Structure and properties of μ_2 -S-[bis(benzenethiolato)tetranitrosyldiiron] in solution*

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Dinuclear iron tetranitrosyl complex with the composition $[Fe_2(SPh)_2(NO)_4]$ (1) was synthesized and its single crystals and polycrystals were studied by X-ray diffraction, IR spectroscopy, and elemental analysis. The decomposition products of complex 1 were investigated by electrochemical method and mass spectrometry. The mass spectrum of a solution of complex 1 shows two groups of ions: the primary decomposition products of 1 in solution (the complex ions $[Fe(SPh)(NO)_2(NO_2)]^-$, $[Fe(SPh)_2(NO)]^-$, and $[Fe(SPh)_2(NO)_2]^-$) and a series of the ions $[FeO_2 + n(NO)]^-$ and $[FeO_3 + n(NO)]^-$ (n = 0—4), which are formed in secondary reactions. The structures of the complexes, which were formed through the Fe—NO bond dissociation and the replacement of the NO ligand by aqua and oxygen ligands in complex 1, and the structure of the complex $[FeO_3]^-$ were studied by quantum chemical modeling.

Key words: NO donors, sulfur nitrosyl iron complexes, thiophenolates, X-ray diffraction study, mass spectrometry.

In recent years, nitrogen monoxide donors have attracted considerable attention as a new class of antitumor agents due to the specific role of NO in the malignant tumor growth.¹ Nitrogen monoxide changes the level of apoptosis (the evolutionary self-destruction) of tumor cells, the p53 gene activity, and the neoangiogenesis (the neoplasms of tumor-feeding vessels)² and suppresses the activity of the key mammalian repair protein O6-methylguanine DNA methyltransferase.³ However, different classes of the known synthetic NO donors are not used as therapeutic drugs for the treatment of malignant diseases, and have found application only as enhancers (to a different degree depending on their chemical nature) of the efficacy of chemotherapeutic agents or radiotherapy.^{1–8}

Iron nitrosyl complexes with thiol-containing ligands belong to one of the forms of natural carriers (depots) of NO.⁹ The direct cytotoxic action of the iron nitrosyl complex Na[Fe₄S₃(NO)₇] on human and mouse melanoma cells was investigated.¹⁰ However, this complex generates NO upon photoactivation and cannot be used as an antitumor agent because of the high toxicity toward normal cells. Therefore, there is a need in new antitumor compounds, NO donors, having high efficacy and

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low toxicity. It is known that Roussin's red salt esters $[Fe_2(SR)_2(NO)_4]$ containing alkyl substituents (R = Et, Bu^t, or $n-C_5H_{11}$)^{11–14} are stable in solution and efficiently generate NO upon thermal activation or photoactivation.¹⁵ Nitrosyl complexes with aryl substituents generate NO in physiological solutions without additional activation and exhibit high antitumor activity and low toxicity. Our investigations confirmed that the iron benzenethiolate nitrosyl complex [Fe₂(SPh)₂(NO)₄] (1) has the direct cytotoxic effect on human tumor cells of different genesis.^{16,17} The toxicity of this complex ($LD_{100} = 60 \text{ mg kg}^{-1}$) is substantially lower than that of the known clinical antitumor agent cisplatin ($LD_{100} = 16 \text{ mg kg}^{-1}$).

In this connection, it is of interest to study the structures and properties of complex **1** in the solid state and solution with the aim of designing new drugs and investigating the mechanisms of the direct (not only adjuvant) antitumor activity of iron nitrosyl complexes as a new class of chemotherapeutic agents. It is known that the majority of NO donors, including NO donors of the class under study,¹⁸ have adjuvant activity, *i.e.*, the ability to enhance the antitumor effect of clinical antitumor agents, due to which the latter can be used in lower doses.

In the present study, complex 1 was synthesized according to a new procedure, which is more efficient than the methods described previously.^{13,14,18} This method al-

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lowed us to obtain the previously unavailable single crystals of **1**. The structures of complex **1** and its derivatives that are formed in aerobic solutions were studied by X-ray diffraction, quantum chemistry, and mass spectrometry.

