New class of neutral paramagnetic binuclear sulfur-containing iron nitrosyl complexes

S. M. Aldoshin, N. A. Sanina, O. A. Rakova, G. V. Shilov,*
A. V. Kulikov, Yu. M. Shulga, and N. S. Ovanesyan

Institute of Problems of Chemical Physics, Russian Academy of Sciences,
142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (096) 515 3588. E-mail: sanina@icp.ac.ru

Neutral paramagnetic binuclear iron nitrosyl complexes, whose structures and properties differ from those of the known Roussin's red salt esters, were synthesized for the first time. The iron nitrosyl complexes $[Fe_2(\mu_2\text{-}SR)_2(NO)_4]\cdot nH_2O$ (η^1-S, η^1-N; n = 1 or 2; R is 5-amino-1,2,4-triazol-3-yl (**1**), 1,2,4-triazol-3-yl (**2**), 1-methyltetrazol-5-yl (**3**), or benzothiazol-2-yl (**4**)) were prepared by the exchange reactions of $Na_2Fe_2(S_2O_3)_2(NO)_4$ with heterocyclic thiols. According to the results of X-ray diffraction analysis, complex **1** has a centrosymmetrical dimeric structure in which the iron atoms are linked through the μ-N—C—S structural fragment. Each Fe atom is bound to the N atom of one ligand and the S atom of another ligand. The isomer shifts of complexes **1**—**4** have virtually equal values (δ_{Fe} = 0.291(1)—0.304(1) mm s^{-1} at T = 85 K), which are twice as large as δ_{Fe} for Roussin's red salt esters. The iron atoms in complexes **1**—**4** have the low-spin configuration d^7 (Fe^+). The ESR spectra of polycrystalline powders of complexes **1**—**4** consist of a single Lorentzian line with g = 2.032 and a width of 6—10 mT. The temperature dependence of the magnetic susceptibility of complex **1** in the temperature range of 80—300 K is adequately described by the Curie—Weiss law with $\theta \approx 8$ K; the effective magnetic moment per iron atom is 1.85 μB.

Key words: synthesis, sulfur-containing iron nitrosyl complexes, heterocyclic thiols, complexes of the g ~2.03 family, X-ray diffraction analysis, ESR, Mössbauer spectroscopy.

Iron nitrosyl complexes, which serve as NO donors, attract attention of scientists in the fields of biochemistry, biophysics, and medicine in connection with studies of the mechanisms of reactions of NO and its intermediates *in vivo* and the design of new efficient adjuvants for chemotherapy and radiotherapy as well as of a new generation of cardiovascular pharmaceuticals.[1—4]

It is known[3,5—8] that the reactions of nitrogen monoxide with endogenous iron(II) and low-molecular-weight thiols (cysteine, glutathione, penicillamine, *etc.*) in cells afford nitrosyl complexes existing in two forms, *viz.*, the mononuclear $[Fe(NO)_2(SR)_2]^-$ and binuclear $[Fe_2(SR)_2(NO)_4]$ complexes. These forms are in dynamic equilibrium, which depends on the concentration of thiols, the latter being determined by the physiological conditions in an organism.[7,8] The structures of binuclear Fe—S nitrosyl complexes are extensively discussed and there is no consensus of opinion regarding this problem. The reason is that the binuclear form $[Fe_2(SR)_2(NO)_4]$ is extremely unstable both *in vivo* and *in vitro*, which hinders the isolation and investigation of the physicochemical properties of these complexes. The results of X-ray diffraction analysis and NMR spectroscopy[9—12] provided evidence that the $[Fe_2(SR)_2(NO)_4]$ compounds (R = Alkyl, pyridine, or pyrimidinyl) have structures of Roussin's red salt esters (in which the iron atoms are linked through the S—R bridge) analogous to the structures of the active region of nitrosyl [2Fe-2S] nonheme proteins. According to an alternative point of view,[7,8] binuclear iron complexes are dimeric associates of mononuclear iron dinitrosyl complexes, which can readily be determined in solutions from an ESR signal with $g \approx 2.03$. To establish the true structures of such compounds, it is necessary to design new molecular systems based on Fe—S nitrosyl complexes, which are structural and spectral analogs of nitrosyl adducts of active regions of [2Fe-2S] proteins, and study their properties. Bifunctional heterocyclic thiols can be used as ligands for the preparation of new stable iron nitrosyl thiolates. These thiols possess a high coordination potential[13—15] due to the presence of the μ-N—C—S structural fragment (Fig. 1).

In the present study, we synthesized binuclear S-containing iron nitrosyl complexes with heterocyclic ligands, *viz.*, 5-amino-1,2,4-triazol-3-yl, 1,2,4-triazol-3-yl, 1-methyltetrazol-5-yl, and benzothiazol-2-yl, and investigated their properties by X-ray diffraction analysis and ESR, IR, and Mössbauer spectroscopy.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1614—1620, August, 2003.

