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Synthesis, structure, and NO-donor activity of the paramagnetic complex $[Fe_2(SC_3H_5N_2)_2(NO)_4]$ as a model of nitrosyl [2Fe-2S] proteins

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The neutral dinuclear iron nitrosyl complex $[Fe_2(SC_3H_5N_2)_2(NO)_4]$ (**1**) of the "g = 2.03" family with a ligand analogous to natural mercaptohistidine was synthesized by the metathesis reaction of the thiosulfate ligands in the $[Fe_2(S_2O_3)_2(NO)_4]^{2-}$ anion with imidazolidine-2-thiolate ligands. The electrochemical determination of nitrogen oxide in solution showed that compound **1** has a lower NO-donor ability compared to the iron complexes with 1-methylimidazole-2-thiol and imidazole-2-thiol synthesized earlier. Study of the magnetic properties of polycrystals of **1** demonstrated that the effective magnetic moment at room temperature is *ca.* 2.45 μ_B and corresponds to a molecule containing a pair of the noninteracting spins S = 1/2. This is evidence that each iron coordination unit in complex **1** contains one unpaired electron, and the iron atom is in the low-spin state.

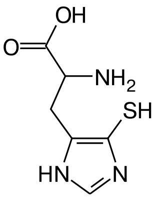
Key words: NO donors, iron nitrosyl complexes with the imidazolidine-2-thione ligand, heterocyclic ligands, X-ray diffraction analysis, ^{57}Fe Mössbauer spectroscopy, magnetism.

Endogeneous nitrogen monoxide reacts with cellular substrates and plays the key role in the living activity.[1–3] In studies of the reaction mechanisms of NO intermediates, the synthesis of analogs of cellular nitrosyl adducts has gained increasing importance.

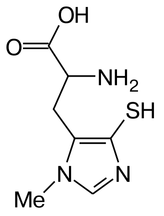
Iron nitrosyl complexes are produced in reactions of endogeneous NO with active sites of non-heme [Fe-S] proteins *in vivo*.[4–6] In recent years, it has been reliably established that iron nitrosyl complexes with thiol-containing ligands (cysteine and glutathione) play important roles in oranisms, such as cellular NO storage and transport.[7] We have prepared stable crystalline mono- and dinuclear iron nitrosyl complexes with the use of azaheterocyclic thiols, *viz.*, thio derivatives of triazole,[8,9] tetrazole,[10] pyridine,[11] and imidazole.[12,13] These compounds are of interest from the point of view of fundamental investigation of the bond nature of the $\{Fe(NO)_2\}$ fragment and practical medicine for the design of new generation drugs based on synthetic models of natural NO donors.[14,15]

Hence, the purpose of the present study was to synthesize and investigate the iron nitrosyl complex with imidazolidine-2-thione as a structural analog of ergothionine.

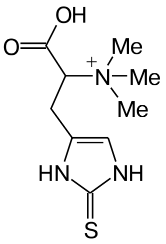
Mercaptohistidines, small aromatic thiols, are known to be different in many respects from other natural thiols, most of which are cysteine derivatives.[16] The aromatic rings of imidazole in mercaptohistidines impart unusual reactivity to the thiol group, whose active form, *viz.*, the thiolate anion, exists in a wide pH range.[17,18] The *in vitro* studies of model mercaptohistidines demonstrated that these compounds are efficient acceptors of radicals, can protect from damage by peroxynitrite and active oxygen-containing intermediates,[19–22] and, consequently, have potential physiological activity. Taking into account the existence of tautomerism of thiols,[17,23,24] it was of particular interest to reveal whether imidazolidine-2-thione is coordinated to the iron atoms in the thiol or thione form. Since the exchange interactions in dinuclear complexes, their total spin, and the spin density distribution in dinuclear iron nitrosyl complexes are responsible for the reactivity, it was also important to study the magnetic properties of complex **1**.