Experimental

The IR spectra were recorded on a Spectrum BX-II Fouriertransform spectrometer in KBr pellets (1 mg of the compound per 300 mg of KBr). The mass spectra were obtained on a highresolution time-of-flight mass spectrometer with orthogonal ion injection.¹⁹ The solutions for experiments were prepared as follows: complex 1 (0.0039 g) was dissolved in DMSO (10 mL), which was purified according to the procedure described previously,²⁰ 0.2 mL of the solution was taken, and MeOH (0.8 mL), which was purified according to a known procedure,²⁰ was added. The resulting solution $(2 \cdot 10^{-5} \text{ mol } L^{-1})$ was analyzed by mass spectrometry after 3-4 min. The ions were extracted from the samples with the use of an atmospheric electrospray ionization source without forced supply of the solution (the flow rate was 0.1 μ L min⁻¹, the inner diameter of the quartz capillary was 50 μ m, the voltage between the capillary and the inlet of the mass spectrometer was ~3 kV). Dry argon at ~20 °C was used as the curtain gas and the buffer gas. The working resolution of the time-of-flight mass spectrometer was ~10 000. The accuracy of the determination of the ion mass was not lower than 10 ppm.

 μ_2 -S-[Bis(benzenethiolato)tetranitrosyldiiron] (1). Distilled water was saturated with argon for 30 min. A mixture of $Na_2S_2O_3 \cdot 5H_2O$ (Aldrich) (0.508 g, 3.2 mmol), $Na_{2}[Fe_{2}(S_{2}O_{3})_{2}(NO)_{4}] \cdot 4H_{2}O$ (0.588 g, 1.0 mmol), which was synthesized according to a procedure described previously,²¹ granulated NaOH (Aldrich) (0.2 g, 5.1 mmol), and PhSH (Aldrich) (0.52 mL, 5.1 mmol) were placed in a flask. Then water (40 mL) was added, the reaction mixture was vigorously stirred at ~20 °C for 2 h, and the product was extracted with dichloromethane (Aldrich) in air (3×15 mL). The combined red extract was concentrated to 1/5 of the initial volume, filtered through a porous filter No. 4, and kept in air for several hours until the solvent was evaporated. The dark-blue crystals that formed were dried in air. The yield of the product was 0.319 g (87%). Found (%): Fe, 24.82; S, 14.20; N, 12.38; C, 32.03; H, 2.20. Fe₂S₂C₁₂H₁₀N₄O₄. Calculated (%): Fe, 24.89; S, 14.22; N, 12.44; C, 32.01; H, 2.22. IR, v/cm⁻¹: 1778, 1763, 1723, 1583, 1478, 1441, 1303, 1181, 1118, 1092, 1071, 1024, 999, 916, 834, 734, 694, 688.

X-ray diffraction study. The unit cell parameters and the X-ray reflection intensities were obtained on an automated Enraf-Nonius CAD-4 X-ray diffractometer (Mo-K α radiation, graphite monochromator). Crystals of **1** are monoclinic, space group $P2_1/c$, $C_{12}H_{10}Fe_2N_4O_4S_2$, M = 450.06, a = 10.730(3) Å, b = 11.018(2) Å, c = 7.509(3) Å, $\beta = 110.40(3)^\circ$, V = 832.1(4) Å³, Z = 2, $d_{calc} = 1.796$ g cm⁻³, μ (Mo-K α) = 20.18 cm⁻¹. The intensities of 2154 reflections were measured in a quadrant of reciprocal space ($2\theta \le 55^\circ$) by the $\omega/2\theta$ -scanning technique from a crystal of dimensions $0.08 \times 0.09 \times 1.05$ mm. The intensities of all reflections were corrected for absorption by the semiempirical method.²² After the exclusion of systematic absences and merging of equivalent reflections, $F^2(hkl)$ and $\sigma(F^2)$ for 1900 independent reflections with the use of the SHELXS-97 program package²³ and refined by the full-matrix least-squares method based on F^2 with anisotropic displacement parameters for nonhydrogen atoms using the SHELXL-97 program package²⁴.

All nonhydrogen atoms of molecules 1 were located by direct methods followed by difference Fourier maps. However, the isotropic and subsequent anisotropic least-squares refinement of the parameters of all these atoms was unsuccessful: the R and wR_2 factors remained very high, and the difference Fourier maps had high residual electron density peaks. This was a consequence of the unusual twinning in the exposed crystal of 1. It was impossible to take into account the twinning in monoclinic crystals with the monoclinic angle β substantially different from 90° with the use of a standard procedure implemented in the SHELXL-97 program package. It appeared that this crystal with another equivalent (centered) unit cell has the monoclinic angle $\beta' \approx 90^\circ$, and its twinning was taken into account in this unit cell with the use of the SHELXL-97 program package; the ratio of the volumes of two scattering components was approximately 0.514 : 0.486(2). After taking into account the twinning in the crystal of 1, the structure refinement by the least-squares method in the initial unit cell met with success.

