4)	117.3(4)
C(2)—C(1)—C(4)	118.3(5)	C(1)—C(2)—C(3)	126.0(5)
C(1)—C(2)—H(2)	113(3)	C(3)—C(2)—H(2)	121(3)
O(2)—C(3)—C(2)	124.8(4)	O(2)—C(3)—C(5)	116.3(4)
C(2)—C(3)—C(5)	118.9(4)	C(1)—C(4)—H(41)	111(4)
C(1)—C(4)—H(42)	114(4)	C(1)—C(4)—H(43)	106(5)
H(41)—C(4)—H(42)	108(6)	H(41)—C(4)—H(43)	114(6)
H(42)—C(4)—H(43)	103(6)	C(3)—C(5)—H(51)	110(5)
C(3)—C(5)—H(52)	110(4)	C(3)—C(5)—H(53)	111(5)
H(51)—C(5)—H(52)	104(6)	H(51)—C(5)—H(53)	107(7)
H(52)—C(5)—H(53)	114(6)		

Results were obtained by a computer simulation according to standard procedures for microanalysis (Cameca). Since the complex contained light elements C, H, and O in addition to metallic components Fe and Y, we failed to perform the complete analysis of mass concentrations. Therefore, concentrations of Fe and Y obtained are relative. However, it should be mentioned that the absence of correction coefficients, which take into account effects of the interaction between

electrons and X-ray irradiation and atoms of a compound, makes an error of less than 20 rel. %. This allows one to make rather reliably a notion about the concentration distribution of Fe and Y atoms in the volume of a sample studied.

Results and Discussion

Two new complexes **1** and **2** were isolated from the mother liquor after electrochemical dissolution of the YFe_2 intermetallide and treatment of the electrolyte. It is shown that the IR spectra of both complexes are nearly identical and are represented mainly by intense bands at 1520, 1530, and 3600 cm^{-1}. It is known that the first two bands are typical of stretching vibrations of C—O bonds of chelate acetylacetonate ligands.[13] The bands in the range of 3600 cm^{-1} are most likely due to hydroxyl groups of crystal hydrate water, which enters the composition of these complexes.

According to the X-ray data (Fig. 1), a molecule of **1** has the structure of diaquabisacetylacetonatoiron(II) $Fe(acac)_2 \cdot 2H_2O$ and is referred to the isostructural series of similar complexes of bivalent metals Mg, Mn, Co, and Ni, whose structures have previously been described[14–17] and discussed in detail in reviews (Refs. 18—20).

Unlike compounds listed, which were studied by the photomethod, the structure of iron complex **1** is determined from the diffractometric data. This makes it possible to measure structural parameters with a higher accuracy, in particular, to localize all hydrogen atoms and to refine their position and thermal parameters.

It is shown in Fig. 1, that in the center-symmetric molecule acetylacetonate ligands chelately coordinate an iron atom to form six-membered metallocycles, and the metal coordination is supplemented by two H_2O molecules arranged on the axial coordinate at the lengthened distance. A polyhedron is a tetragonally distorted octahedron.

The Fe—O distances in the equatorial plane are 2.034(3) and 2.041(3) Å, Fe—O(w) 2.213(3) Å. The average lengths of the O—C and C—C bonds in the cycle are 1.262(6) and 1.406(7) Å, respectively, and correspond to the structure with delocalized bonds in a metallocycle in the form of an envelope inflected along the O...O line by 14.7°. In the crystal, the complexes are united in layers parallel to (100) due to the O—H...O-type H-bonds toward shortest distances between molecules. These directions are the y axis and the direction of slipping along the z axis. Only weak van der Waals forces act between the layers.

Parameters of H-bonds: $O(w)...O(1)_{(1-x,5-y,1-z)}$ 2.934(4), O(w)—H(1w) 0.86(8), H(1w)...O(1) 2.14(8) Å, angle O(w)—H(1w)—O(1) 158(3)°; $O(w)...O(2)_{(1-x,2-y,1-z)}$ 2.999(5), O(w)—H(2w) 0.61(8), H(2w)...O(2) 2.41(8) Å, angle O(w)—H(2w)—O(2) 164(3)°.

The magnetic properties of complex **1** turned out to be unexpected. The dependence of the static magnetic susceptibility χ on the applied magnetic field is presented in Fig. 2. The temperature dependence of the reverse magnetic susceptibility is presented in Fig. 3 (curve *1*). Effective magnetic moments calculated for an

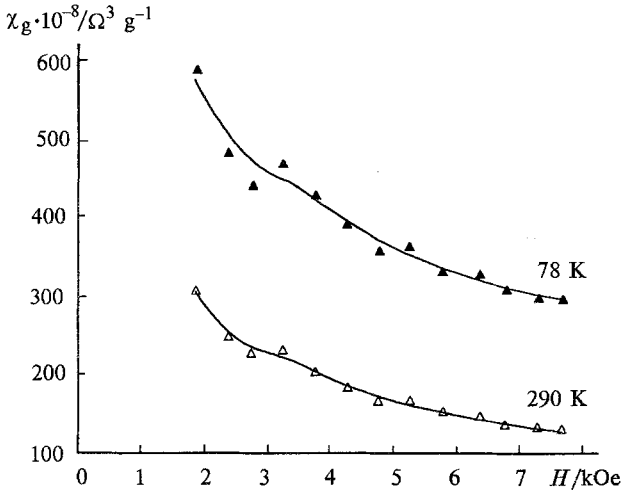

Fig. 2. Dependence of the gram magnetic susceptibility of complex **1** on the value of the applied magnetic field.