1066-5285/03/5208-1702 $25.00 © 2003 Plenum Publishing Corporation

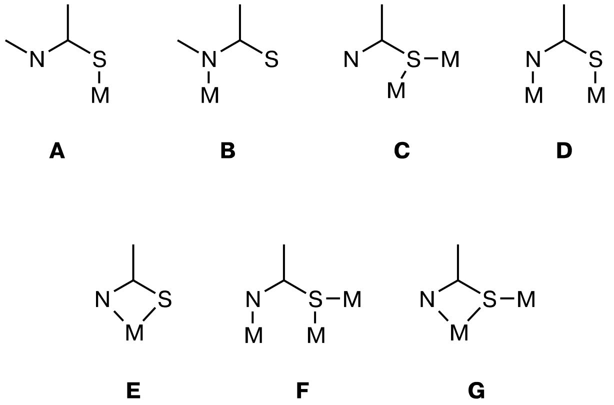


Fig. 1. Modes of coordination of the thioamide group to metals.[15]

Results and Discussion

Iron nitrosyl complexes **1—4** were synthesized by replacing the thiosulfate ligands in the $Na_2[Fe_2(S_2O_3)_2(NO)_4]$ complex by heterocyclic nitrogen-containing ligands

$$Na_2[Fe_2(S_2O_3)_2(NO)_4] + 2\,RSH + 2\,NaOH \longrightarrow$$

$$\longrightarrow [Fe_2(SR)_2(NO)_4] + 2\,Na_2S_2O_3 + 2\,H_2O. \qquad (1)$$

Reaction (1) proceeds through the formation of the mononuclear iron complexes $[Fe(S_2O_3)_2(NO)_2]^{3-}$ [10,11] followed by the replacement of the thiosulfate groups by the thionate groups to form a binuclear structure.

The ligand can be coordinated to the iron atom (see Fig. 1) in a monodentate fashion through either the sulfur atom, η^1-S (**A**), or the nitrogen atom, η^1-N (**B**), as a bridge either through the sulfur atom, μ_2-S (η^2-S) (**C**), or through the sulfur and nitrogen atoms, μ_2-S,N (η^1-S, η^1-N) (**D**), in a chelate mode μ_1-S,N (η^1-S, η^1-N) (**E**), or in a combined mode μ_3-S,N (η^2-S, η^1-N) (**F**), μ_2-S,N (η^2-S, η^1-N) (**G**).[15] The presence of substituents (NH_2, COOH, OH, *etc.*) in heterocyclic thiols additionally extends the coordination possibilities of the ligands.

The Mössbauer spectra of polycrystalline nitrosyl complexes **1—4** have virtually equal isomer shifts, which are almost twice as large (Table 1) as those for complexes with structures of Roussin's red salt esters.[11,12] Such a substantial change in the Mössbauer parameters may indicate that the structures of all the compounds synthesized differ from the structures of all known binuclear complexes.

According to the results of X-ray diffraction analysis, complex **1** has a centrosymmetrical dimeric binuclear structure (Fig. 2). However, the Fe(1) and Fe(2) atoms in complex **1** are linked through the μ-N(3)—C(1)—S(1) and μ-N(3a)—C(1a)—S(1a) structural fragments, unlike the binuclear complex with pyridine-2-thione $[Fe_2(\mu_2\text{-}SC_5H_4N)_2(NO)_4]$ (**5**) and the binuclear complex with pyrimidine-2-thione $[Fe_2(\mu_2\text{-}SC_4H_3N_2)_2(NO)_4]$ (**6**) studied earlier[11,12] in which the iron atoms are linked by the

Table 1. Parameters of the Fe^{57} Mössbauer spectra of binuclear thionate complexes **1—4** at 85 and 296 K and the differences in the vibration frequencies of nonequivalent NO groups $\Delta\nu_{NO}$

Complex	δ_{Fe}*	ΔE_Q**	Γ***	$\Delta\nu_{NO}$ /cm^{-1}
	mm s^{-1}			
	at 85 K/296 K			
$[Fe_2(C_2H_3N_4S)_2(NO)_4]\cdot 2H_2O$ (**1**)	0.304(1) 0.216(1)	0.997(2) 0.943(1)	0.305(2) 0.237(2)	73
$[Fe_2(C_2H_2N_3S)_2(NO)_4]\cdot H_2O$ (**2**)	0.293(1) 0.223(1)	1.181(1) 1.223(1)	0.329(2) 0.238(2)	73
$[Fe_2(C_2H_2N_4S)_2(NO)_4]\cdot H_2O$ (**3**)	0.298(1) 0.223(1)	1.024(1) 1.004(1)	0.260(2) 0.252(2)	75
$[Fe_2(C_7H_4NS_2)_2(NO)_4]\cdot H_2O$ (**4**)	0.291(1) 0.216(1)	1.008(1) 0.994(1)	0.258(2) 0.245(2)	62