All independent H atoms of molecule 1 were located in difference Fourier maps in the intermediate step of the anisotropic refinement. The coordinates and individual isotropic thermal parameters of the H atoms were refined by the least-squares method. In the last cycle of the full-matrix refinement, the absolute shifts of all 129 variable parameters in the structure of 1 were smaller than 0.001 σ . The final *R* factors were R = 0.030 and $wR_2 = 0.075$ based on 1770 observed reflections with $I \ge 2\sigma(I)$; R = 0.039 and $wR_2 = 0.085$ based on all 1900 independent observed reflections; the goodness-of-fit S = 1.05 (the values of wR_2 and *S* have been determined previously²³). In the final difference Fourier map, $-0.34 \le \Delta \rho \le 0.33$ e Å⁻³.

Electrochemical determination of NO. The concentration of nitrogen monoxide generated by complex 1 in solution was measured with the use of an amiNO-700 sensor of the inNO Nitric Oxide Measuring System (USA). The concentration of NO was detected during 200 s (with a step of 0.2 s) in a solution of the NO donor $(0.4 \cdot 10^{-5} \text{ mol } \text{L}^{-1})$. The sensor was calibrated with the use of a standard aqueous NaNO₂ solution (100 µmol L⁻¹; supplied with an electrode), which was added to a mixture consisting of KI (Aldrich, 20 mg), 1 *M* H₂SO₄ (reagent grade, 2 mL), and water (20 mL). Solutions of complex 1 were prepared in 1% aqueous DMSO with the use of a phosphate buffer, pH 6.5; in the course of the measurements, the temperature of the solutions was maintained at 25 °C.

Results and Discussion

Single-crystalline and polycrystalline samples of complex 1 were synthesized according to a procedure that has advantages over those described previously^{13,14,18} in its simplicity and cheapness, based on the exchange of the thiosulfate ligands for the benzenethiolate ligands in an alkaline medium (Scheme 1).

Water (instead of acetonitrile or THF) was used as the solvent. The reaction was performed in one step and gave complex 1 in 87% yield.



1

The structure of dinuclear molecule 1 in the crystal is shown in Fig. 1. Selected bond lengths and bond angles are given in Table 1. Molecule 1 is centrosymmetric; its center coincides with the crystallographic center of inversion *i*(000). Molecule 1 has the approximate symmetry C_{2h} , *i.e.*, has an approximate twofold axis passing through the centers of the Fe and Fe['] atoms and an approximate plane of symmetry passing through the centers of the S and S['] atoms and all atoms of two Ph substituents.

In molecule 1, the Fe atom forms five single covalent bonds with the adjacent Fe', S, S', N(1), and N(2) atoms. The coordination environment of the Fe atom can be described as a distorted tetrahedron with one additional vertex occupied by the Fe' atom or a strongly distorted trigonal bipyramid with the base formed by the Fe', N(1), and N(2) atoms and with two opposite vertices occupied by the S and S' atoms. In molecule 1, the Fe–Fe, Fe–S, and Fe–N covalent bond lengths and the corresponding bond angles are very similar to those found previously in nitrosyl complexes containing other aromatic substituents $(C_6H_4F, C_5H_4N, and C_4H_3N_2)$ at the sulfur atoms.^{25–27}

In molecule 1, individual atoms deviate from the plane formed by the Fe, S, Fe', and S' atoms by the following distances: O(1), -2.304(3) Å; N(1), -1.437(2) Å; O(2),



Fig. 1. Structure of centrosymmetric molecule **1** in the crystal. The primed atoms are related to the unprimed atoms by a center of symmetry.

Table 1. Experimental and theoretical bond lengths (*d*) and bond angles (ϕ) in the structure of **1**

Parameter	Experiment	Calculations		
		B3LYP/6-31G*	PBE/SBK	
Bond		$d/{ m \AA}$		
Fe—Fe'	2.699(1)	2.549	2.655	
Fe—S	2.260(1)	2.246	2.253	
Fe-S'	2.259(1)	2.246	2.253	
Fe-N(1)	1.675(2)	1.630	1.656	
Fe-N(2)	1.666(2)	1.630	1.656	
S-C(1)	1.785(2)	1.803	1.817	
O(1)=N(1)	1.182(3)	1.171	1.175	
O(2)=N(2)	1.167(3)	1.171	1.172	
Angle		φ/deg		
Fe'-Fe-S	53.32(3)	55.0	53.7	
Fe'-Fe-S'	53.33(3)	55.0	53.7	
Fe'-Fe-N(1)	120.75(8)	121.6	120.8	
Fe'-Fe-N(2)	121.56(8)	121.7	121.0	
S-Fe-S´	106.65(3)	110.1	107.4	
S-Fe-N(1)	105.56(8)	105.6	105.6	
S-Fe-N(2)	110.61(7)	105.6	105.6	
S' - Fe - N(1)	110.03(8)	109.4	109.8	
S' - Fe - N(2)	105.86(9)	109.5	109.7	
N(1)-Fe- $N(2)$	117.7(1)	116.5	118.2	
Fe-S-Fe'	73.35(3)	69.9	72.6	
Fe-S-C(1)	111.68(7)	112.5	111.4	
Fe'-S-C(1)	112.39(8)	112.5	111.4	
Fe-N(1)-O(1)	170.2(2)	171.0	169.9	
Fe-N(2)-O(2)	168.1(2)	171.0	169.9	
S - C(1) - C(2)	124.3(2)	119.9	119.7	
S-C(1)-C(6)	115.4(2)	119.9	119.7	

Note. The primed atoms are related to the unprimed atoms by a center of symmetry (-x, -y, -z).