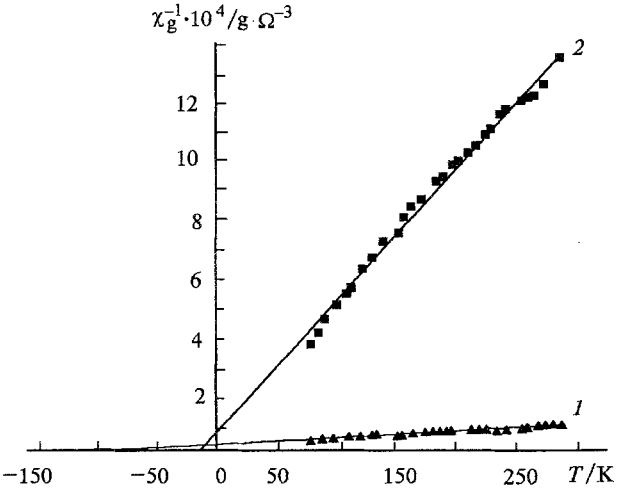

Fig. 3. Temperature dependences of the reverse value of the gram magnetic susceptibility for complexes **1** (*1*) and **2** (*2*).

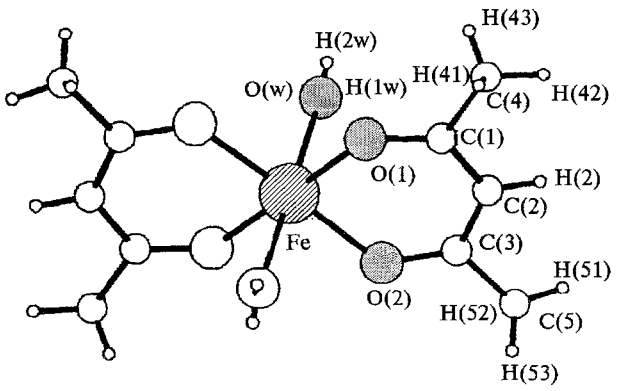

Fig. 1. Structure of complex **1**.

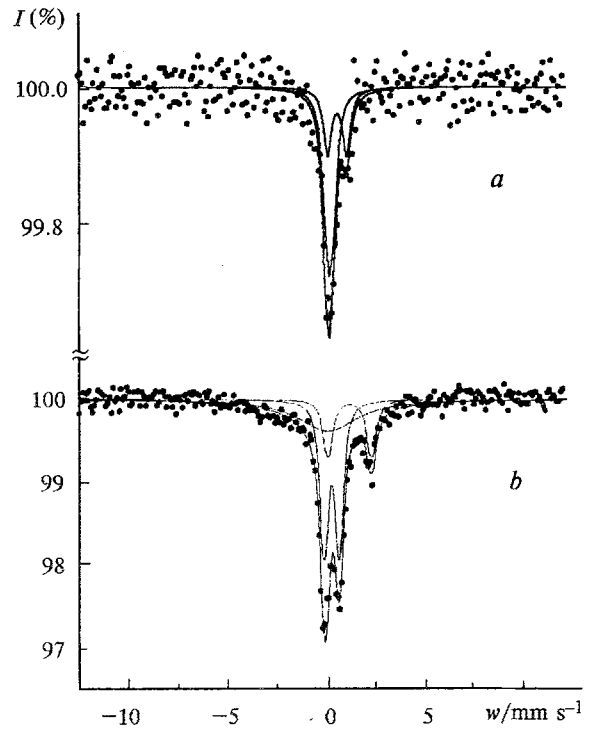

Fig. 4. Mössbauer spectra of complexes **1** (*a*) and **2** (*b*).

iron(II) acetylacetonate molecule turned out to be anomalously high compared to the high-spin state of Fe^{2+} (4.9 μ_B), equaling approximately 9 μ_B at room temperature. It is seen from Fig. 3 (curve *1*) that the dependence $\chi^{-1}(T)$ as a whole obeys the Curie—Weiss law in the whole temperature range with a negative Weiss constant θ. At the same time, the susceptibility of complex **1** depends on the value of the applied magnetic field (see Fig. 2), which indicates the presence of a ferromagnetic admixture in the sample, resulting in a strong increase in magnetic moments. Weak exchange interactions of the antiferromagnetic type are probably caused by intermolecular interactions in the crystal. Thus, it can be assumed that the single crystal of **1** is covered with an X-ray amorphous film of compounds or a compound with ferro- or ferrimagnetic properties. In fact, the bag-shaped region (I.s. = 0.11 mm s^{-1}, population density ~38 %) is present in the Mössbauer spectrum of the complex (Fig. 4, *a*) in addition to the doublet corresponding to high-spin two-valence iron (I.s. = 1.27 mm s^{-1}, Q.s. = 2.21 mm s^{-1}, population density ~19 %). This line can correspond to the superfine structure of highly dispersed magnetic ordered iron-containing clusters. One more doublet found in the spectrum is related to Fe^{3+} in the O^{2-} surroundings (I.s. = 0.37±0.05 mm s^{-1} and Q.s. = 0.76±0.05 mm s^{-1}, population density ~43 %).