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

** ΔE_Q is the quadrupole splitting.

*** Γ is the line width.

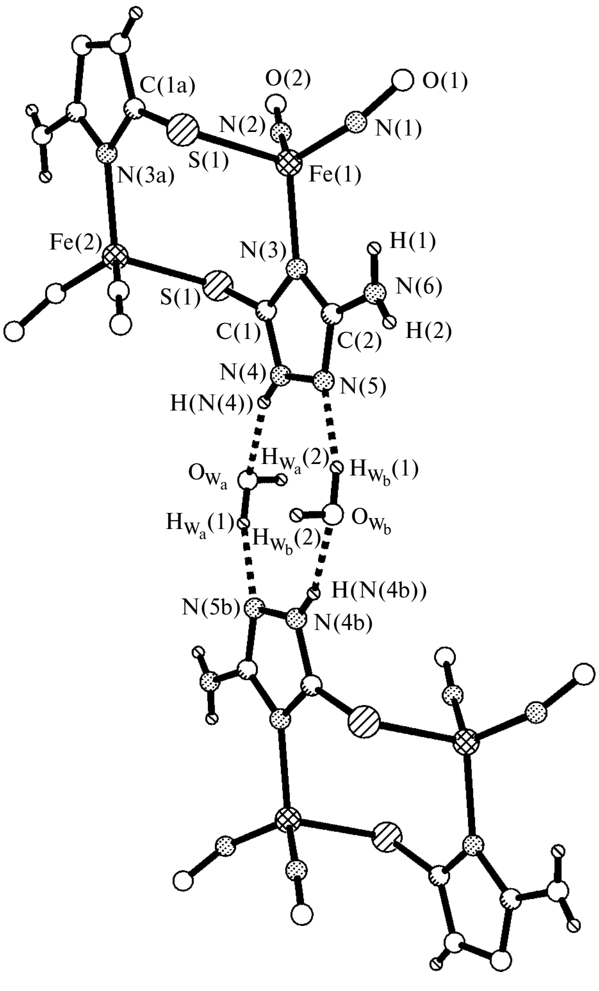
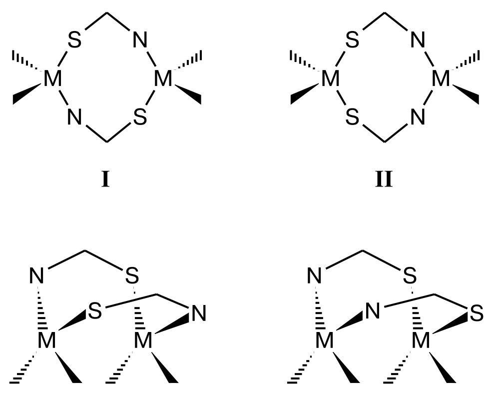


Fig. 2. Fragment of the crystal structure of $[Fe_2(SC_2H_3N_4)_2(NO)_4]\cdot 2H_2O$.



I **II**

III **IV**

Fig. 3. Isomerism of $[M_2(\mu_2\text{-}SR)_2L_4]$ (η^1-S, η^1-N).[13]

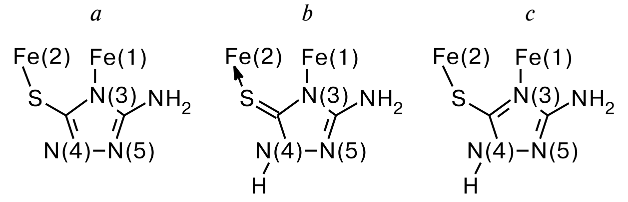
bridging sulfur atoms, whereas the nitrogen atoms of the heterocycles are not involved in coordination. Each iron atom in **1** is coordinated by the nitrogen atom of one ligand and the sulfur atom of another ligand (see Fig. 1, the coordination mode **D**). The iron atoms have a tetrahedral configuration and are separated by a distance of 4.04 Å, in contrast to the binuclear complexes studied earlier in which the Fe...Fe distance is ~2.7 Å.[10—12,16—19]

In complexes in which heterocyclic thiols are coordinated in the mode **D**, the following four isomers can occur (Fig. 3): *trans*-head-to-tail (I), *trans*-head-to-head (II), *cis*-head-to-tail (III), and *cis*-head-to-head (IV).[13] In complex **1**, 5-amino-1,2,4-triazole-3-thione is coordinated in the *trans*-head-to-tail fashion.

Binuclear complexes **1** are linked in dimeric associates through intermolecular hydrogen bonds involving the water molecules W_a and W_b. The H(N(4)) atom of the triazole ring forms an intermolecular hydrogen bond with the oxygen atom of the water molecule W_a (H(N(4))...O_{W_a}, 1.89 Å; N(4)...O_{W_a}, 2.82 Å; N(4)H(N(4))O_{W_a}, 169.1°). The N(5) atom of the triazole ring forms an intermolecular hydrogen bond with the $H_{W_b}(1)$ atom (N(5)...$H_{W_b}(1)$, 2.08 Å; N(5)...O_{W_b}, 2.79 Å; N(5)$H_{W_b}(1)O_{W_b}$, 163.0°). The molecules W_a and W_b are not linked by a hydrogen bond with each other; the O_{W_a}...O_{W_b} distance is 4.47 Å. Conceivably, the $H_{W_a}(2)$ and $H_{W_b}(2)$ atoms are disordered due to rotation of the hydrogen atom about the O_{W_a}—$H(1)_{W_a}$ and O_{W_b}—$H(1)_{W_b}$ bonds.

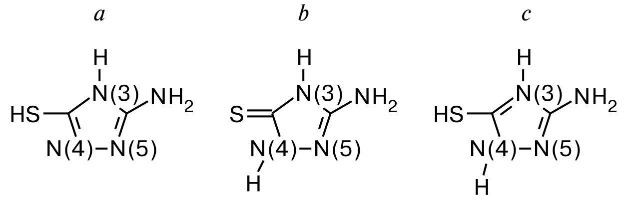
In complex **1**, the Fe—S bond (2.305 (1) Å) is elongated by ~0.04 Å compared to the bridging Fe—S η^2-S-bond in thionate complexes **5** (2.28 Å) and **6** (2.262 Å) studied earlier.[11,12] The C—S distance in complex **1** (1.726(2) Å) is 0.04—0.05 Å shorter than the corresponding distances in complexes **5** and **6** (1.81 (**5**) and 1.790 Å (**6**)). This fact may be evidence for a weakening of the Fe—S bond in complex **1**.[14,20,21] The length of the Fe—N(3) bond between the iron atom and the nitrogen atom of the heterocyclic ligand in complex **1** is 2.020(2) Å. This bond was found for the first time in binuclear sulfur-containing nitrosyl complexes. In the iron complexes, the Fe—N bond is, generally, formed by a donor-acceptor mechanism and its length varies over a broad range depending on the oxidation state of the iron atom and the size of the heterocycle: 1.97 Å in $[Fe(phen)_3]^{3+}$ (phen is 1,10-phenanthroline),[22] 2.042 Å in $[Fe(NO)_2(1\text{-}MeIm)_2]$ (MeIm is methylimidazole),[5] 2.165 Å in $[Fe(pym)_3]^-$ (pym is 2-mercaptopyrimidine),[23] 2.170 Å in $[Fe(bipy)_2(NCS)_2]$ (bipy is 2,2′-bipyridyl),[24] and 2.24 Å $[Fe(py)_4(NCS)_2]$ (py is pyridine).[25]