2.263(3) Å; N(2), 1.417(2) Å; C(1), 1.578(3) Å. The S atom has a pyramidal configuration and deviates from the plane passing through three atoms (Fe, Fe['], and C(1)) bound to S by 0.928(1) Å. The independent Ph ring in molecule **1** is planar within $\pm 0.008(2)$ Å for six C atoms. The average C—C bond length is 1.383(9) Å and it is almost equal to the average (for C,H-substituted benzene rings)²⁸ bond length (1.384(13) Å). It should be noted that the mean plane of this Ph ring passes almost along the bisector of the Fe–S–Fe['] bond angle and is almost perpendicular to the plane passing through the Fe, S, Fe['], and S['] atoms; the dihedral angle between these two planes is 89.15(7)°.

In the crystal structure of **1** (Fig. 2), all short intermolecular contacts are close to, or somewhat smaller than, the sums of the corresponding van der Waals radii.

In protic solvents, complex 1 eliminates NO only within a particular time after the dissolution (Fig. 3); the intense elimination of NO was observed after the induction period of 10-12 s. The kinetic curves are non-monotonic



Fig. 2. Projection of the crystal packing of complex 1 along the b axis.

and have a maximum at ~100 s. In a 1% aqueous DMSO solution under aerobic conditions (see Fig. 3, curve 1), the maximum amount of nitrogen monoxide generated by complex 1 is approximately five times larger than that obtained under anaerobic conditions (see Fig. 3, curve 2). It should be noted that the amount of NO generated by complex 1 under aerobic conditions is approximately 20 times smaller than the maximum amount of NO generated upon hydrolysis of the related iron pyrimidinethiolate complex, which we have studied previously under the same conditions.²⁷ As in the case of hydrolysis of the iron pyrimidinethiolate complex,²⁷ it is noteworthy that the maximum number of NO molecules per iron nitrosyl complex is smaller than the minimum stoichiometric number (equal to unity). The question is how to explain this fact. It is known that in solutions of iron dinitrosyl complexes, N₂O is generated due apparently to the dimerization of intermediate nitroxyl HNO. This transformation of NO leads to a decrease in the observed concentration of NO. In our opinion,²⁷ the iron-containing nitrosyl intermediate that is formed as a result of the Fe-NO bond dissociation serves as a reducing agent for the transformation of molecular NO into the NO⁻ anion. The stronger reducing properties of this intermediate compared to those of the starting complex are attributed to the increase in the electron density on the Fe atom due to the coordination of a water molecule. The amount of NO eliminated as a result of the

decomposition of the complex under aerobic conditions is several times larger than that eliminated under anaerobic conditions, which we have previously attributed²⁷ to the faster electron transfer to the oxygen molecule from the intermediate. This competitive redox reaction results in an decrease in the percentage of reduced NO molecules, which are transformed in subsequent reactions, and, as a consequence, the detected concentration of nitrogen monoxide increases.



Fig. 3. Plot of the amount of nitrogen monoxide generated by complex 1 under aerobic (1) and anaerobic (2) conditions vs the time $(0.4 \cdot 10^{-5} M \text{ solutions in } 1\%$ aqueous DMSO, pH 6.50, 25 °C).

The formation of other intermediates in the course of decomposition of complex 1 in protic media was studied by mass spectrometry. Figure 4 shows the mass spectrum of a solution of complex 1 in methanol. All main detected ions were identified based on the analysis of the isotopic distribution of the ion peaks and the measurements of the precise ion masses. The mass spectrum shows two groups of ions. The first group includes the complex ions $[Fe(SPh)_2(NO)_2]^-$, $[Fe(SPh)_2(NO)]^-$, and $[Fe(SPh)(NO)_2(NO_2)]^-$, which are the primary decomposition products of the starting complex 1 in solution under electrospray conditions. The second group includes two series of ions, $[FeO_2 + n(NO)]^-$ and $[FeO_3 + n(NO)]^-$ (n = 0-4), that are formed in the secondary reactions. The measured differences in the m/z values for the ions in the series, which are close to the mass of the main isotope of NO (29.998), definitely indicate that the ions observed in the mass spectrum belong to the series $[FeO_2 + n(NO)]^{-1}$ and $[FeO_3 + n(NO)]^-$. The results of processing of the mass spectrum are presented in Table 2, which gives the experimental m/z values for the peaks corresponding to the main isotopes. The peak of the $[Fe(SPh)_2(NO)_2]^-$ ion has the maximum intensity; the intensities of the peaks of other ions in the spectrum were normalized to the maximum intensity and are given in the relative scale.

