

Experimental and quantum chemical modeling of the influence of the pH of the medium on the NO-donor activity of the mononuclear nitrosyl iron complex $[\text{Fe}(\text{SC}(\text{NH}_2)_2)_2(\text{NO})_2]\text{Cl} \cdot \text{H}_2\text{O}^*$

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The electrochemical method and quantum chemical modeling were used to study the NO-donor activity of the mononuclear nitrosyl complex with the thiourea ligand and the influence of the pH of the medium on the reaction. It is shown experimentally that this complex evolves nitrogen monoxide and the character of this process depends on the pH of the medium. For a neutral medium, the curve of nitrogen monoxide evolution reaches a plateau, whereas the curve increases linearly with time for an alkaline medium. The quantum chemical modeling (using DFT methods with the B3LYP and BP86 functionals) of possible processes in an aqueous solution of the complex in neutral and alkaline media allowed us to propose the schemes of the NO-donation reaction, which explain the experimental data on the pH effect.

Key words: iron–sulfur nitrosyl complexes, NO-donor activity, electrochemical study, quantum chemical calculations, density functional theory, functionals B3LYP and BP86, PCM approximation.

Numerous studies carried out in recent years reliably established that nitrogen monoxide NO, having a wide range of biological effect and the ability to affect various systems of the organism, enzyme activity, and processes of cell fission and decay, is involved in cancerogenesis processes.¹ Depending on the local concentration *in vivo*, NO can affect cellular targets in different ways: products of its reactions can stimulate cancer development or inhibit tumor cell growth. It was shown that NO changed the level of tumor cell apoptosis. activity of gene p53, vascularization (formation of neoplasms of tumor-feeding blood vessels)² and suppressed the activity of the key repair protein of mammals, *viz.*, O(6)-methylguanine-DNA methyltransferase.³ All these facts make it possible to consider NO-donor compounds as a new class of anticancer agents.⁴ Therefore, it is especially urgent to search for novel compounds: exogenic NO-donating drugs (NODD) having a direct anticancer effect.^{5–10} The dinitrosyl iron complexes (DNIC), which are NO donors, are of interest. Some of them have already found use in anticancer therapy, since they evolve NO in a necessary therapeutic concentration.^{11–17}

The mechanism of NO evolution and the intermediate and final products of this reaction remain unknown up to

now, although the NO-donor activity of the nitrosyl iron complexes are being intensively studied by various methods.^{18–21} We use the electrochemical method and quantum chemical modeling to study this problem.^{22–24} The binuclear sulfur-containing nitrosyl iron complexes have yet been objects of our studies so far. In the present work, we studied the mononuclear complex $[\text{Fe}(\text{SC}(\text{NH}_2)_2)_2(\text{NO})_2]^+\text{Cl}^- \cdot \text{H}_2\text{O}$ (**1a**)²⁵ and complex **1b** obtained after NO detachment. The former is especially interesting for two reasons. First, complex **1a** is water-soluble since containing a single-charge cation and, hence, it is promising from the point of view of preparing convenient pharmaceutical forms. Second, complex **1a** is convenient for quantum chemical modeling due to a small number of atoms.

The purpose of this work is to study the NO-donor activity of complex **1a** and the influence of the pH of the medium on the reaction using the electrochemical method and quantum chemical modeling.

Experimental

Amperometric study of NO-donation. The concentration of NO generated by complex $[\text{Fe}(\text{SC}(\text{NH}_2)_2)_2(\text{NO})_2]\text{SO}_4 \cdot \text{H}_2\text{O}$ (**2**) in solutions was measured with an amiNO-700 sensor electrode of the inNO Nitric Oxide Measuring System (USA) and detected within 500 s (with an increment of 0.2 s) in a solution of the NO donor in a concentration of $1.49 \cdot 10^{-5}$ mol L⁻¹. A standard

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aqueous solutions of NaNO_2 ($100 \mu\text{mol L}^{-1}$), which was added to a mixture consisting of 20 mg of KI (Aldrich), 2 mL of 1 M H_2SO_4 (reagent grade), and 18 mL of bidistilled water, was used for electrode calibration. The working solutions of complex **2** were prepared in an aqueous solution using a phosphate buffer with pH 7.0 (HydriionTM, Aldrich) and a tris-HCl buffer with pH 9.0 (prepared from 0.2 M tris(oxy)methyl)aminomethane and 0.1 M HCl according to an earlier described procedure²⁶) under anaerobic conditions. The values of pH in solutions were measured using an HI 8314 membrane pH meter (HANNA Instruments, Germany). All experiments were carried out in a temperature-maintained cell at 25 °C with vigorous stirring.

