2088 Russian Chemical Bulletin, International Edition, Vol. 60, No. 10, pp. 2088—2093, October, 2011

Synthesis and structure of binuclear iron(II) complex with the cage-like ligand as a model of methane monooxygenase

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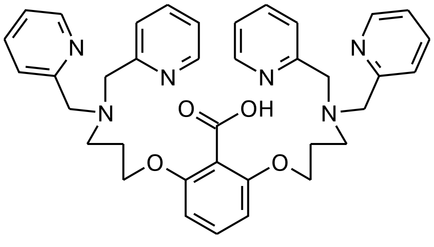
A binuclear iron(II) complex, $[Fe^{II}_2L(OTf)_2](OTf)$ (**1**), with the cage-like ligand LH = $[(PyCH_2)_2N(CH_2)_3O]_2C_6H_3COOH$ containing an immobilized carboxylate was synthesized and characterized in order to model an active center of soluble methane monooxygenase (sMMO). Studies on the oxidation of cyclohexane with hydrogen peroxide or O_2 involving this complex showed that the complex **1** does not catalyze the indicated reactions. Consideration of crystal structure of complex **1** gives an explanation of its inactivity in the reaction of O_2 activation.

Key words: modeling methane monooxygenase, binuclear iron(II) complexes, biomimetic oxidation, activation of O_2.

The nature created an efficient catalyst for the direct selective oxidation of methane to methanol under the environmental conditions — in aqueous medium at ambient temperature and pressure, *viz.*, an enzyme methanemonooxygenase (MMO), which exists in the soluble (sMMO) and the membrane-bound forms having different structures.[1] The absence of similar direct chemical process of low-temperature oxidation of methane to methanol stimulated attempts to model the natural phenomenon.[2—4] Since no efficient chemical models of MMO are yet developed, any efforts in this direction seem of undoubted interest.



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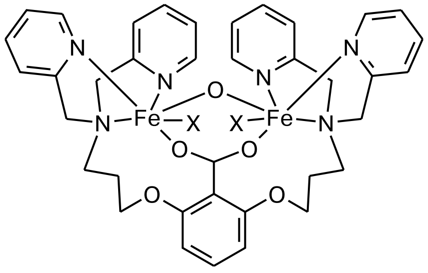

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2: X = H_2O (**a**), 2X = BzO (**b**)

The crystal structure of sMMO from *Micrococcus capsulatus (Bath)*[5] (further, MMO) shows that the active center (AC) of the enzyme contains two iron atoms linked *via* a carboxylate bridge, *i.e.*, from the chemical point of view the AC of MMO is a binuclear μ-carboxylate iron complex incorporated into the protein globule (Fig. 1). Complexes based on simple ligands frequently are labile in solutions and, therefore, not always can adequately model a well balanced structure of the enzyme AC. Proceeding from this, we have designed[6,7] polydentate cage-like ligand (LH) with the immobilized carboxylate **1** and synthesized on its basis binuclear μ-carboxylate iron(III) complexes of the composition $[Fe_2^{III}OLX_n]^{m+}$ (**2**, X = H_2O, $n = 2$, $m = 3$ (**a**); X = OBz, $n = 1$, $m = 2$ (**b**)), which model the ferri-form of MMO.

These complexes catalyzed oxidation of methane to methanol with hydrogen peroxide at room or slightly elevated temperature (2—7 cycles of catalysis (TON) at 20—60 °C)[8] and in the experiments with cyclohexane and *cis*-1,2-dimethylcyclohexane showed the signs of monooxygenase mechanism of oxidation of alkanes, in particular, incorporation of the ^{18}O oxygen isotope from $H_2{}^{18}O$ into the product and stereoselectivity of the process.[9] Since efficiency of the process was low, we assumed that this was due to the insufficient stability of the active complex in solution caused by flexibility of the cage-like ligand used by us.[6] In addition, it is known that the oxidized form of MMO poorly "works" with hydrogen peroxide.[10] This could have been the other reason of unsatisfactory effi-

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 2051—2056, October, 2011.