Mercaptohistidine



Ovothiol



Ergothionine

The aim of the present study was to synthesize a new iron nitrosyl complex with the imidazolidine-2-thione ligand of composition $[Fe_2(SC_3H_5N_2)_2(NO)_4]$ (**1**), estab-

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lish its structure by X-ray diffraction, IR spectroscopy, and ^{57}Fe Mössbauer spectroscopy, and investigate the NO-donor activity of complex **1** compared to the already known nitrosyl complexes, μ_2-(*N*,*C*,*S*)-[bis(1-methylimidazole-2-thiolate)tetranitrosyldiiron] (**2**)[13] and μ_2-(*N*,*C*,*S*)-[bis(imidazole-2-thiolate)tetranitrosyldiiron] (**3**).[12]

Experimental

The following commercial reagents were used: $Na_2S_2O_3 \cdot 5H_2O$ (Aldrich), NaOH (Aldrich), 2-mercaptoimidazolidine (Aldrich), KI (Aldrich), and H_2SO_4 of reagent grade (GOST 4204-77). The $Na_2[Fe_2(\mu_2\text{-}S_2O_3)_2(NO)_4] \cdot 4H_2O$ complex was synthesized according to a known procedure.[25] All operations associated with the preparation of solutions, the reactions, and isolation of complex **1** were carried out under nitrogen. The solvents (anhydrous acetone, ethanol, and DMSO) were purified according to a known procedure.[26] The elemental analysis for C, H, N, S was carried out at the Analytical Center of the Institute of Problems of Chemical Physics of the Russian Academy of Sciences. The IR spectra (ν/cm^{-1}) were recorded on a SPECTRUM BX-II Fourier spectrometer. Samples were prepared as KBr pellets (1 mg of the compound under study per 300 mg of KBr).

μ_2-(*N*,*C*,*S*)-[Bis(imidazolidine-2-thiolate)tetranitrosyliron], $[Fe_2(SC_3H_5N_2)_2(NO)_4]$ (1). Complex **1** was synthesized by the addition of an aqueous solution (15 mL) of a mixture of $Na_2[Fe_2(\mu_2\text{-}S_2O_3)_2(NO)_4] \cdot 4H_2O$ (0.88 g, 2 mmol) and $Na_2S_2O_3 \cdot 5H_2O$ (0.76 g, 4 mmol) to an aqueous alkaline solution (25 mL; 0.29 g, 7.25 mmol of NaOH) of imidazolidine-2-thione (0.78 g, 7 mmol). The black precipitate that formed was rapidly filtered off and dried under a stream of nitrogen. Extraction with a 1 : 4 ethanol—acetone mixture followed by removal of the solvents afforded black needle-like crystals of compound **1** in 11% yield. Found (%): C, 16.50; H, 2.68: Fe, 25.42; N, 25.07; S, 14.61. $Fe_2S_2C_6H_{10}N_8O_4$. Calculated (%): C, 16.53; H, 2.77; Fe, 25.61; N, 25.70; O, 14.68; S, 14.71. IR, ν_{max}/cm^{-1}: 3286 (s), 1786 (v.s), 1720 (v.s), 1636 (m), 1509 (s), 1464 (m), 1454 (m), 1400 (m), 1318 (m), 1280 (s), 1241 (m), 1190 (m), 1041 (m), 1019 (m); ν(NO) 1786, 1720.

Complexes **2** and **3** were synthesized according to known procedures,[28,29] respectively.

X-ray diffraction study. The unit cell parameters and the three-dimensional set of reflection intensities were measured on an automated Enraf-Nonius CAD 4 X-ray diffractometer using Mo-Kα monochromatic radiation ($\lambda = 0.71070$ Å). The intensities of all reflections were corrected for absorption by the semiempirical method;[27] the maximum/minimum transmission factors were 0.868/0.577. The structure was solved by direct methods and refined anisotropically by the full-matrix least-squares method with the use of the SHELXS-97 program package.[28] All nonhydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atom of the NH group was located in a difference Fourier map. The positions of the other hydrogen atoms at the carbon atoms were calculated geometrically and refined isotropically. The position of the hydrogen atom at the nitrogen atom was refined independently.