Quantum chemical calculations were carried out by the density functional theory (DFT) with the full geometry optimization for open electronic shells of the initial and formed complexes by the Gaussian 03 program (version D)²⁷ using the BP86 local functional, the B3LYP hybrid functional, and the 6-311++G**/6-31G* basis set taking into account solvation in an aqueous solution in terms of the polarized continuum model (PCM). The calculations showed the absence of imaginary frequencies. This indicates that all optimized geometries correspond to energy minima.

Results and Discussion

NO-Donor activity of complex 1a. Effect of the pH of the medium. It was established for anaerobic conditions that an aqueous solution of cationic complex **1a** evolved NO with an induction period of ~10 s in neutral and alkaline media (Fig. 1). A high initial rate of NO generation with a maximum at ~160 s and an NO concentration of 31.7 nmol L^{-1} (mole of complex)⁻¹ is observed at pH 7. The total amount of NO in the system remains approximately constant and then decreases to ~ 28.7 nmol L^{-1} (mole of complex)⁻¹ (see Fig. 1, curve 1), possibly indicating the further conversion of evolved nitrogen monoxide. The evolution of NO at pH 9 is described by a dependence close to linear, and in ~500 s

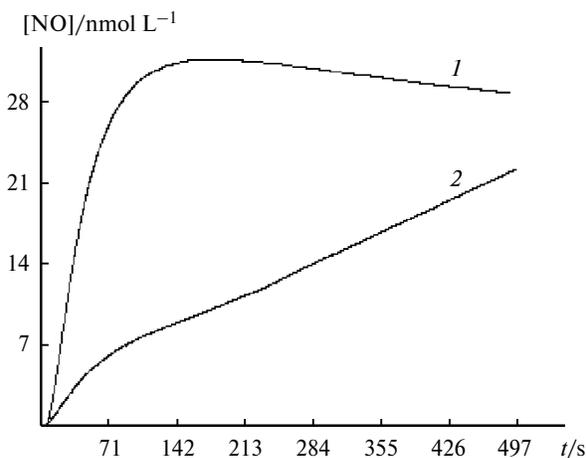


Fig. 1. Time dependences of the concentration of NO evolved by complex **2** ($1.45 \cdot 10^{-5} \text{ mol L}^{-1}$) in an aqueous solution at 25 °C under anaerobic conditions at pH 7 (1) and 9 (2).

complex **1a** generates ~ 22 nmol L^{-1} (mole of complex)⁻¹ nitrogen(II) oxide under these conditions, and the total amount of NO in the system continues to increase monotonically (see Fig. 1, curve 2). Evidently, NO generation by cationic complex **1a** proceeds *via* different mechanisms depending on the acidity of the solution. It is most likely that in an alkaline solution the hydroxide ion participates in the decomposition of complex **1a**, leading to the prolongation of NO evolution.

It should be mentioned that complex **1a** requires no additional photo-, thermo-, or enzymatic activation compared to other NO donors. For example, a comparison of the NO-donor ability of complex **1a**, diazenium-1,2-di-olates (NONOates, which form a class of highly efficient NO donors),²⁸ and cationic binuclear tetranitrosyl complexes CysAm and Pen obtained earlier^{23,29} suggests a high nitrosylating ability of the new cationic mononuclear complex (Table 1).

The amount of NO evolved from complex **1a** is far from the stoichiometric one; however, this amount is quite sufficient for NO therapy. In this case, the prospect of changing the rate and duration of NO evolution by the variation of the acidity of the medium also appears.

Quantum chemical simulation of NO-donation. The problem of search for the mechanism of NO-donation was studied^{22,23} using quantum chemical modeling. An obvious scheme was proposed: Fe—NO bond dissociation with the NO ligand substitution by the aqua ligand. The dissociation of the binuclear complex to two mononuclear complexes was considered as the first step. In this case, the problem is facilitated by the existence of mononuclear complex **1a**. The initial structure (**1a**) and the structure obtained after NO ligand detachment (**1b**) were optimized. The optimized geometries of complexes **1a** and **1b** are shown in Fig. 2, and their electronic characteristics are given in Table 2.