In complex **1**, the aminotriazole heterocycle can be coordinated to the Fe and S atoms in three different modes (Fig. 4). The distribution of the bond lengths in the heterocycle is most similar to structure **1**′, which corresponds to the starting thiol tautomeric form of the heterocycle (Fig. 5, *a*). However, the presence of the H(N(4)) atom is in contradiction with this coordination mode. In addition, if this coordination mode were in existence by analogy with the complexes studied earlier, dimer **1** would occur as a doubly charged anion rather than as a neutral molecule, as evidenced by the results of X-ray diffraction analysis. Therefore, the coordination mode can be either **1**″ or **1**‴ (see Fig. 4), which correspond to the thione (see Fig. 5, *b*) or thiol (see Fig. 5, *c*) tautomeric forms, respectively. Both these tautomeric forms were observed in the mononuclear $[Fe(SC_2H_3N_3)(SC_2H_2N_3)(NO)_2]\cdot 1/2H_2O$ complex (**7**) studied by us earlier[26] with the difference that the ligand is coordinated in a monodentate fashion through the



1′ **1**″ **1**‴

Fig. 4. Possible coordination modes of 5-amino-1,2,4-triazole-3-thione.



1′ **1**″ **1**‴

Fig. 5. Possible tautomeric forms of 5-amino-1,2,4-triazole-3-thione.

S atom. A comparison of the distribution of the bond lengths in the heterocycles of complexes **1** and **7** counts in favor of coordination mode **1**$''$ (see Fig. 4) corresponding to the thione tautomeric form (see Fig. 5, *b*). In this case, the N(3) atom forms the Fe—N bond after the proton abstraction, and the S atom is involved in the donor-acceptor Fe←S bond. If, by analogy with the iron complexes studied earlier, the NO groups are considered as electroneutral, complex **1** is also electroneutral and the Fe atom has the d^7 electronic configuration, like in mononuclear paramagnetic complex **7**.

Analysis of the Fe—N—O structural fragments in complex **1** compared with those in binuclear complexes **5—7** also demonstrated that these fragments are strongly nonequivalent. The Fe—N(2)—O(2) fragment containing shorter N—O and Fe—N bonds (Table 2; N(2)—O(2), 1.156(3) Å; Fe—N(2), 1.677(2) Å) is more linear, as evidenced by the angle of 170.8(3)°. In the Fe—N(1)—O(1) fragment, the bonds are longer (N(1)—O(1), 1.174(3) Å; Fe—N(1), 1.695(2) Å) and the angle has the smallest value (157.5(2)°) of all the known complexes[11,12,19] due, apparently, to the intermolecular O(1)...S′ Coulomb interaction. The Fe—N—O angles in complex **1** differ by 13.3°, unlike those in the binuclear complexes with (η^2-S) in which this difference is, on the average, 2—4°.[11,12,16] In addition, the N(1)—Fe—N(2) angle in complex **1** (112.4(1)°) is 5—7° smaller than the corresponding angles in the binuclear complexes studied earlier.[11,12,19] It can be assumed that these differences in the structure of the iron nitrosyl fragments in complex **1** are caused by the redistribution of the charges on the NO groups.

Table 2. Selected interatomic distances (*d*) and bond angles (ω) in complex **1**

Distance	*d*/Å	Angle	ω/deg
Fe—N(1)	1.695(2)	O(1)—N(1)—Fe	157.5(2)
Fe—N(2)	1.677(2)	O(2)—N(2)—Fe	170.8(2)
Fe—S	2.305(1)	N(1)—Fe—N(2)	112.4(1)
Fe—N(3)	2.020(2)	N(2)—Fe—N(3)	112.4(1)
N(1)—O(1)	1.174(3)	N(1)—Fe—N(3)	112.2(1)
N(2)—O(2)	1.156(3)	N(2)—Fe—S	103.44(9)
S—C(1) [a]	1.726(2)	N(1)—Fe—S	107.31(9)
N(3)—C(1)	1.359(3)	N(3)—Fe—S	108.58(7)
C(1)—N(4)	1.321(3)	C(1)[a]—S—Fe	101.88(8)
N(4)—N(5)	1.369(3)	C(1)—N(3)—C(2)	104.31(18)
N(5)—C(2)	1.327(3)	C(2)—N(3)—Fe	130.72(16)
N(6)—C(2)	1.348(3)	N(4)—C(1)—N(3)	108.7(2)
N(3)—C(2)	1.360(3)	C(1)—N(3)—Fe	124.96(15)
		N(4)—C(1)—S [a]	124.0(2)
		N(3)—C(1)—S [a]	127.3(2)
		C(1)—N(4)—N(5)	110.5(2)
		C(2)—N(5)—N(4)	103.6(2)
		N(5)—C(2)—N(6)	123.6(2)
		N(5)—C(2)—N(3)	112.8(2)
		N(6)—C(2)—N(3)	123.6(2)

[a] −*x*, −*y* + 1, −*z* + 1.