The crystallographic data were deposited with the Cambridge Structural Database (CCDC 614393).

^{57}Fe Mössbauer spectra were recorded on a WissEl constant-acceleration instrument with the use of ^{57}Co in a Rh matrix as the source. Low-temperature spectra were measured with the use of a CF-506 temperature-controlled continuous-flow helium cryostat (Oxford Instruments). The Mössbauer spectra were processed by the least-squares method assuming the Lorentz line shape for individual spectral components.

Magnetic measurements. The magnetic moment of a powdered sample (M) and its dependences on the temperature (T) and the magnetic field strength (H) were studied on a Quantum Design MPMS 5XL SQUID magnetometer in a constant magnetic field at a strength of H = 0—50 kOe at 2—300 K.

Electrochemical determination of the NO concentration generated by iron nitrosyl complexes **1—3** in solution was performed with the use of an amiNO-700 sensor electrode of the inNO Nitric Oxide Measuring System (Innovative Instruments, Inc., Tampa, FL, USA). The NO concentration was fixed for ~200 s (with a step of 0.2 s) in a 1% aqueous dimethyl sulfoxide (DMSO) solution at an NO donor concentration of 0.1 μmol L^{-1}. The electrochemical sensor was calibrated against a standard aqueous $NaNO_2$ solution at a concentration of 100 μmol L^{-1}, which was added to a mixture of KI (20 mg) in water (18 mL) and 1 *M* H_2SO_4 (2 mL). All experiments were carried out in aerobic solutions at 25 °C; pH was measured using an HI 8314 membrane pH meter (HANNA instruments, Germany). The experimental data were processed and the decomposition rate constants for complexes **1—3** were calculated with the use of the Origin 6.1 program package.

Results and Discussion

Complex **1** was synthesized by the exchange of thiosulfate ligands with imidazolidine-2-thione ligands according to a known procedure[12,13] by the reaction

$$[Fe_2(S_2O_3)_2(NO)_4]^{2-} + 2\ S_2O_3{}^{2-} \longrightarrow$$

$$\longrightarrow 2\ [Fe(S_2O_3)_2(NO)_2]^{3-} \xrightarrow[-4\ S_2O_3{}^{2-}]{2\ C_3H_5N_2S^-,\ OH^-}$$

$$\longrightarrow \underset{\mathbf{1}}{[Fe_2(SC_3H_5N_2)_2(NO)_4]}. \tag{1}$$

Complex **1** is readily soluble in DMSO and acetone, partially soluble in methanol, poorly soluble in ethanol, and insoluble or immediately decomposes in most organic solvents.

Study by ^{57}Fe Mössbauer spectroscopy (at T = 290 K) demonstrated that the product of reaction (1) in an aqueous alkaline solution was composed of a mixture of two iron-containing phases, *viz*., the iron nitrosyl complex with the imidazolidine-2-thione ligand, **1**, characterized by the isomer shift $\delta_{Fe} = 0.157(1)$ mm s^{-1} and the quadrupole splitting $\Delta E_Q = 1.021$ (2) mm s^{-1} and an iron complex with the parameters $\delta = 0.399(2)$ mm s^{-1} and $\Delta E_Q =$ 0.798 (2) mm s^{-1}. Earlier, we have observed the formation of impurity phases containing the octahedral

Table 1. Crystallographic parameters and the X-ray diffraction data collection and refinement statistics for complex **1**