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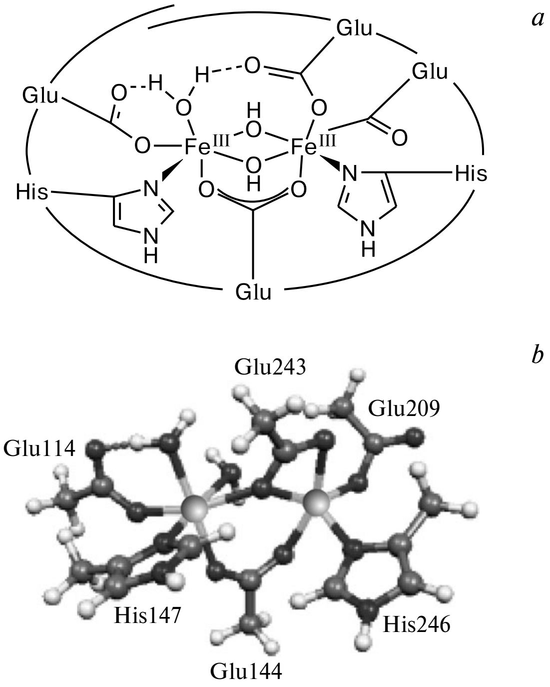
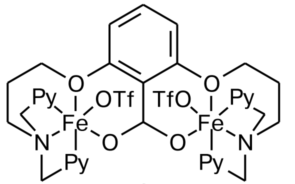


Fig. 1. The scheme of the active center of MMO in the oxidized, ferri-, (*a*) and reduced, ferro-, (*b*) forms.

ciency of our model. In order to check this assumption, in the present work we synthesized an iron(II) complex **3** with the same cage-like ligand **1**, which can be considered as a possible model of the reduced form of MMO, and studied its reactions with O_2 and H_2O_2 in the presence and in absence of an alkane.



3

Experimental

All the solvents were no less than 99.5% in purity and were used either as obtained, or after drying with CaH_2 (methanol) or molecular sieves (3 Å). Cyclohexane was distilled over metallic sodium. Other reactants were of commercial purity (99%, Aldrich). Syntheses were carried out under argon in a glove box or using the Schlenk-type vacuum glassware. Elemental analysis was performed in the Microanalytical Laboratory of IPChPh of RAS. Absorption spectra in the UV and visible regions were recorded on Specord M-40 or Varian 300 BioUV/vis spectrophotometers. IR spectra were recorded on Specord 75-IR and Specord M-82 spectrometers. Mass spectrometric measurements with the electrospray ionization (ESI) were performed on a high-resolution time-of-flight mass spectrometer in the Institute of Energy Problems of Chemical Physics of RAS.[11] ^{1}H NMR spectra in acetonitrile-d_3 were recorded on a Varian UNITY spectrometer (300 MHz), chemical shifts are given in the δ scale relatively to the resonance of residual protons of the solvent.

X-ray diffraction analysis for the complex **3** was performed in the Laboratory of Crystallography of Departement of Chemistry of the University of Minnesota. A crystal (of approximate size 0.32×0.26×0.20 mm) was placed on a glass capillary tip 0.1 mm in diameter on a Bruker SMART Platform CCD diffractometer to collect data at 173(2) K using Mo-Kα radiation (graphite monochromator). The structure was solved using the SIR97 program. All the nonhydrogen atoms were positioned geometrically and refined in the anisotropic full-matrix approximation on F^2, whereas all the hydrogen atoms were placed in the ideal positions and refined in the isotropic approximation. Four molecules of CH_2Cl_2 were localized based on the electron density, but only one of them was well resolved, the other three were disordered between two or three positions. Electron density from the molecules of CH_2Cl_2 was removed using the PLATON program.

Oxidation of alkanes in the presence of complex **3** was performed at 20 °C in glass vessels (10 mL) as described earlier.[7] Products of oxidation were analyzed on a Hewlett—Packard 5880A chromatograph with a flame-ionizing detector and a Carbowax 20M capillary column.