It is known[27] that the charge on the NO group in metal nitrosyl complexes correlates with the M—N—O angle and the Fe—N distance. The closer is the angle to 180° and the shorter is the Fe—N bond, the higher is the positive charge on NO. An increase in the positive charge of the NO groups is accompanied by an upfield shift of the NO stretching vibrations. The IR spectrum of complex **1** has two absorption bands at 1732 and 1805 cm^{-1} assigned to stretching vibrations of the nitrosyl groups. The difference between the frequencies of two absorption bands is 73 cm^{-1}, whereas this values in the spectra of complexes **5—7** was at most 43 cm^{-1}.[11,12] Most likely, the observed substantial splitting of the bands (73 cm^{-1} for **2**, 75 cm^{-1} for **3**, and 62 cm^{-1} for **4**) can also be associated with the nonequivalence of the NO groups in the Fe—N—O fragments. A comparison of the Fe—N—O and N—Fe—N angles in the dinitrosyl fragments and $\Delta\nu_{NO}$ for complexes **1—4** (see Table 2) with the corresponding values for the compounds studied earlier[11,12,19,28] also confirms the conclusion that the larger the difference in these angles, the larger the difference in $\Delta\nu_{NO}$. Nevertheless, the NO stretching vibrations in the spectra of complexes **1—4** are observed in the range typical of the neutral NO groups. This fact is consistent with the results of the study.[29]

In the Mössbauer spectra of neutral binuclear complexes **1—4** in which the iron atoms are linked through the μ-N—C—S bridges, the isomer shifts (see Table 1) are, on the average, 0.12 mm s^{-1} ($T = 85$ K) higher than the corresponding values in the spectra of neutral thionate complexes in which the iron atoms are coordinated only through the μ_2-S ligand[11,12] and are 0.03 mm s^{-1} higher than the isomer shift for neutral mononuclear complex **7**.[26] This fact implies a decrease in the 4s electron density and an increase in the 3d electron density on the iron atoms in the new complexes, which is manifested in an increase in the Fe—S bond length by 0.03 Å and the involvement of the N atom (instead of the more covalent S atom) in the coordination sphere of the iron atom.

Based on the d^7 configuration of Fe$^+$ and taking into account that the Fe...Fe distance is longer than 4 Å, one would expect that binuclear complexes **1—4** will be paramagnetic. Actually, all the complexes under consideration gave an ESR signal as a Lorentzian line with $g \sim 2.032$ and a width of 6—10 mT (for complex **1**, the line width is 7 mT). The number of unpaired electrons per iron atom, which was estimated based on measurements of the intensity of the ESR signal from a sample of a known weight, is 1.0±0.2.

Formally, the 3d^7 configuration in a tetrahedral coordination has the spin S = 3/2 with three unpaired electrons on the dπ orbitals. In the case under consideration, the total spin of the paramagnetic center is determined by

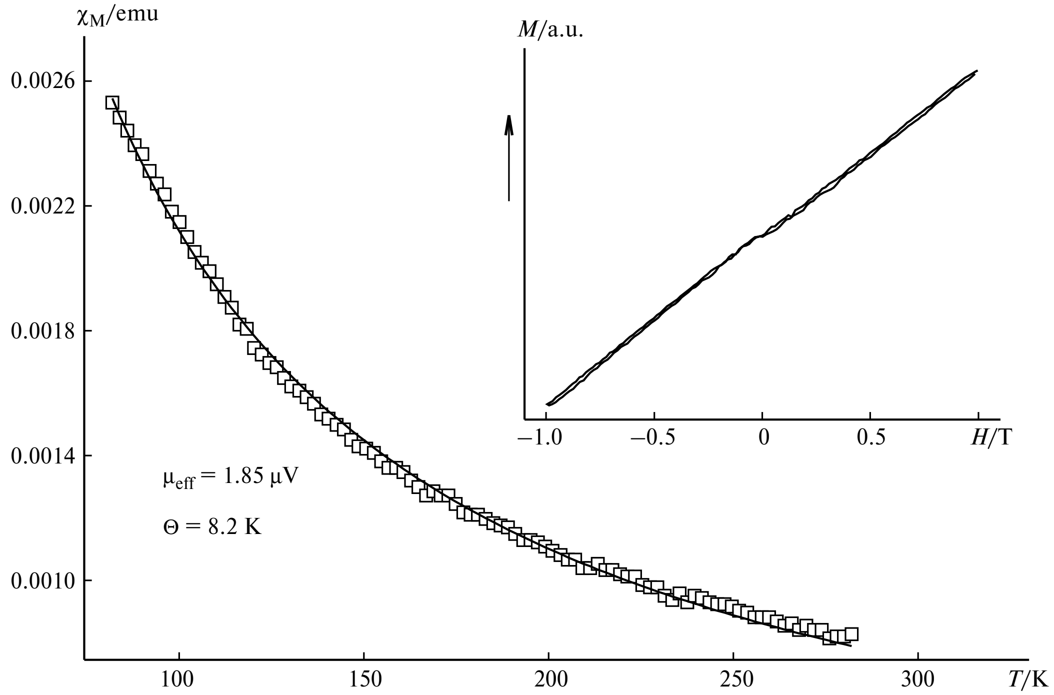


Fig. 6. Plot of the specific magnetic susceptibility of complex **1** *vs.* temperature. The experimental points are indicated by squares. The solid line represents the dependence obtained by fitting according to the equation $\chi_{M'} = C\mu_{eff}^2/(T + \Theta)$, where C and Θ are constants (C is a known constant and Θ is a fitting constant); μ_{eff} is the effective magnetic moment (determined by fitting). The dependence of the magnetization M of the sample under study on the external magnetic field H is shown in an inset.