The energetics of the Fe–NO bond dissociation and the replacement of the NO ligand by the aqua ligand and the oxygen ligand in dinuclear complex 1 and the related mononuclear complex $[Fe(SPh)(NO)_2]$ was studied by quantum chemical modeling. The calculations were carried out by the density functional theory at the B3LYP level of theory with the 6-31G* basis set using the Gaussian 03 program²⁹ and by the PBE method³⁰ with the extended basis set for the SBK pseudopotential³¹ using the



Fig. 4. Mass spectrum of a solution of the complex $[Fe_2(SPh)_2(NO)_4]$ in methanol $(2 \cdot 10^{-5} \text{ mol } L^{-1})$. The inset shows the mass spectrometric isotopic distribution of the ion peak corresponding to the complex ions $[Fe(SPh)_2(NO)_2]^-$; *N* is the number of ions.

Table 2. Mass spectrometric data for a solution of the complex $[Fe_2(SPh)_2(NO)_4]$ (1) in methanol

Ion	m/z	I _{rel}
[NO ₃] ⁻	61.993	0.12
$[FeO_2]^-$	87.930	0.03
[FeO ₃] ⁻	103.926	0.33
[SPh] ⁻	109.018	0.01
[FeNO ₃] ⁻	117.929	0.08
[FeNO ₄] ⁻	133.923	0.03
$[FeN_2O_4]^-$	147.926	0.02
$[FeN_2O_5]^-$	163.921	0.14
$[FeN_3O_5]^-$	177.925	0.20
$[FeN_3O_6]^-$	193.917	0.91
$[FeN_4O_6]^-$	207.921	0.69
$[Fe(SPh)N_3O_4]^-$	270.941	0.13
[Fe(SPh) ₂ NO] ⁻	303.962	0.25
$[Fe(SPh)_2(NO)_2]^-$	333.959	1.00

PRIRODA program (see Ref. 32).* The zero-point energy contribution was taken into account in the comparison of the energies of the optimized structures. The total energies were calculated at the B3LYP level of theory with the use of the 6-311++G** basis set. The structures of the calculated complexes in different spin states are shown in Figs 5 and 6.

The geometry of the starting complex **1** is satisfactorily described at both the B3LYP and PBE levels. Thus the typical differences in the bond lengths are about 0.01 Å (see Table 1). The largest difference (0.04 Å) is observed for the Fe—N bond lengths determined at the B3LYP level. The elimination of the NO ligand from the diamagnetic dinuclear complex results in the doublet state of the system, the energy of the quartet state being higher by a few kcal mol⁻¹ (Table 3). These states differ only in the mutual orientation of the local spins of the moieties Fe(NO) (S = 1) and Fe(NO)₂ (S = 1/2) (see Table 3).

The quantitative calculations of the N—O bond energy in complex 1 present certain difficulties due to the use of the single-determinant approximation in the density functional theory. The absolute values of the spin density on both the iron atoms and the nitrosyl ligands, which were estimated for the starting complex 1 in the singlet state based on the solution with disturbed symmetry, are significantly smaller than the idealized theoretical values (3 and 1, respectively). For all other complexes under consideration, the distribution of the spin densities on the Fe atom and the NO ligands is in better agreement with the expected distribution (Table 4, B3LYP data). Hence, the solution found for complex 1 (the geometry with disturbed symmetry) does not have the necessary spin structure, although it

^{*} The calculations were carried out with the use of the PRIRODA program at the Interdepartmental Supercomputer Center of the Russian Academy of Sciences.



Fig. 5. Calculated structures of the dinuclear complexes in different spin states: $[Fe_2(\mu-SPh)_2(NO)_3]$ (**3a,b**: S = 1/2 (**a**) and 3/2 (**b**)), $[Fe_2(\mu-SPh)_2(NO)_3(H_2O)]$ (**4a,b**: S = 1/2 (**a**) and 3/2 (**b**)), and $[Fe_2(\mu-SPh)_2(NO)_3(O_2)]$ (**5a,b**: S = 1/2 (**a**) and 3/2 (**b**)). Here and in Fig. 6, the distances are given in Å and the angles are given in degrees; the results of the PBE/SBK calculations are given in parentheses.