The ligand **1** was synthesized according to the procedure described earlier[7] and purified by gradient chromatography on a silica gel column; R_f 0.15 (methanol—ethyl acetate (1 : 1)), R_f 0.5 (methanol), R_f 0.05 (methanol—ethyl acetate—acetonitrile (1 : 1 : 0.5)). IR (KBr), ν/cm^{-1}: 1716 (COOH), 1592, 1569, 1458, 1434, 1374, 1298, 1251, 1101, 761 The ^{1}H NMR spectrum of ligand **1** agrees with that given in the work.[7]

Sodium salt of ligand 1 (LNa). A solution of sodium methoxide (20.2 mg) in anhydrous methanol (2 mL) was added to a solution of ligand **1** (237 mg, 0.375 mmol) in methanol (2 mL) with stirring, the stirring was continued for 1 h, followed by concentration to dryness. IR (KBr), ν/cm^{-1}: 1592, 1569, 1457, 1434, 1386, 1245, 1251, 1095, 763. Disappearance of the vibration band of the carboxy group at 1716 cm^{-1} was observed in the IR spectrum.

Synthesis of complex [Fe$^{II}_2$L(OTf)$_2$](OTf) (3). A solution of $Fe(OTf)_2(MeCN)_2$ (330 mg) in acetonitrile (2 mL) was added dropwise to a solution of the sodium salt of ligand **1** (245 mg, 0.375 mmol) in acetonitrile (2 mL) placed in a Schlenk flask with stirring, the stirring was continued for 5 h, the solvent was half evaporated, an equal amount of anhydrous diethyl ether was added, and the mixture was kept in refrigerator. A white precipitate that formed was dissolved in the CH_2Cl_2—MeCN (9 : 1) mixture and filtered. Hexane was layered on top of the mixture and this was left for 18 h at room temperature. The next day, large cubical colorless crystals of complex **3** suitable for X-ray diffraction analysis were grown on the walls. Complex **3** is stable in air in the crystalline state, but slowly loses the solvate, as well as is oxidized on storage in acetonitrile. IR (KBr), ν/cm^{-1}: 1605, 1560 (ν^{as} (COO$^-$)), 1463, 1422 (ν^{s} (COO$^-$)), 1310, 1265, 1238, 1222, 1159, 1031, 800, 637. MS (ESI), *m/z*, (I_{rel} (%)): 247.7 [LFe$_2$]$^{3+}$ (100), 446.0 [LFe$_2$(OTf)]$^{2+}$ (20), 1041.0 [LFe$_2$(OTf)$_2$]$^{2+}$ (4). Found (%): C, 39.43; H, 3.29; N, 6.80; S, 7.85. $C_{40}H_{39}N_6O_{13}S_3F_9Fe_2 \cdot 0.5CH_2Cl_2$. Calculated (%): C, 39.45; H, 3.23; N, 6.82; S, 7.80. ^{1}H NMR (acetonitrile-d_3), δ: 120, 99.06, 53.28, 17.00, 7.45, 5.37, 3.12, 2.05, −2.65, −14.02.

Results and Discussion

Binuclear iron(III) complexes with the cage-like ligand **1** synthesized earlier can be considered as the structurally functional models of the AC of ferri-MMO (see Fig. 1, *a*), though not efficient enough. From the point of view of structural resemblance, they contain two iron atoms linked *via* a carboxylate bridge. In addition, they have four labile coordination sites (two on each iron atom) necessary for catalysis, which are arranged toward each other and provide a possibility of supposed bridged mechanism[12] of activation of O_2 with the formation of the active oxidant, *viz.*, bis-μ-oxo-binuclear iron complex. The use of the cage-like ligands allows one to maintain integrity of this structure even under conditions of very low concentrations of the complex in solutions usually used in catalysis. In these model complexes, the labile coordination sites are occupied either by molecules of water, complex **2a**, or with the bidentate carboxylate, in particular, with benzoate, complex **2b**.