These results confirm that unusual magnetic properties of single crystals of bivalent iron acetylacetonate can be caused by superparamagnetic species of the ferromagnetic alloy of which the electrode consists. These species form a film on the crystal surface. In addition, the presence of superparamagnetic clusters of iron γ-oxide also fixed on the surface cannot be excluded.

Table 3. X-ray spectral microanalysis data

Region of measurements	Composition (wt. %)	
	Fe	Y
Chip surface	15.03	0.00
of crystal	15.18	0.02
(volume of crystal)	14.64	0.03
	16.25	0.03
Crystal covering	21.36	5.62

According to the X-ray spectral microanalysis data (Table 3), yttrium and iron in the ~1 : 4 mass ratio are found in the covering of the crystal, while only iron is present in the crystal volume (the content of yttrium is less than 0.1 mass %).

It can be seen from Fig. 3 (curve *2*) that the dependence of χ^{-1} for compound **2** obeys the Curie law. The effective magnetic moment is unchanged in the 77 to 300 K temperature interval, 5.4 μ_B per iron atom. This value can be caused[21] by high-spin iron(II) ions. A weak dependence of the magnetic susceptibility on the applied magnetic field (Fig. 5) means that a small amount of a ferro- or ferrimagnetic admixture is present.

The Mössbauer spectrum of complex **2** (see Fig. 4, *b*) consists of two doublets. Parameters of one of them are similar to those of the monoline with I.s. = 0.26 mm s^{-1} and Q.s. = 0.29 mm s^{-1}. It can be referred to the cluster of the $[Y_{1-a}Fe_a]_n$ alloy and $a \leq 1$. The parameters of the doublet with I.s. = 0.68 mm s^{-1} and Q.s. = 0.97 mm s^{-1} occupy an intermediate position between those characteristic of the Fe^{III} state and the high-spin Fe^{II} state.

The X-ray spectral microanalysis data for this compound concerning iron and yttrium (Fe : Y ≈ 1 : 19)

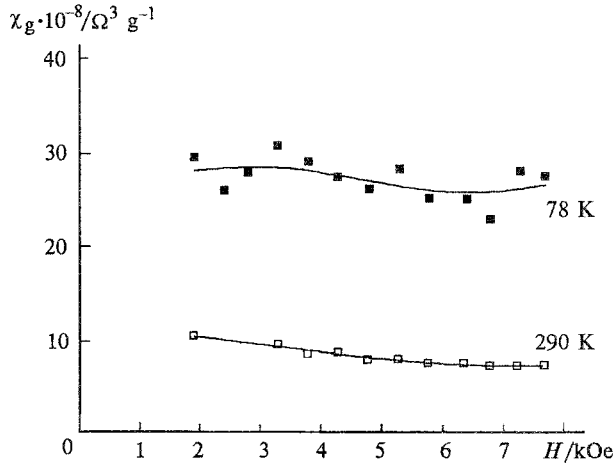

Fig. 5. Dependence of the gram magnetic susceptibility of complex **2** on the applied magnetic field.

coincide as a whole with those obtained by atomic absorption spectroscopy.

Like the spectrum of complex **1**, the IR spectrum of complex **2** contains vibrations at 1520, 1530, and 3600 cm^{-1}, which are most likely related to acetylacetonate ligands and hydroxyl groups of crystal hydrate water. Taking into account the data presented above, one can assume that compound **2** is the acetylacetonate oligomeric complex containing high-spin bivalent iron and yttrium. Like for complex **1**, the presence of superparamagnetic clusters, which act as a ferromagnetic admixture, can be considered to be established.

Thus, two new compounds are the main products of the modified electrochemical dissolution of the iron—yttrium [YFe_2] alloy in acetylacetone:

1. Monocrystalline complex **1**, which is diaquabisacetylacetonatoiron(II). Single crystals of this complex are covered with an X-ray amorphous film containing finely dispersed $[Y_{1-a}Fe_a]_n$ clusters and, probably, superparamagnetic species of γ-Fe_2O_3.

2. Polycrystalline acetylacetonate complex **2**, which is likely an oligomer containing ions of high-spin two-valence iron and yttrium and highly dispersed clusters of the ferromagnetic intermetallide of which the electrode consists.

In our opinion, both of these complexes can be promising for the synthesis of complex oxides using sol—gel technology.

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