the Fe(d^7) ions (S = 3/2) in the dimer and two NO groups bound to this ion (S = 1/2). Upon the formation of a covalent bond, each π* electron of the NO group is paired with one of the dπ electrons of Fe giving rise to the total spin of the paramagnetic center S_t = 1/2. The electroneutrality of the NO groups assumed by us implies that the electron pair of the bond is evenly divided between Fe and NO. The shift of the electron pairs to the Fe atom leads to the $Fe^{-}(d^9)$—$2(NO^{+})$ configuration. The shift of electrons to the NO group leads to the $Fe^{3+}(d^5)$—$2(NO^{2-})$ configuration; the total spin S_t is 1/2.

The dependence of the magnetization of complex **1** on the external magnetic field in the range from −1 to +1 T represents a straight line (Fig. 6), which is evidence that the sample contained no ferromagnetic impurities. The temperature dependence of the magnetic susceptibility in the range of 80—273 K is well described by the Curie—Weiss law with $\theta \approx 8$ K; the effective magnetic moment per Fe atom (μ_{eff}) is 1.85 μB. This value of μ_{eff} is close to the purely spin value for one unpaired electron (1.73 μB). The absence of a strong exchange interaction is consistent with a large distance between the iron atoms in complex **1**.

Therefore, the results of our study (X-ray diffraction analysis, Mössbauer spectroscopy, ESR spectroscopy, and magnetic susceptibility measurements) provide evidence for the d^7 configuration of the Fe^{+} ion and electroneutrality of the NO groups in the new neutral paramagnetic binuclear iron complexes. Based on the results of Mössbauer and IR spectroscopy and elemental analysis data, it can be concluded that complexes **2**—**4**, like the $[Fe_2(\mu_2\text{-}SR)_2(NO)_4]$ complex (R is benzimidazolyl) studied by us earlier,[30] are structurally similar to complex **1**.

In the solid state, all the complexes synthesized are more stable upon storage in air at 16—18 °C in the dark and in the absence of atmospheric moisture compared to the thionate complexes in which the iron atoms are coordinated through the η^2-S ligand.[11,12] Complexes **1**—**4** decompose upon storage for 7—8 months, whereas the complex with pyridine-2-thiol decomposes within a few days. It should be noted that Roussin's red salt decomposes under analogous conditions within one day.

It is known[31,32] that most of low-molecular-weight thiols in cells (cysteine, glutathione, penicillamine) contain the amino group whose nitrogen atom, along with the sulfur atom, can be coordinated to the iron atom. This can give rise to binuclear structures of a new type different from Roussin's red salt esters. New neutral paramagnetic binuclear iron nitrosyl complexes **1**—**4** can be used as stable models for studying mechanisms of further transformations of nitrosyl adducts of [2Fe-2S]-proteins *in vivo*.

Experimental

The studies were carried out with the use of $Na_2S_2O_3 \cdot 5H_2O$ (Merck), NaOH (Aldrich), 3-amino-5-mercapto-1,2,4-triazole

(Aldrich), 2-mercaptobenzothiazole (Aldrich), 3-mercapto-1,2,4-triazole (Merck-Schuchardt), and 5-mercapto-1-methyl-1*H*-tetrazole (Aldrich). The complex $Na_2[Fe_2(\mu_2\text{-}S_2O_3)_2(NO)_4]\cdot 2H_2O$ was synthesized according to a procedure described earlier.[33] All operations associated with the synthesis and isolation of the complexes were carried out under nitrogen. The solutions were prepared using distilled water from which oxygen was removed by evacuation at 0—2 °C for several hours.

The IR spectra were recorded on a Spectrum BX-II Fourier spectrometer in KBr pellets (1 mg of the compound under study and 300 mg of KBr).

Synthesis of complexes 1—4. An alkaline solution (10 mL) of thiol (10 mmol) was added to an aqueous solution (10 mL) of $Na_2[Fe_2(\mu_2\text{-}S_2O_3)_2(NO)_4]\cdot 2H_2O$ (2 mmol) and $Na_2S_2O_3\cdot 5H_2O$ (4 mmol). The filtrate was kept at 6—8 °C for 6 days. Complexes **1** and **2** were recrystallized from anhydrous methanol. Complex **3** was recrystallized from dichloromethane. Complex **4** was recrystallized from anhydrous acetone and dried *in vacuo* over $CaCl_2$.

Bis(5-amino-1,2,4-triazole-3-thiolate)bis(tetranitrosyl)iron dihydrate, $[Fe_2(C_2H_3N_4S)_2(NO)_4]\cdot 2H_2O$ (1). Black single crystals of complex **1**. The yield was 0.478 g (52%). Found (%): Fe, 22.40; S, 12.73; N, 33.70; C, 9.46; H, 1.54. $C_4H_8Fe_2N_{12}O_6S_2$. Calculated (%): Fe, 22.58; S, 12.90; N, 33.87; C, 9.67; H, 1.61. IR (KBr), ν/cm^{-1}: 3518, 3468, 3353, 3168, 2995, 2928, 1805, 1732, 1645, 1630, 1560, 1529, 1501, 1446, 1384, 1321, 1293, 1272, 1234, 1152, 1114, 1068, 1036, 8864, 738, 669, 615, 542, 498; 1732, 1805 (NO).