In the nature, MMO are functionally active in the ferro-state (see Fig. 1, *b*). Moreover, it is known that the ferri-MMO, unlike cytochrom P-450, poorly works in the "shunted" system with hydrogen peroxide.[10] Therefore, it seemed interesting to synthesize iron(II) complexes with the cage-like ligands and study their reactions with molecular oxygen and alkanes. It could have been expected that the change in the oxidation state of iron would not lead to significant changes in the structure of the model as a whole. In the first attempts to synthesize such a complex based on the cage-like ligand **1**, we used the benzoate anion to form the second (labile) carboxylate bridge (Scheme 1, reaction (1)), however, in this case isolation of individual crystalline product failed.

Scheme 1

$$\mathrm{LH + 2\,Fe(ClO_4)_2 + PhCOOH + 2\,Et_3N \longrightarrow}$$
$$\mathrm{\longrightarrow [Fe^{II}{}_2L(PhCOO)](ClO_4)_2 + 2\,Et_3NH(ClO_4)} \qquad (1)$$

$$\mathrm{LNa + 2\,Fe(OTf)_2(MeCN)_2 \longrightarrow}$$
$$\mathrm{\longrightarrow \underset{\textbf{3}}{[Fe^{II}{}_2L(OTf)_2](OTf)}} \qquad (2)$$

Complex **3** was obtained by the reaction (2) from the sodium salt of ligand **1** (LNa) (see Scheme 1). Initially, we suggested that water, hydroxide ion, or triflate anion (OTf, trifluoromethanesulfonate) can be the second bridge in it.[13] However, according to the X-ray diffraction data (Table 1 and 2), complex **3** has completely different structure. In the solid state, the complex **3** is a white powder, whereas its solution in acetonitrile in the absence of O_2 has a light yellow color and does not exhibit characteristic absorption in the electron spectrum. According to the IR spectroscopic data, the value ν^{as}—ν^{s} for the corresponding vibrations of the COO-group of complex **3** is 138 $\mathrm{cm^{-1}}$, that confirms a bridged bidentate coordination of the carboxy group bound to ligand **1** with the iron atom. The mass spectrometric and elemental analysis data agree with the composition suggested for the complex **3**. The mass spectrometric data also indicate that in acetonitrile the iron ions preserve their bonding with the ligand even at very high dilution. In the ^{1}H NMR spectrum of complex **3** in acetonitrile-d_3, all the signals are in the region from −14 to 120 ppm. This fact indicates that complex **3** is a high-spin Fe(II) complex.[14] On storage in air, the light yellow solution of complex **3** in acetonitrile acquires brown color indicating oxidation of the iron ion. However, according to the electron spectra and ^{1}H NMR spectra, oxidation of complex **3** gives, together with complex **2**, other unidentified iron(III) complexes, as well. These results agree with the data in the work[7] on the studies of electrochemistry of complex **2** (X = H_2O, OAc, OBz). Two irreversible diffusion controlled cathode peaks are observed on the voltammograms of complex **2**, which correspond to the process $\mathrm{Fe^{III}Fe^{III} \rightarrow Fe^{II}Fe^{III} \rightarrow Fe^{II}Fe^{II}}$. The irreversible character of the peaks indicates the fact that even on the cyclic voltammetry time scale, the reduced states generated initially are kinetically unstable. Irreversibility

Table 1. Crystallographic data and parameters of the X-ray diffraction experiment for the complex **3**

Parameter	Value
Molecular formula	$\mathrm{[C_{40}H_{39}N_6O_{10}S_2F_6Fe_2][OTf] \cdot 4CH_2Cl_2}$
Molecular weight	1530.382
Crystal system	Triclinic
Space group	$P\bar{1}$
Cell sizes	
a/Å	10.934(2)
b/Å	17.817(4)
c/Å	18.289(4)
α/deg	110.466(4)
β/deg	105.834(4)
γ/deg	97.179(4)
V/Å^3	3114(1)
Z	2
d_{calc}/g cm^{-3}	1630
μ/cm^{-1}	0.0998
Region of scanning, θ/deg	1.38—25.09
Total number of reflections	30209
Number of independent reflections	10986
R_{int}	0.0642
Number of observed reflections	7609
GOF on F^2	1.009
$R\,[I > 2\sigma(I)]$	
R_1	0.0616
wR_2	0.1518