Fig. 6. Calculated structures of the mononuclear complexes in different spin states.

Com lex	p- $E_{\rm rel}$ /kcal mol ⁻¹	$q_{\rm Fe}$	ρ_{Fe}	q _{NO}	ρ _{NO}	$q_{\rm S}$	ρ_S	< <i>S</i> ² >	$\langle S^2_A \rangle^b$
				B3LYP/6-31	G* calculations				
1 ^c	_	0.62	±2.41	-0.23	± 0.77	-0.19	0	2.62	10.82
3a	0	0.60,	3.19,	-0.34, -0.24,	-1.36, 1.16,	-0.35	-0.015	4.49	14.82
		0.89	-3.15	-0.25	1.18				
3b	3.2	0.66,	3.25,	-0.36, -0.25,	-1.37, 1.19,	-0.37	0.10	6.58	10.70
		0.91	3.24	-0.25	1.19				
4 a	0	0.76,	3.30,	-0.41, -0.24,	-1.41, 1.17,	-0.39	-0.04	4.60	15.19
41.	1.6	0.85	-3.19	-0.28	1.21	0.41	0.00		11.07
40	1.0	0.81, 0.87	3.37, 3.22	-0.41, -0.25, -0.28	-1.43, -1.18, 1 11	-0.41	0.08	0.00	11.07
59	0	0.07	_2 19	-0.30 -0.26	1.08 _1.18	_0.37	0.03	4 23	13.87
Ja	0	0.91,	3.20	-0.20, -0.27	-1.19	-0.37, -0.34	0.03,	т.25	15.07
5b	-7.0	1.01.	3.01.	-0.29, -0.24	-1.09, -1.17	-0.37.	0.21.	6.35	9.78
		0.86	3.22	-0.26	-1.19	-0.33	0.06		,
6	_	0.85	3.25	-0.27	-1.20	-0.28	0.12	2.51	4.91]
7a	0	0.90	3.29	-0.33, -0.29	-1.25, -1.21	-0.31	0.12	2.62	5.44
7b	15.8	0.91	3.42	-0.33, -0.28	0.56, -1.14	-0.30	0.10	4.88	4.37
8a	43.8	0.48	_	-0.28	_	-0.23	_	_	_
8b	0	0.69	3.28	-0.38	-1.39	-0.31	0.05	3.12	2.61
9a	2.7	0.93	-2.51	-0.22, -0.22	1.06, 1.07	-0.17	0.09	2.48	4.97
9b	0	1.01	3.46	-0.10, -0.25	-0.93, -1.18	-0.22	0.28	5.40	5.36
10	_	0.93	2.81	-0.18	-1.09	-0.20	0.10	2.82	2.37
				PBE/SBK	calculations				
1	0	0.50	_	-0.23	_	-0.02	_	_	_
3a	0	0.68,	1.99,	-0.40, -0.25,	-0.57, 0.21,	-0.12	-0.03	_	_
		0.52	-0.79	-0.25	0.21				
3b	5.2	0.66,	2.63,	-0.33, -0.31,	-0.57, -0.29,	-0.17,	0.17,	—	—
		0.64	1.16	-0.30	-0.30	-0.12	0.14		
4 a	0	0.76,	1.94,	-0.44, -0.27,	-0.53, 0.25,	-0.12,	-0.05,	—	—
4h	2.2	0.48	-0.90	-0.27	0.26	-0.08	-0.02		
40	2.5	0.70,	2.62,	-0.29, -0.30,	-0.07, -0.21,	-0.19,	0.15,	—	—
5a	0	0.03	2.19	-0.23 -0.27	-0.23 -0.42, 0.24	-0.13 -0.05	0.13	_	_
	-	0.55	-0.82	-0.25	0.23	-0.08	0.02		
5b	4.7	0.71,	2.42,	-0.26, -0.25,	-0.42, 0.29,	-0.06,	0.01,	_	_
		0.55	-1.00	-0.24	0.27	-0.09	0.03		
6	0	0.72	1.68	-0.29, -0.26	-0.42, -0.42	-0.14	0.13	_	—
7a	0	0.76	1.76	-0.32, -0.28	-0.51, -0.51	-0.20	0.18	—	—
7b	25.0	0.73	2.21	-0.33, -0.26	0.16, 0.27	-0.16	0.23	—	—
8a	24.9	0.52	—	-0.37	—	-0.09	—	—	—
8b	0	0.72	2.64	-0.38	-0.78	-0.26	0.09	_	—
9a	0	0.64	-0.56	-0.16, -0.15	0.19, 0.28	-0.07	-0.03	_	—
9b	10.5	0.65	1.23	-0.19, -0.17	-0.14, -0.09	-0.04	0.33	_	_
10	0	0.94	1.90	-0.26	-0.57	-0.09	0.21	_	_