As can be seen from the values of $\langle S^2 \rangle$, adequate spin states were obtained for both complexes by using the BP86 functional. Therefore, conclusions about the electronic state can be drawn in this case. In complex **1a**, its positive charge is predominantly concentrated on the Fe atom with the formal oxidation state +1, the NO ligands have a partial negative charge, and the thiourea ligands are partially positively charged. As a whole, it can formally be accepted that in this cation the central iron(I) ion is bound to the neutral ligand environment. As can be seen from Table 2,

Table 1. Maximum amount of NO (nmol L^{-1}) generated by aqueous solutions of nitrosyl iron complexes **2**, CysAm, Pen, and NONOates at 25 °C for 500 s in an inert medium

pH of medium	1	NONOates ²⁸	CysAm ²³	Pen ²⁹
7	31.7	4	35	50
9	22.0	2	10	60

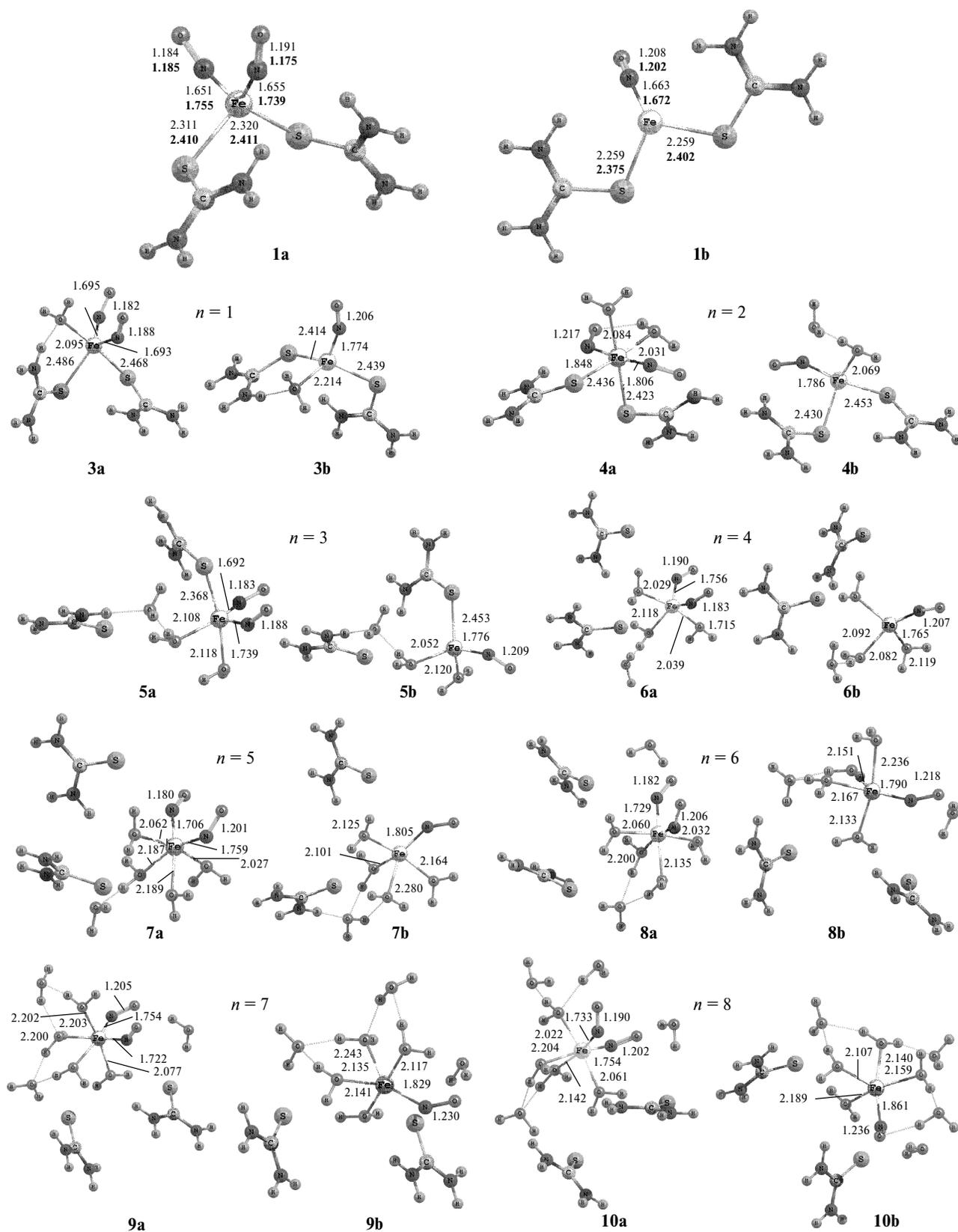


Fig. 2. Optimized with the B3LYP functional (those with the BP86 functional are solid) geometries of the initial complex **1a**, a complex without ligand NO **1b**, possible aqua complexes with the number of water molecules $n = 1-8$ (**3a-10a**), and the corresponding complexes formed after the detachment of the NO ligand (**3b-10b**).