Table 2. Selected bond distances (*d*) and bond angles (ω) for the complex **3**

Parameter	Value
Bond*	d/Å
Fe(1)—O(1) [COO]	2.031(2)
Fe(1)—O(5) [OTf]	2.131(3)
Fe(1)—N(2) [Py]	2.150(3)
Fe(1)—N(3) [Py]	2.179(3)
Fe(1)—O(2) [ether]	2.204(3)
Fe(1)—N(1) [amine]	2.208(3)
Fe(2)—O(3) [COO]	2.020(2)
Fe(2)—N(5) [Py]	2.151(3)
Fe(2)—O(8) [OTf]	2.174(11)
Fe(2)—N(6) [Py]	2.174(4)
Fe(2)—N(4) [amine]	2.210(3)
Fe(2)—O(4) [ether]	2.276(3)
O(1)—C(1) [COO]	1.275(4)
O(3)—C(1) [COO]	1.255(4)
Angle	ω/deg
O(1)—Fe(1)—O(5)	94.73(10)
O(1)—Fe(1)—N(2)	166.00(11)
O(1)—Fe(1)—N(3)	91.01(11)
O(1)—Fe(1)—O(2)	78.42(9)
O(1)—Fe(1)—N(1)	100.96(11)
O(3)—Fe(2)—N(5)	165.11(12)
O(3)—Fe(2)—O(8)	98.0(7)
O(3)—Fe(2)—N(6)	92.70(11)
O(3)—Fe(2)—N(4)	98.63(11)
O(3)—Fe(2)—O(4)	77.25(10)
C(1)—O(1)—Fe(1)	133.6(2)
C(1)—O(3)—Fe(2)	133.0(2)

* The fragment in the structure of complex **3** bearing the bond is given in square brackets.

of the peaks can indicate a retardation of the step of reverse electron transfer due to the structural rearrangement of the complexes, which accompanies this step.[15] A suggestion has been made that this rearrangement is not related to the change in the nuclearity of the complex, rather it is accompanied by only small changes in the coordination pattern of iron atoms with the ligands.

Table 3 shows the results of oxidation of cyclohexane with molecular oxygen and hydrogen peroxide in the presence of complex **3** and, for comparison, the data obtained earlier[7] for the complexes **2a**,**b** with two molecules of water or bidentate carboxylate fragment as the labile ligands. From the data in Tables 3, it follows that complex **3** is not able to catalyze oxidation of alkanes in acetonitrile at room temperature. A small effect observed in the case of hydrogen peroxide is apparently due to the appearance of complex **2** in the solution as a result of oxidation of complex **3**. Attempts to detect formation of the oxygen intermediates in the reaction of complex **3** with O_2 at low temperatures (−40 °C in MeCN and −60 °C in CH_2Cl_2) were also undertaken, but did not give positive results.

The X-ray crystallographic data for complex **3** (Fig. 2) allowed us to make some suggestions with respect to its inactivity in the oxidation reaction. In the structure of complex **3**, two out of total three triflate anions are coordinated to the iron atoms, whereas the third triflate anion is placed in the outer coordination sphere as a counter ion. For the complex cation, a C_2 axis of symmetry is approximately observed, which passes through the C(5)...C(2)—C(1) atoms, but the two centers, *i.e.*, Fe(1) and Fe(2), somewhat differ: the average distances to the coordinated atoms are 2.151 Å (Fe(1)) and 2.1675 Å (Fe(2)). Each center is placed in the distorted octahedral configuration, with the distances Fe—N being within 2.15—2.21 Å (see Table 2), which are typical of the high-spin iron(II) complexes.[14] The NMR spectroscopic data indicate that the high-spin state is retained for complex **3** in the solution in acetonitrile. The oxygen donors are placed opposite to the facial coordinated group of nitrogen donors, $(PyCH_2)_2N$: the carboxylate group and the ether oxygen (O_{ether}) are in the *trans*-position to the pyridine donors N_{Py}, and the triflate one is in the *trans*-position to N_{am}. The largest difference between the two centers is observed for the bonds with the triflate (Fe(1)—O(5) 2.131 Å, Fe(2)—O(8) 2.174 Å) and ether donors (Fe(1)—O(2) 2.204 Å, Fe(2)—O(4) 2.276 Å). Instead of expected *syn-syn*-conformation for the bridged carboxylate fragment present in complex **2**, the more rare *anti,anti*-conformation was found.[16,17] Because of this, the distance between the iron atoms is increased to 6.28 Å. Apparently, such a conformation of the carboxylate fragment is stabilized by the formation of the six-membered cycles upon coordination of the ether oxygen atom to the iron atom. Approximately equal distances $Fe—O_{COO}$ for the atoms Fe(1) and Fe(2), as well as close distances C—O in the carboxylate, indicate delocalization of electrons in the latter. The $Fe—O_{COO}$ bond is relatively short for the *anti*,*anti*-conformation, its length is comparable with the corresponding value for the *syn*,*syn*-conformation,[18] that is apparently due to the chelate effect. The $Fe—O_{ether}$ bond is longer than is commonly observed for this bond[18] due to the *trans*-effect of the pyridine donor and, possibly, as a result of the strain imposed by the formation of bicyclic structure upon coordination of the O_{ether} atoms to the iron atom (see Fig. 2). The too high value for the bond