Parameter	Characteristic
Molecular formula	$C_6H_{10}Fe_2N_8O_4S_2$
Molecular weight	434.04
T/K	293(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	6.422(2)
b/Å	7.618(2)
c/Å	8.194(2)
α/deg	100.93(2)
β/deg	100.93(2)
γ/deg	90.08(3)
V/Å^3	386.2(2)
Z	1
d_{calc}/g cm^{-3}	1.866
μ(Mo-Kα)/mm^{-1}	2.177
Crystal dimensions/mm	0.065×0.10×0.25
θ_{max}/deg	25
Number of measured reflections	2712
Number of reflections with $F_0 > 4\sigma(F_0)$	1357
R_{int}	0.0315
Number of parameters in refinement	109
$R(F)$ ($I > 2\sigma(I)$)	0.0321
$R_w(F^2)$	0.0503
S	0.983
$\Delta\rho_{max}$, $\Delta\rho_{min}$/e Å^{-3}	0.254, –0.236

Fe^{3+} ions, which were characterized by the analogous or similar Mössbauer parameters, in the synthesis of dinuclear nitrosyl [2Fe-2S] complexes with other azaheterocyclic thiols.[9—13] Presumably, these are compounds of composition FeL_3, where L is heteryl-2-thiolate (compositions and the structures of these compounds are presently under study). The percentage of a Fe^{3+} ion impurity is, as a rule, no higher than 7—10%. In the case of complex **1**, we obtained 50% of the impurity. Extraction with acetone from the powdered product afforded complex **1** as the pure phase in a substantially lower yield compared to compounds **2** (86%) and **3** (63%). Attempts to use other solvents for extraction with the aim of increasing the yield of the reaction product failed because of low solubility of complex **1** in most organic solvents.

The crystal and molecular structure of compound **1** was established by single-crystal X-ray diffraction. The crystallographic data and the X-ray data collection and refinement statistics are given in Table 1. Selected bond lengths and bond angles are listed in Table 2. The X-ray diffraction study demonstrated (Fig. 1) that complex **1** has a centrosymmetric dinuclear structure, in which, like in nitrosyl complexes **2** and **3**, each iron atom forms bonds with the sulfur atom of one ligand, the nitrogen atom of another ligand, and two NO groups. Selected bond lengths and bond angles and the Mössbauer and IR parameters of complexes **1—3** are given in Table 3.

The C—S bond length in the imidazolidine-2-thione ligand of complex **1** determined by X-ray diffraction is 1.741 Å, which is substantially larger than the C=S double bond length (1.684 Å).[29] Presumably, the thiol form of the ligand (RS^-) makes a large contribution to the resulting complex.

An analysis of the main bond lengths and bond angles in the $Fe(NO)_2$ fragment demonstrated that the Fe—N—O angles in complex **1** are more linear compared to those in compounds **2** and **3** (see Table 3). The lengths of the bonds between iron and the nitrogen atoms of the NO groups decrease, whereas the N—O bond lengths increase. The NO groups in **1** are more equivalent than those in **2** and **3**, which is confirmed by a decrease in the difference

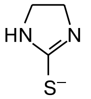
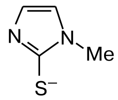
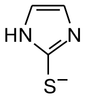
Table 2. Selected geometric parameters for complex **1***