Table 2. Electronic characteristics of complexes **1a** and **1b** calculated by the UDFT/BP86/6-31G* and UDFT/B3LYP/6-31G* methods

Complex	S	Q					ρ					$\langle S^2 \rangle_{\text{calc}}$	$\langle S^2 \rangle_{\text{annih}}$	$\langle S^2 \rangle_{\text{theor}}$
		Fe	NO ¹	NO ²	SR ¹	SR ²	Fe	NO ¹	NO ²	SR ¹	SR ²			
UDFT/BP86/6-31G*														
1a	1/2	0.67	-0.24	-0.26	0.34	0.41	1.30	-0.26	-0.23	0.09	0.11	0.84	0.76	0.75
1b	1	0.51	-0.27	—	0.39	0.37	2.39	-0.56	—	0.10	0.08	2.22	2.00	2
UDFT/B3LYP/6-31G*														
1a	1/2	0.92	-0.24	-0.31	0.31	0.32	3.31	-1.16	-1.25	0.06	0.06	2.59	5.34	0.75
1b	1	0.90	-0.45	—	0.27	0.28	3.39	-1.46	—	0.04	0.03	3.23	2.74	2

Note. S is the spin of the complex, Q is the charge on the fragment, ρ is the spin population of the fragment; the average values of the squared spin: $\langle S^2 \rangle_{\text{calc}}$ is the calculated value, $\langle S^2 \rangle_{\text{annih}}$ is the value after annihilation, and $\langle S^2 \rangle_{\text{theor}}$ is the theoretical value.

the localization of the unpaired electron on the iron(1) atom corresponds to spin 1/2. The spin populations of the fragments (ρ) are non-integral and of different signs, which is due to MO delocalization and spin polarization effects.

No significant change in the charge distribution occurs upon the detachment of one NO group. Another unpaired electron appears on the Fe atom due to the Fe—N covalent bond dissociation, and the second electron of this bond is localized on the N atom of free oxide NO. The delocalization of MO results in the appearance of the spin density on the remained NO ligand.

Almost the same electronic structure was obtained when using the B3LYP functional, although a total spin of 1/2 corresponds to spin 3/2 on the Fe atom and spin -1/2 for each NO ligand in this case. This spin density distribution in the complex corresponds well to the wavefunction in the one-determinant approximation [$d_1\alpha d_2\alpha d_3\alpha \pi_a\beta \pi_b\beta$], where d_i are the orbitals predominantly localized on the Fe atom, and π_a and π_b are the orbitals localized on different NO groups.³⁰ This wavefunction is not an eigenfunction of the operator S^2 because contains impurity components with $S = 1/2, 3/2$, and $5/2$. Therefore the average value of squared spin S^2 for such a wavefunction (2.59) differs from the theoretical value (0.75) for the doublet state.

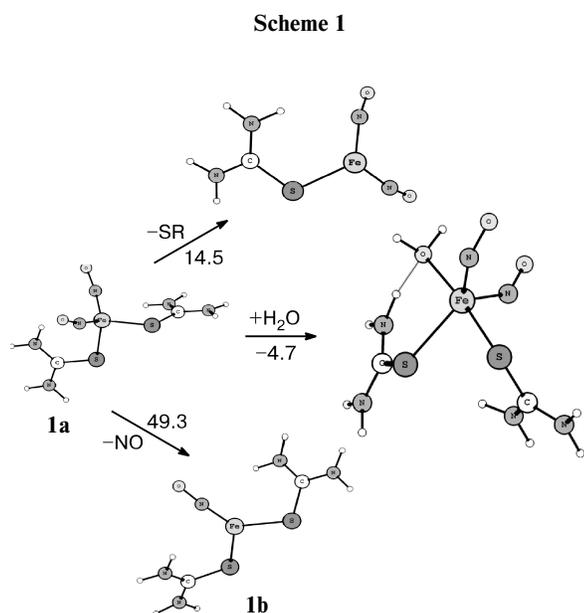
The contribution of the component with $S = 5/2$ is very high, since after annihilation of the components with $S = 3/2$ the average value becomes $S^2 = 5.34$. Since several doublets can correspond to the system with five unpaired electrons, when projecting this one-determinant state onto the state with a regular spin symmetry, a strong correlation of spins of d-electrons in the Fe atom (Hund's rule) should be taken into account. This spin configuration corresponds to the formation of homeopolar bonds Fe—NO, which is not accompanied by a noticeable change in the electronic configuration of the Fe atom. The detachment of the NO ligand with the formation of complex **1b** does not result in substantial changes in the charges on the atoms and in their spin populations.