Bis(1,2,4-triazole-3-thiolate)bis(tetranitrosyl)iron monohydrate, $[Fe_2(C_2H_2N_3S)_2(NO)_4]\cdot H_2O$ (2). Black polycrystalline powder. The yield was 0.732 g (85%). Found (%): Fe, 24.75; S, 14.07; N, 30.95; C, 10.43; H, 1.27. $C_4H_6Fe_2N_{10}O_5S_2$. Calculated (%): Fe, 24.89; S, 14.22; N, 31.11; C, 10.66; H, 1.33. IR (KBr), ν/cm^{-1}: 3454, 2945, 1805, 1796, 1732, 1530, 1460, 1384, 1352, 1327, 1270, 1177, 1084, 1048, 1003, 974, 890, 870, 816, 712, 669, 650, 533; 1732, 1796, 1805 (NO).

Bis(1-methyltetrazole-5-thiolate)bis(tetranitrosyl)iron monohydrate, $[Fe_2(C_2H_3N_4S)_2(NO)_4]\cdot H_2O$ (3). Black polycrystalline powder. The yield was 0.620 g (70%). Found (%): Fe, 23.18; S, 13.18; N, 34.68; C, 9.78; H 1.71. $C_4H_8Fe_2N_{12}O_5S_2$. Calculated (%): Fe, 23.33; S, 13.33; N, 35.00; C, 10.00; H, 1.67. IR (KBr), ν/cm^{-1}: 1794, 1732, 1468, 1454, 1429, 1384, 1350, 1313, 1271, 1240, 1130, 1090, 1035, 1005, 870, 754, 723, 704, 669, 610, 532; 1732, 1794 (NO).

Bis(benzothiazole-2-thiolate)bis(tetranitrosyl)iron monohydrate, $[Fe_2(C_7H_4NS_2)_2(NO)_4]\cdot H_2O$ (4). Dark-red polycrystalline powder. The yield was 0.950 g (88%). Found (%): Fe, 19.14; S, 21.63; N, 14.38; C, 28.69; H, 1.67. $C_{14}H_{10}Fe_2N_6O_5S_4$. Calculated (%): Fe, 19.24; S, 21.99; N, 14.43; C, 28.86; H, 1.71. IR (KBr), ν/cm^{-1}: 3454, 1790, 1729, 1449, 1402, 1385, 1312, 1272, 1239, 1090, 1034, 1020, 1004, 933, 870, 752, 723, 669, 609, 535, 507; 1729, 1790 (NO).

Elemental analysis was carried out in the Analytical Center of the Institute of Problems of Chemical Physics of the Russian Academy of Sciences.

X-ray diffraction analysis of complex 1. X-ray diffraction data were collected on a KM-4 single-crystal diffractometer (KUMA DIFFRACTION, Poland) at 200 K from a black parallelepiped-shaped single crystal of dimensions ~0.2×0.3×0.5 mm. Compound **1** crystallized in the triclinic system: a = 8.006(2), b = 7.809(2), c = 8.471(3) Å, α = 64.42 (3), β = 71.46(3), γ = 67.01(3)°, V = 432.6(2) Å^3, space group $P\bar{1}$, Z = 1, ρ_{calc} = 1.912 g cm^{-3}. The unit cell parameters were determined and refined based on 25 reflections in the θ angle range of 5—10°. A total of 3540 reflections (2156 independent reflections with $I > 2\sigma(I)$) were measured in the angle range $0 < \theta < 35°$ using the $\omega/2\theta$ scanning technique and MoKα radiation (graphite monochromator).

The structure was solved by direct methods and refined using the SHELXL-97 program package.[34] The nonhydrogen atoms of the structure were refined anisotropically. The positions of all hydrogen atoms in the structure were revealed from difference Fourier syntheses and refined isotropically to R_1 = 0.0394, $_wR_2$ = 0.1023, GOOF = 0.837.

The atomic coordinates and isotropic thermal parameters were deposited with the Cambridge Structural Database. The selected interatomic distances and bond angles are given in Table 2.

Mössbauer spectra were recorded on a WissEl instrument in a constant acceleration mode using Co^{57} in a Rh matrix as the source. The spectra were measured at low temperatures using a CF-506 temperature-controlled continuous-flow helium cryostat (Oxford Instruments). The spectra were processed by the least-squares method assuming the Lorentzian form of individual spectral components.

The ESR spectra were recorded (3-cm range) on a Radiopan SE/X 2544 spectrometer under conditions excluding distortions of the spectra. The amount of spins in the sample was determined by comparing the intensities of the ESR spectra of the sample and a powder of $CuSO_4\cdot 5H_2O$.

Magnetic measurements were carried out using a EG&G PARC M-4500 vibration magnetometer in the temperature range of 80—300 K and $-1\ \text{T} \le H \le 1\ \text{T}$.

We thank Yu. G. Morozov and V. A. Kogan (Rostov State University) for studying the magnetic properties of the complexes.

This study was financially supported by the Russian Foundation for Basic Research (Project No. 02-03-33344) and INTAS (Grant 99-00209). The experiments were carried out using facilities of the Joint Use Center of the Russian Foundation for Basic Research (Project No. 00-03-40141).