Bond	d/Å	Parameter	Value	Parameter	Value
Fe—S	2.312(1)	Bond angle	ω/deg	Bond angle	ω/deg
Fe—N(1´)	1.982(2)	S—Fe—N(1´)	108.38(8)	Fe´—N(1)—C(2)	129.3(2)
Fe—N(01)	1.687(3)	S—Fe—N(01)	106.2(1)	Fe´—N(1)—C(5)	122.4(2)
Fe—N(02)	1.673(3)	S—Fe—N(02)	104.8(1)	C(2)—N(1)—C(5)	107.8(3)
O(1)—N(01)	1.165(3)	N(1´)—Fe—N(01)	106.0(1)	S—C(2)—N(1)	125.4(2)
O(2)—N(02)	1.170(3)	N(1´)—Fe—N(02)	113.5(1)	S—C(2)—N(3)	121.4(2)
S—C(2)	1.741(3)	N(01)—Fe—N(02)	117.5(1)	N(1)—C(2)—N(3)	113.2(3)
N(1)—C(2)	1.308(4)	Fe—S—C(2)	99.7(1)	C(2)—N(3)—C(4)	111.7(3)
N(1)—C(5)	1.483(4)	Fe—N(01)—O(1)	167.2(3)	N(3)—C(4)—C(5)	101.5(2)
N(3)—C(2)	1.339(4)	Fe—N(02)—O(2)	170.7(3)	N(1)—C(5)—C(4)	105.3(2)
N(3)—C(4)	1.438(4)	N—H...S″	176(3)		
C(4)—C(5)	1.525(4)	Torsion angle	ψ/deg	Torsion angle	ψ/deg
N(3)—H(3)	0.83(2)**	Fe—S—C(2)—N(1)	–78.5(3)	S—Fe—N(1´)—C(2´)	–79.2(3)
H(3)—S″	2.61(2)**	S—C(2)—N(1)—Fe´	6.4(4)	N(1´)—Fe—S—C(2)	102.8(1)

* The symmetry codes: (´) $-x$, $-y$, $-z$, (″) $-x$, $-y$, $1 - z$.

** The hydrogen bond lengths and the N(3)—H(3)...S″ angles.

Table 3. Selected bond lengths, bond angles, and parameters of the Mössbauer (at 290 K) and IR spectra of sulfur-containing iron nitrosyl complexes **1—3** of composition $Fe_2(SL)_2(NO)_4$

Complex	L	N—O	Fe—N	Fe—N—O	Fe—N_{get}	Fe...Fe	Fe—S	δ_{Fe}*	ΔE_Q**	ν_{NO}	$\Delta\nu_{NO}$
		Å		/deg	Å			mm s^{-1}		cm^{-1}	
1		1.165(3) 1.170(3)	1.687(3) 1.673(3)	167.2(3) 170.7(3)	1.982(2)	4.030	2.312(1)	0.155(4)	1.015(2)	1786 1724	62
2		1.149(6) 1.164(6)	1.696(5) 1.667(5)	164.3(5) 170.2(4)	2.013(4)	4.010	2.283(2)	0.180(1)	0.928(4)	1782 1748 1716	66
3		1.148(4) 1.158(5)	1.690(3) 1.674(3)	165.5(4) 170.5(4)	2.010(3)	4.102	2.299(1)	0.196(1)	1.109(2)	1781 1748 1716	65

* δ_{Fe} is the isomer shift relative to α-Fe.

** ΔE_Q is the quadrupole splitting.

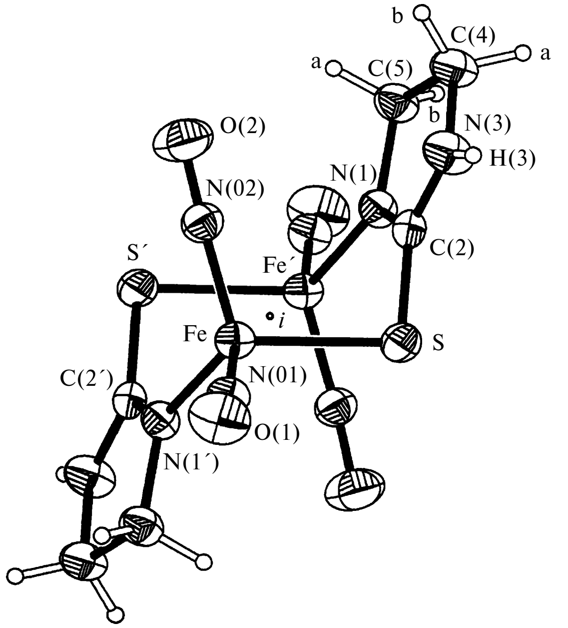


Fig. 1. Molecular structure of complex **1**. The atoms are represented by anisotropic displacement ellipsoids drawn at the 35% probability level.