The energy expenses to the dissociation of complex **1a** with the formation of complex **1b** are 52.9 (BP86) and 23.0 (B3LYP) kcal mol⁻¹ in the calculations taking into account the aqueous medium in the PCM (polarized continuum model) approximation. This significant difference is explained by the fact that the local functional BP86 substantially exceeds the energy of the Fe—NO bond. The latter can be caused by the overestimation of the energy of mixing of the antibonding orbitals of the Fe—N and N—O bonds in the given complex,³¹ whereas the dissociation energy of the Fe—N bond can be underestimated by B3LYP functional because of admixing of the high-spin states to the ground state. However, it is evident in both cases that the energy of NO ligand detachment from complex **1a** is too high for the reaction to proceed *via* this route.

Therefore, the reaction mechanism is different. Such transformations of complex **1a** should occur primarily that would substantially decrease the energy of the Fe—NO bond. Since this system contains only the initial complex and water, it is reasonable to estimate the energies of formation of possible iron aqua complexes and dissociation energies of the Fe—NO bond in them. Another possible way for nitrosyl complex transformation in solution is the cleavage of the Fe—SR bond, which is well studied for the binuclear nitrosyl complexes^{22,32} and is characteristic, most likely, of mononuclear complexes.

The processes that occur in an aqueous solution of complex **1a** and the corresponding changes in the Gibbs energies (kcal mol⁻¹) are presented in Scheme 1. It is seen that only the addition of a water molecule can be spontaneous.

The optimized geometries for possible aqua complexes **3a—10a** with the number of water molecules $n = 1-8$ and for complexes **3b—10b** formed upon NO monoxide detachment are presented in Fig. 2. The energies of NO ligand detachment are given below. All calculations were performed with the B3LYP hybrid functional, since the dependence of the energy of the optimized aqua complex on the coordination number of the Fe atom was observed