Table 3. Oxidation of cyclohexane in the presence of complexes **2** and **3***

Entry	Complex	Oxidant	TON	Ref.
1	**3**	O_2	0	The present work
2	**3**	H_2O_2	0.4	The present work
3	**2a** (X = H_2O)	H_2O_2	6.5	7
4	**2b** (X = PhCOO)	H_2O_2	4.5	7

* **Reaction conditions:** [Fe] = 0.7 mmol L^{-1}, [Fe] : [H_2O_2] : [RH] = = 1 : 400 : 1000, MeCN, 20 °C, 0.5 h.

distances with the triflate anion as compared to the normal[13] value can indicate formation of a hydrogen bond with the solvate molecule of CH_2Cl_2 (see Ref. 19). The most unexpected for us in the structure of complex **3** were the changed type of conformation of the carboxylate fragment and the fact of coordination of the ether oxygen donors of the ligand to the iron atom in the acetonitrile solution. Though coordination of the ether O atoms to the iron atom is possible, there are little examples of iron(II) complexes with ordinary ethers.[18] It is obvious that stabilization of the ether coordination in complex **3** is due to the chelate/macrocyclic effects of the ligand, which forms a binuclear core containing four thermodynamically favorable six-membered rings. If such a structure of complex **3** is retained in solution, the iron atoms are so far from each other that the bridged activation of O_2 in this system becomes impossible. If we yet assume that in solution the ether donor is displaced by the molecule of acetonitrile, then a vast amount of unproductive conformations is possible due to the flexibility of the ligand molecule, which because of known instability of the $Fe(O_2)$-intermediates for the mononuclear iron complexes will hardly lead to the formation of relatively stable bridged peroxide. According to the modern concept,[1] a diferryl center ($Fe^{IV}Fe^{IV}$) is the active intermediate of MMO. The diferryl intermediate (apparently, in the form of bis-μ-oxo-complex) is preceded by a bridged peroxide intermediate. For the reliable formation of these intermediates by activation of molecular oxygen, a favorable conformation of the binuclear iron complex in solution is necessary, whose probability of formation in the case under study can be low because of high flexibility of the ligand **1**. The presence of the second bridge should significantly increase the probability of favorable conformation, however, the hope on the formation of the second bridge involving an exogenic ligand did not come up to expectations. Freezing the favorable conformation of the binuclear iron complex with such a type of the ligand is also possible by incorporation of this complex either into the cavity of a cavitand of the calixarene or cyclodextrin type, or into the cavity of a globular polypeptide.[20] In the latter case, stabilization of inorganic catalyst in the protein crystal and occurrence of a catalytic process at low temperature gives a possibility to detect the short-lived oxygen intermediates.[21] Finally, an increase in probability of favorable conformation can be reached by the direct design of the cage-like ligand itself, including removal of the ether oxygen donors from its structure. The problem of development of adequate models of AC of MMO based on such a type of the ligands is closely related to the search for the optimum balance between flexibility and rigidity of the cage-like ligand. In fact, according to the quantum chemical calculations,[22] the polypeptide cage