in the positions of the NO stretching bands in the IR spectra. The smallest difference Δ_{NO} is observed for **1** (see Table 3). Unlike the IR spectra of compounds **2** and **3**, which show three NO absorption bands, the IR spectrum of compound **1** has two bands of this type. The NO stretching bands are shifted to higher frequencies. In terms of the formalism[30] and taking into account the X-ray diffraction data, this is evidence that the electron density is shifted from the NO groups to the iron atoms. Therefore, the charge on the NO group decreases. The observed substantial decrease in the length of the bond between the iron atom and the nitrogen atom of the heterocycle in **1** and a decrease in the interatomic Fe...Fe distance (by 0.072 Å compared to that in **3**) in complex **1** (see Table 3) suggest that the complex with imidazolidine-2-thione would be more stable in protic media than complexes **2** and **3**. Actually, intensive decomposition of complexes **2** and **3** is observed during first seconds in 1% aqueous DMSO solutions at 25 °C and pH 7 under aerobic conditions (Fig. 2). Activationless decomposition of complex **1** occurs only within 12 s after dissolution of the sample, and NO is generated over a longer period of time. The plots of the concentration of NO eliminated from the complexes *vs.* the time indicate that nitrogen oxide reacts with oxygen dissolved in water according to the scheme proposed in our study.[13]

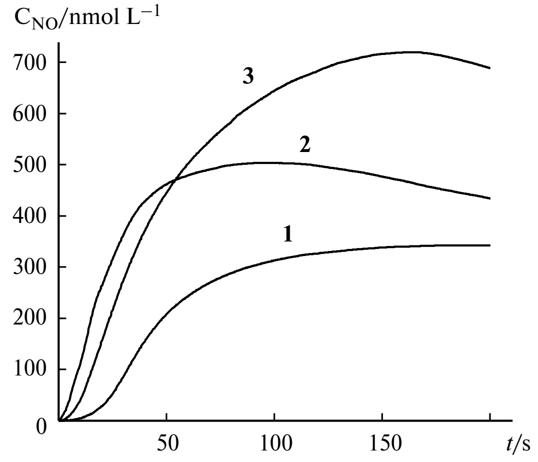


Fig. 2. Plot of the amount of NO generated by iron nitrosyl complexes **1—3** ($1 \cdot 10^{-4}$ mol L^{-1}) in 1% aerobic DMSO aqueous solutions *vs.* the time at 25 °C and pH 7.0.

The ^{57}Fe Mössbauer spectrum of polycrystals of complex **1** is a single doublet, which confirms the structural equivalence of the iron atoms at room temperature. In the spectra of **1**, δ_{Fe} decreases (see Table 3), *i.e.*, the s-electron density on the iron nuclei increases, which would lead to a decrease in the Fe—S bond length. However, we observed a slight elongation of the Fe—S bond (see Table 3). Apparently, this is associated with the fact that the negative charge on the S atom of imidazolidine-2-thione differs from the charge on the imidazolethione fragment of complex **3** and the charge on the 1-methylimidazole-2-thione fragment of complex **2** containing, unlike **1**, the aromatic ring.

The temperature dependence of the magnetic susceptibility of complex **1** is a nonmonotonic curve (Fig. 3). At room temperature, the effective magnetic moment of compound **1** (Fig. 4) approaches $g(2(S + 1)S)^{1/2} = 2.45$, which corresponds to a molecule containing a pair of the noninteracting spins S = 1/2. A decrease in the temperature below 100 K leads to a decrease in the effective magnetic moment μ_{eff}, which is evidence for antiferromagnetic exchange interactions in the dimers. The 3d^7 configuration of the iron ion (oxidation state +1) in a tetrahedral coordination has the spin S = 3/2 formed by three unpaired electrons on the dπ orbitals. The total spin of the paramagnetic center is formed by the individual Fe(d^7) ion (S = 3/2) and two NO groups coordinated to this ion (S = 1/2). Due to strong exchange interactions between the π*-NO electrons and the dπ electrons of the Fe atom, the total spin of the paramagnetic center is $S_t = 1/2$.