Table 3. Electronic characteristics ^{<i>a</i>} of the complexes $[Fe_2(\mu-SPh)_2(NO)_3(X)]$ (X = NO, the free coordination site, H ₂ O, and O ₂
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^{*a*} E_{rel} is the relative energy; q_{Fe} , q_{NO} , and q_S are the charges on the Fe atom, the NO group, and the S atom, respectively; ρ_{Fe} , ρ_{NO} , and ρ_S are the spin density on the Fe atom, the NO group, and the S atom, respectively; $\langle S^2 \rangle$ is the square of the spin.

 b The average square of the spin after the annihilation of the wave function term with the spin 1, 2, 3/2, and 5/2 for the singlet, triplet, doublet, and quartet states, respectively.

^c Characteristics of the singlet state with disturbed symmetry.

has the intrinsic stability. This is also evident from the average square of the spin, which, as can easily be shown, can be calculated by the equation

$$\langle S^2 \rangle = (n_{\rm a} + n_{\rm b})/2 + (n_{\rm a} - n_{\rm b})^2/4$$

for the single-determinant function containing n_a unpaired electrons with the spin α and n_b unpaired electrons with the spin β .

The electronic configuration of the starting complex is $d_1 \alpha d_2 \alpha d_3 \alpha \pi_1 \beta \pi_2 \beta d_1 \beta d_2 \beta d_3 \beta \pi_1 \alpha \pi_2 \alpha$, where the d_i and π_i orbitals are located predominantly on the Fe atoms and the NO ligands, respectively; the orbitals belonging to another Fe(NO)₂ unit are primed. Hence, $n_a = n_b = 5$ for the starting complex; after removal of one NO group, $n_a = 5$, $n_{\rm b} = 4$ for the doublet states of the system (complexes **3a**, 4a, and 5a), and $n_a = 6$, $n_b = 3$ for the quartet states (complexes **3b**, **4b**, and **5b**). Therefore, $\langle S^2 \rangle = 5$ would be expected for complex 1 and $\langle S^2 \rangle = 4.75$ would be expected for complexes 3a, 4a, and 5a. The former value is inconsistent with the results of calculations (2.60), whereas the latter value is in good agreement with the experimental values (4.49, 4.60, and 4.23, respectively). The underestimated spin densities on the Fe atoms and the NO ligands in complex 1 are indicative of a substantial admixture of the singlet state with filled electron shells, whose energy is higher than that of the singlet state with disturbed symmetry by 21.0 kcal mol⁻¹ (see Ref. 33). This leads to a considerable underestimation of the bond energy of the NO ligand in the complex (up to $1.3 \text{ kcal mol}^{-1}$), as well as of the energy consumption for its decomposition into two mononuclear complexes (up to 6.2 kcal mol^{-1}). In the mononuclear Fe dinitrosyl complex with the doublet ground state, when there is no need to find the solution with disturbed symmetry, this artifact is virtually absent, and the Fe-NO bond dissociation energy estimated at the B3LYP level³⁴ is 29.2 kcal mol⁻¹.

For the quartet states of complexes **3b**, **4b**, and **5b**, the calculated values of $\langle S^2 \rangle$ (6.58, 6.66, and 6.35, respectively) are also in satisfactory agreement with the theoretical value of 6.75. The good agreement with the theoretical values (2.75, 4.75, and 3) is observed also for the mononuclear complexes in the doublet (**6**, **7a**, **9a**, and **10**), quartet (**9b**), and triplet (**8b**) states, respectively. Therefore, it can be expected that the relative energies of these complexes with the spins S = 1/2 and 3/2, as well as the energies of the addition of neutral H₂O and O₂ ligands to coordinatively unsaturated complexes, would be obtained with satisfactory accuracy.

The results of calculations for the open-shell complexes at the PBE level of theory (see Table 3) show that the spin density distribution substantially differs from the idealized distribution. Hence, these calculations are poorly informative for the estimation of the energy changes in the reactions. For this purpose, we used the results of calculations at the B3LYP level and the data for the spin states with the lowest energies for all systems.