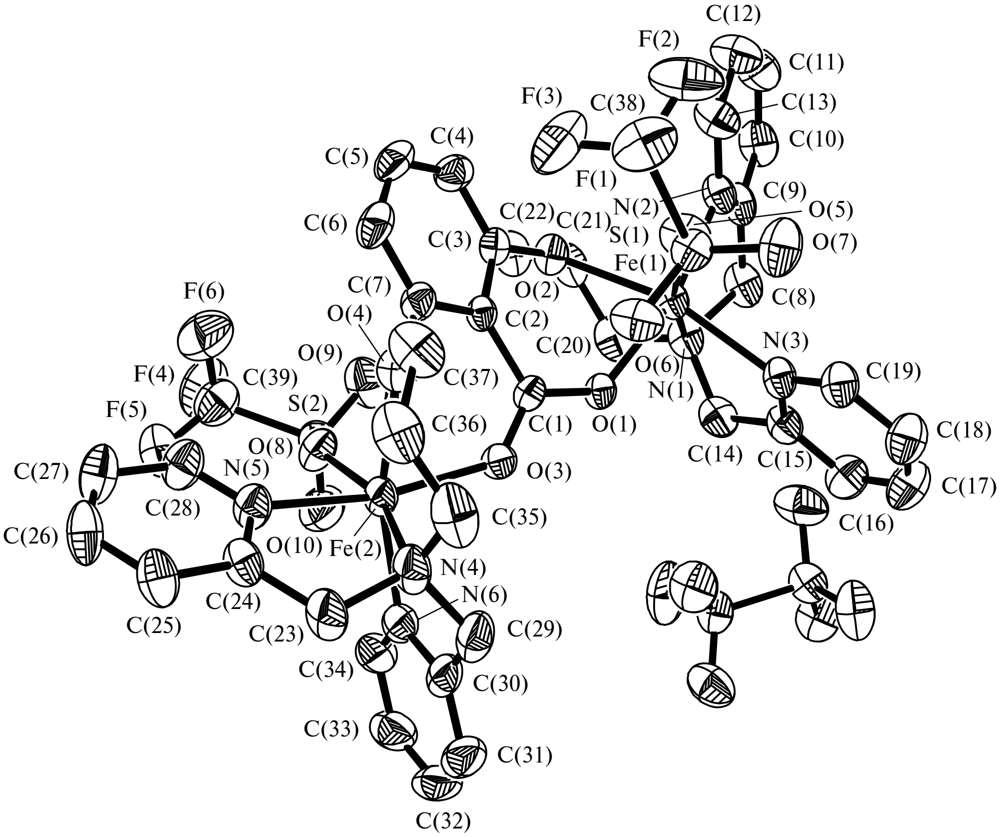


Fig. 2. The structure of complex **3** according to the X-ray crystallographic data.

of the AC of MMO is involved into the conformational movements directed on optimization of the formation of oxygen intermediates along the reaction pathway. It is obvious that the work in this direction should be continued.

In conclusion, according to the crystal structure of complex **3**, instead of expected formation of the second bridge between the iron atoms involving a labile ligand during formation of the complex, we observed coordination of the ether oxygen atoms of the ligand **1** and "inversion" of the carboxylate fragment with the formation of unusual *anti*,*anti*-conformation in the rigid enough structure. This leads to the elongation of the Fe...Fe distance and impossibility to form a bridged peroxide intermediate, a necessary condition for the activation of molecular oxygen. Due to this, the complex **3**, unlike the complex **2**, reproduces neither structural, nor functional features of the AC of MMO.

The authors are grateful to W. W. Brennessel and V. G. Young, Jr. (the Laboratory of Crystallography, Departement of Chemistry of University of Minnesota) for carrying out the X-ray studies for complex **3** and prof. L. Que, Jr. (University of Minnesota) for providing a possibility for A. A. Shteinman to work in his laboratory.

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Received December 24, 2010;
in revised form August 5, 2011