An increase in the magnetic susceptibility at temperatures below 15 K (see Fig. 3) indicates that additional paramagnetic species that are present in the sample of complex **1** under study make a substantial contribution to the magnetic moment. This nonmonotonic dependence of the magnetic susceptibility of the sample of **1** on the temperature can be accounted for by the summation of the contributions of impurity paramagnetic species with the spin 3/2 and dimers with the spin pair of 1/2 to the total magnetic moment. The contribution of an impurity to the total magnetic moment and its dependence on the susceptibility are described by the Curie—Weiss law. The dimers contain pairs of the iron spins, which can interact with each other. The total spin of the dimers decreases with decreasing temperature due to antiferromagnetic exchange interactions between the dimers. This accounts for a decrease in the magnetic susceptibility at temperatures below 75 K. A further decrease in the temperature leads to an increase in the number of the dimers containing paired spins existing in the ground state with the spin of the complex equal to zero, which is characteristic of the tetrahedral coordination.**[31]** The contribution of the paramagnetic impurity increases, resulting in an increase in M at $T < 10$ K.

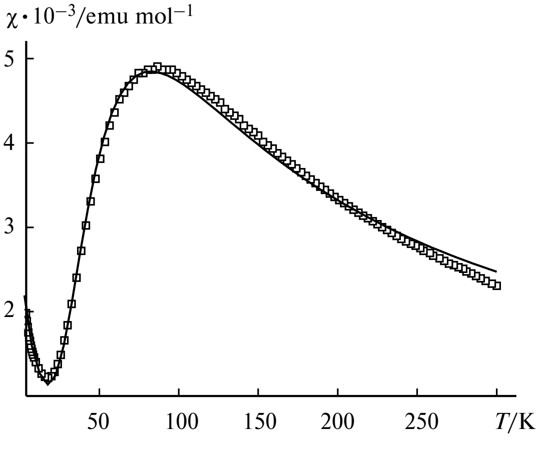


Fig. 3. Magnetic susceptibility χ of complex **1** *vs.* the temperature in a constant magnetic field of 1 kOe. The experimental data are represented by points; the approximation of the experimental dependence by the sum of the contributions of the dimers and monomers is shown by a solid line.

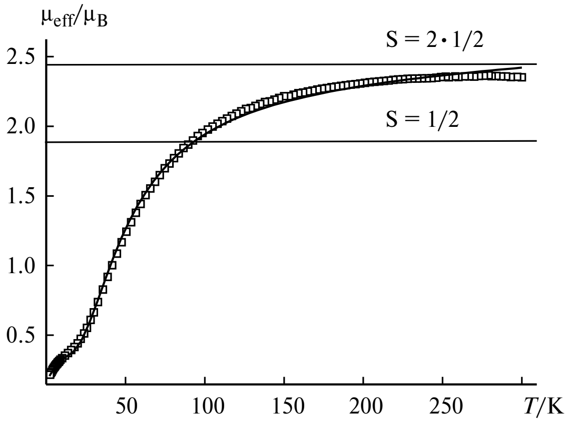


Fig. 4. Plot of the effective magnetic moment μ_{eff} of complex **1** *vs.* the temperature in a constant magnetic field of 1 kOe. The effective magnetic moment is normalized to the Bohr magneton. The effective magnetic moments corresponding to the paramagnetic systems with one and two spins 1/2 in the unit cell are indicated by horizontal lines.