For the coordinatively unsaturated dinuclear (3a) and mononuclear (6) complexes, the binding of the water molecule leads to a decrease in the energy by 8.9 and 11.2 kcal mol⁻¹, respectively. In mononuclear agua dinitrosyl complex 7a, the N–O bond energy is 25.5 kcal mol⁻¹; this energy decreases to 14.6 kcal mol⁻¹ in complex **9b**, which is formed in the case when the O2 molecule rather than H_2O binds at the free coordination site in complex **6**. This process is accompanied by shortening of the Fe-O bonds and elongation of the O–O bond by 0.09 Å. Consequently, the stronger binding of the oxygen molecule leads to a decrease in the energy consumption for the Fe–NO bond dissociation in the mononuclear complex. A similar effect would be expected for the dinuclear complexes, but it was beyond the scope of our study. These results suggest a new mechanism of the influence of oxygen on the intensification of the elimination of NO due to the formation of less stable mixed oxygen nitrosyl complexes of iron.

The calculations at the PBE level of theory for oxygen complexes 5a,b showed that the O2 molecule has the angular coordination, as opposed to the π coordination obtained in the calculations at the B3LYP level (see Fig. 5). It is also noteworthy that the calculations at the PBE level resulted in the transformation into the quartet state $5a \rightarrow 5b$ not due to a change in the mutual orientation of the local spins on the atoms of the Fe units, like in all other cases, but due to a change in the orientation of the spin on O_2 (the spin density is 0.58) from antiparallel to parallel with respect to the spin on the Fe atom. This accounts for the qualitative difference in the mutual arrangement of the quartet and doublet states for the terminal and lateral coordination of O_2 (see Table 3). In addition, we failed to find solutions with the similar local spin density distribution in the calculations at the B3LYP level for the states with the spins S = 1/2 and 3/2. In the doublet complex, the O₂ ligand bears the unpaired electron (the spin density is 1.12), whereas the spin density on this ligand in the quartet complex is small (-0.10).

In mononuclear complexes 9a,b, the O₂ ligands have the same spin density (1.3), *i.e.*, these ligands are analogous to the superoxide anion with the weak O—O bond. This provides prerequisites for the subsequent intramolecular or intermolecular oxidation accompanied by the transformation of the iron oxygen complexes into the oxo complexes. The elucidation of their transformation pathways are beyond the scope of the present study.

Based on the results of the present study, it would be expected that the decomposition of dinuclear complex 1 into two mononuclear complexes is quite probable on the condition of the coordination of the solvent molecule $(6 \rightarrow 7a)$. A decrease in the calculated Fe–NO bond energy in the mononuclear aqua dinitrosyl complex by 3.7 kcal mol⁻¹ compared to the mononuclear dinitrosyl complex with two sulfur-containing ligands³⁴ also indicates that the mononuclear complex should be less stable than the dinuclear complex. This result is in qualitative agreement with the observed induction period for the elimination of NO.

The mass spectra show an intense peak of the $FeO_3^$ ion. To elucidate the nature of this species, we carried out calculations of the energy of the complexes FeO_3^{-} in different spin states and with different geometry at the PBE/SBK level of theory. It appeared that the quartet complex with the symmetry D_{3h} has the lowest energy. The Fe–O bond length in this complex is 1.643 Å. Since only 75% of the spin density is located on the Fe atom, it should formally be described as the Fe^{IV} complex. The doublet FeO_3^- complex has a slightly higher energy (by 1.6 kcal mol⁻¹). The symmetry of the latter complex reduces to $C_{2\nu}$ due to the non-equivalent Fe–O bonds; two bond lengths are 1.626 Å, and one bond length is 1.606 Å. The energy of the quartet Fe^{III} complex containing the peroxo group (O-O, 1.450 Å) is substantially higher (48.6 kcal mol⁻¹). In this complex, there is one short Fe–O distance (1.653 Å) and two long Fe–O distances (1.840 Å). As mentioned above, the formation of the iron trioxo complex can be attributed to the decomposition of the reaction products of the mononuclear nitrosyl complexes with oxygen.

Therefore, we synthesized single crystals of the dinuclear iron benzenethiolate tetranitrosyl complex 1 and studied its structure and its decomposition products in solution. In the mass spectrum of a solution of 1, the primary decomposition products of the starting complex 1 (the complex ions $[Fe(SPh)(NO)_2(NO_2)]^-$, $[Fe(SPh)_2(NO)]^-$, and $[Fe(SPh)_2(NO)_2]^-$) and a series of ions that are formed in the secondary reactions $([FeO_2 + n(NO)]^- \text{ and } [FeO_3 + n(NO)]^-, n = 0-4) \text{ were}$ identified. The Fe-NO bond dissociation and the replacement of the NO ligand by aqua and oxygen ligands in complex 1 were studied by quantum chemical modeling. Presumably, the stronger Fe-O bond and the fact that the oxidation of NO by oxygen is a favorable reaction are responsible for the energetically favorable destruction of the primary oxygen complexes giving Fe-O and Fe=O bonds and new N-O bonds under electrospray conditions in aerobic solutions.

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