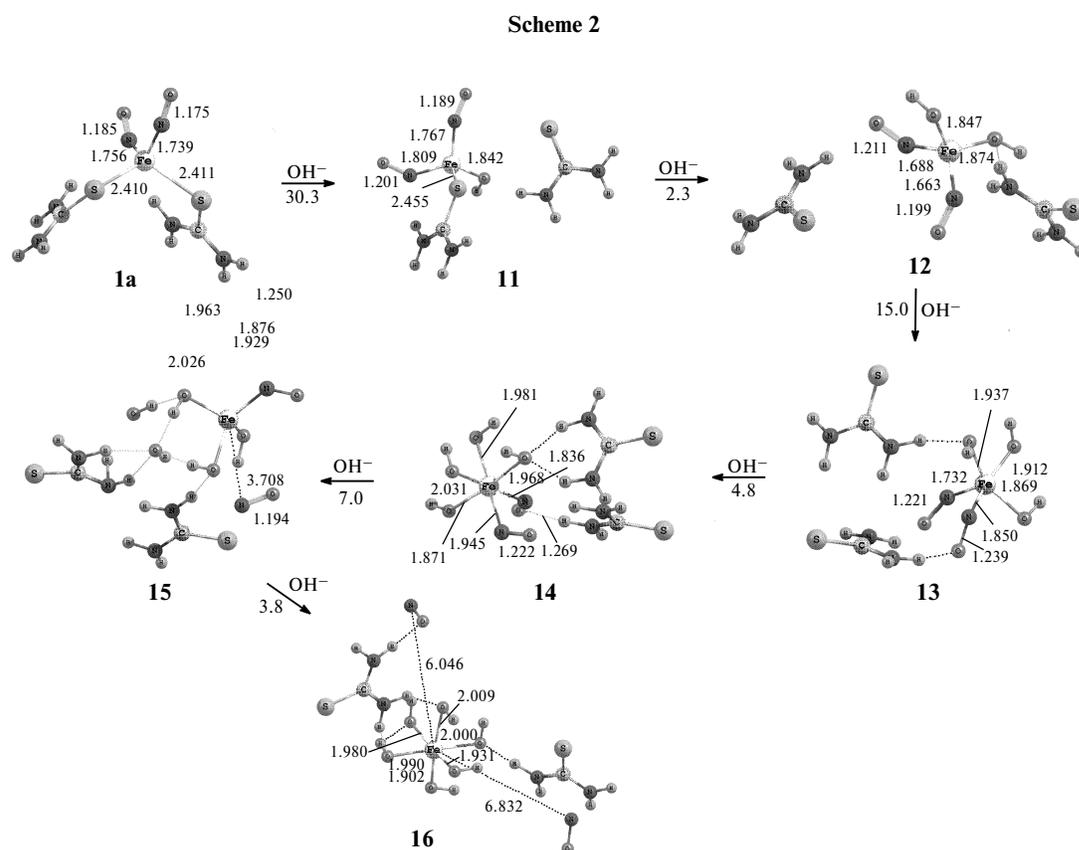


for the BP86 local functional together with a significant overestimation of the Fe–N bond energy. The latter impeded a correct estimation of the energy of NO monoxide detachment. This artifact was not observed in the case of using the B3LYP functional.

n	$-\Delta E/\text{kcal mol}^{-1}$	n	$-\Delta E/\text{kcal mol}^{-1}$
0	-23.0	5	12.3
1	11.8	6	9.3
2	24.4	7	9.6
3	5.5	8	11.7
4	7.6		

As follows from the values of energies of ligand NO detachment, this process is exothermic for all aqua complexes with the number of water molecules $n = 1-8$, unlike the endothermic process for the anhydrous complex ($n = 0$). This explains the high initial rate of NO generation by the initial cation in an aqueous solution, whereas it is rather stable for a long time in the absence of moisture. However, our scheme, *viz.*, the formation of aqua complexes responsible for NO evolution, describes, most likely, only the initial step of NO-donation by the mononuclear cation in an aqueous solution. Then the reaction products undergo the further transformation, most likely, involving evolved monoxide NO in these processes, due to which the experimental curve of its evolution reaches a plateau.

The situation differs drastically for an alkaline medium (Scheme 2). In this case, the substitution of first thiocarbamide and then nitroxide ligands by hydroxide occurs rather than the formation of aqua complexes with a weak



Note. The values of ΔE are presented in kcal mol^{-1} .

Fe—N bond. The reaction of NO detachment from complex **11** is endothermic (16.8 kcal mol⁻¹). The substitution of the second thiocarbamide ligand with the formation of complex **12** is more favorable (-2.3 kcal mol⁻¹). Although the detachment of NO from complex **12** is exothermic (-5.9 kcal mol⁻¹), the addition of hydroxide to form complex **13** is much more favorable (-15.0 kcal mol⁻¹). Complex **14** is initial in fact for NO donation in an alkaline medium, because the nitroxide ligand is replaced by hydroxide in this complex to form complex **15** and finally complex **16**.

The proposed scheme answers the question why the curve of NO evolution for an alkaline medium differs from that for a neutral medium. In an alkaline medium, ligand substitution (as in the case of the S_N2 mechanism) occurs in the first step rather than the dissociation reaction at the Fe—NO bond in the formed aqua complexes (as in the case of the S_N1 mechanism). The initial rate of NO evolution in an alkaline medium is lower than that in a neutral medium, since the thiocarbamide ligand is replaced first and next the nitroxide ligand is substituted. Evidently, this substitution is irreversible and, hence, NO is evolved entirely and is prolonged. On the contrary, in an aqueous medium, the dissociation can be reversible, due to which, most likely, the curve of NO evolution reaches a plateau.

Thus, the NO-donor activity of the mononuclear dinitrosyl complex [Fe(SC(NH₂)₂)₂(NO)₂]Cl·H₂O in alkaline and neutral media. It is experimentally shown that the complex is an NO donor, and the character of its donation depends on the pH of the medium. For a neutral medium, the curve of NO evolution reaches a plateau, whereas that for an alkaline medium increases linearly in time. The quantum chemical modeling shows that the dissociation of the Fe—NO bond proceeds *via* different mechanisms. In a neutral medium, the aqua complexes responsible for NO donation are formed. The NO ligand is substituted by hydroxide in an alkaline medium. The dependence of the mechanism of the studied NO donation on the pH of the medium provides a prospect for controlling nitrogen monoxide evolution by changing this parameter.

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