The experimental dependence $\chi(T)$ is approximated with a satisfactory accuracy by the sum of two equations. The first equation is the Bleaney—Bowers equation for the magnetic susceptibility of a dimer with two spins 1/2. The second equation takes into account the paramagnetic species with the spin 3/2 (Curie—Weiss equation):

$$\chi = \frac{2N\mu_B^2 g^2}{3kT}\left[1 + \frac{1}{3}\exp\left(\frac{-2J}{kT}\right)\right]^{-1}(1-p) + \frac{C}{T-\theta}p, \qquad (2)$$

where N is the number of magnetic centers in the sample, μ_B is the Bohr magneton, k is the Boltzmann constant, T is the temperature, J is the exchange integral, p is the

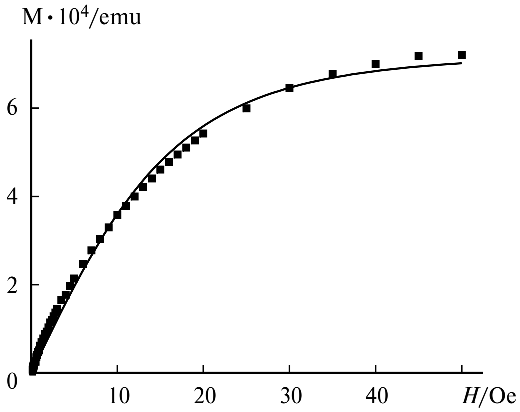


Fig. 5. Plot of the magnetic moment of a sample of complex **1** *vs.* the constant magnetic field *H* at $T = 2$ K. The experimental dependence of the Brillouin function for the spin 3/2 is indicated by a solid line.

fraction of paramagnetic species with the spin 3/2 in the sample, *C* is the Curie constant, and θ is the Weiss constant. The approximation of the dependence $\chi(T)$ by Eq. (2) for $g = 2.0$ revealed the following parameters: $J = -47$ cm^{-1}, $p = 0.017$, and $\theta = -8$ K. Earlier, we have proposed[12] an analogous interpretation for the temperature dependence of the magnetic susceptibility for dinucleariron tetranitrosyl complex **3**. Therefore, the impurity present in polycrystals of complex **1** accounts for no more than 2%. The field dependence of the sample is characteristic of the paramagnet with the spin 3/2 (Fig. 5). A SQUID magnetometer allows investigation of the magnetic moment of the sample as a whole and does not enable one to obtain direct evidence for the contributions of species of different types to its magnetic moment. Hence, we studied the magnetic properties of a polycrystalline sample of **1** by the ESR method and found that the *g* factor of one of the lines is 2.03, which confirms that the complexes belong to the corresponding family.[32,33]

In conclusion, we synthesized the first paramagnetic iron tetranitrosyl complex with imidazolidine-2-thionyl $Fe_2(SC_3H_5N_2)_2(NO)_4$ containing the structural analog of natural aromatic thiol, *viz.*, ergothionine. The X-ray diffraction study demonstrated that the iron atoms in the centrosymmetric dimer are linked to each other by the μ-N—C—S bridge between the thiol ligands and the NO groups. The total spin of the paramagnetic center ($S_t = 1/2$) is formed by the individual Fe(d^7) ion (S = 3/2) and two NO groups bound to this ion (S = 1/2). The nonmonotonic dependence of the magnetic susceptibility on the temperature can be explained by the summation of the contributions to the total magnetic moment of the system of dimers with a pair of the spins 1/2 and the paramagnetic impurity with the spin 3/2. The X-ray diffraction data, the results of ^{57}Fe Mössbauer and IR spectroscopy, and the data from electrochemical analysis show that complex **1** differs from compounds **2** and **3** by higher chemical stability in the solid phase and solution. The NO donor activity of complex **1** is substantially lower compared to that of compounds **2** and **3**. Decomposition of **1** accompanied by elimination of NO occurs at a lower rate in 1% aqueous DMSO solutions.

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