References

1. T. Ueno, Y. Suzuki, S. Fujii, and T. Yoshimura, *Biochem. Pharmacol.*, 2002, **63**, 485.
2. S. Costanzo, S. Menage, R. Purrello, R. P. Bonomo, and M. Fontecave, *Inorg. Chim. Acta.*, 2001, **318**, 1.
3. A. R. Butler and I. L. Megson, *Chem. Rev.*, 2002, **102**, 1155.
4. P. G. Wang, M. Xian, X. P. Tang, X. J. Wu, Z. Wen, T. W. Cai, and A. J. Janczuk, *Chem. Rev.*, 2002, **102**, 1091.
5. N. Reginato, C. T. C. McCrory, D. Pervitsky, and L. J. Li, *J. Am. Chem. Soc.*, 1999, **121**, 43, 10217.
6. R. Basosi, E. Gaggelli, E. Tiezzi, and G. Valensin, *J. Chem. Soc., Perkin Trans. 2*, 1975, 423.
7. A. F. Vanin, *Biokhimiya*, 1998, **63**, 782 [*Biochemistry (Moscow)*, 1998, **63** (Engl. Transl.)].
8. A. F. Vanin, R. A. Stukan, and E. B. Manukhina, *Biophysics*, 1997, **42**, 7.

9. A. R. Butler, C. Glidewell, and M. H. Li, *Adv. Inorg. Chem.*, 1988, **32**. 335.
10. C. Glidewell, R. J. Lambert, M. E. Harman, and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1990, 2685.
11. O. A. Rakova, N. A. Sanina, G. V. Shilov, Yu. M. Shul´ga, V. M. Martynenko, N. S. Ovanesyan, and S. M. Aldoshin, *Koord. Khim.,* 2002, **28**, 364 [*Russ. J. Coord. Chem.*, 2002, **28** (Engl. Transl.)].
12. O. A. Rakova, N. A. Sanina, S. M. Aldoshin, and Y. M. Shulga, *J. Inorg. Biochem.*, 2001, **8**, 309.
13. E. S. Raper, *Coord. Chem. Rev.*, 1997, 165, 475.
14. E. S. Raper, *Coord. Chem. Rev.*, 1985, **61**, 115.
15. P. D. Akrivos, *Coord. Chem. Rev.*, 2001, **213**, 181.
16. C. Glidewell, M. E. Harman, M. B. Hursthouse, I. L. Johnson, and M. Motevalli, *J. Chem. Res. (S)*, 1988, 212.
17. J. T. Thomas, J. H. Robertson, and E. G. Cox, *Acta Crystallogr.*, 1958, **11**, 599.
18. C. Glidewell, D. Baty, R. G. Willis, M. G. Burdon, A. R. Butler, I. L. Johnson, and R. Massey, *Inorg. Chim. Acta*, 1987, **138**, 15.
19. O. A. Rakova, N. A. Sanina, G. V. Shilov, V. V. Strelets, I. B. Borzova, A. V. Kulikov, and S. M. Aldoshin, *Koord. Khim.,* 2001, **27**, 698 [*Russ. J. Coord. Chem.*, 2002, **27** (Engl. Transl.)].
20. A. K. Sen, R. N. Singh, R. N. Handa, S. N. Dubey, and P. J. Squattrito, *J. Molecular. Struct.*, 1998, **470**, 61.
21. J. Jolley, W. I. Cross, R. G. Pritchard, C. A. McAuliffe, and K. B. Nolan**,** *Inorg. Chim. Acta*, 2001, **315**, 36.
22. D. H. Templeton, A. Zalkin, and T. Ueki, *Acta Crystallogr.*, *Sect. A.*, 1966, **21**, 154.
23. I. A. Latham, G. J. Leigh, and C. J. Pickett, *J. Chem. Soc. Dalton Trans.*, 1986, 1986.
24. E. Konig and K. J. Watson, *Chem. Phys. Lett.*, 1970, **6**, 457.
25. M. Gerloch, R. F. McMeeking, and A. M. White, *J. Chem. Soc. Dalton Trans.*, 1975, 2452.
26. S. M. Aldoshin and N. A. Sanina, *Tez. dokl., III Natsional'naya kristallokhimicheskaya konf.* [*Abstrs. of Papers, III All-Russian Crystal-Chemcial Conf.*] *(Chernogolovka, May 19—23, 2003)*, Chernogolovka, 2003, 36 (in Russian).
27. M. Fontecave and J. L. Pierre, *Bull. Soc. Chim. Fr.*, 1994, **131**, 620.
28. N. A. Sanina, O. A. Rakova, S. M. Aldoshin, I. I. Chuev, E. G. Atovmyan, and N. S. Ovanesyan, *Koord. Khim.,* 2001, **27**, 198 [*Russ. J. Coord. Chem.*, 2002, **27** (Engl. Transl.)].
29. J. Lewis, R. J. Irving, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1958, **7**, 32.
30. O. A. Rakova, N. A. Sanina, Yu. M. Shul´ga, V. M. Martynenko, N. S. Ovanesyan, and S. M. Aldoshin, *Dokl. Akad. Nauk,* 2002, **383**, 350 [*Dokl. Chem.*, 2002 (Engl. Transl.)].
31. L. D. Pettit and M. Bezer, *Coord. Chem. Rev.*, 1985, **61**, 97.
32. K. A. Mitchell and C. M. Jensen, *Inorg. Chim. Acta*, 1997, **265**, 103.
33. V. A. Klimova, *Osnovnye mikrometody analiza organicheskikh soedinenii* [*Main Micromethods for Analysis of Organic Compounds*], Khimiya, Moscow, 1975, 21 (in Russian).
34. G. M. Sheldrick, *SHELX-97, Release 97-2, Program for Crystal Structure Refinement,* University of Göttingen, Göttingen (Germany), 1997.

Received August 1, 2002;
in revised form April 15, 2003