Influence of the cation on the properties of binuclear iron nitrosyl complexes. Synthesis and crystal structure of $[Pr^n_4N]_2[Fe_2S_2(NO)_4]$

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The binuclear nitrosyl complexes $Q_2[Fe_2S_2(NO)_4]$, where Q = Me, Et, Pr^n, and Bu^n, were synthesized. The crystals of $[Pr^n_4N]_2Fe_2S_2(NO)_4$ were studied by X-ray analysis. The influence of the cation size on the electronic structure and symmetry of its local environment in the synthesized complexes was examined. The decrease in the isomeric shifts in the ^{57}Fe Mössbauer spectra is related to the increase in the length of the alkyl substituent chain of the quaternary tetraammonium cation and is consistent with changing the structural parameters: a decrease in the bond angle of the Fe—NO bond and stretching vibrations of the NO groups due to changes in intermolecular contacts.

Key words: synthesis, binuclear iron-sulfur nitrosyl complexes, X-ray analysis, Mössbauer spectroscopy.

The role of iron-sulfur proteins in respiration processes, photosynthesis, nitrogen fixation, synthesis of hormones, and metabolism of sulfur and carbon is well known.[1—3] These proteins are also representatives of a whole class of transport proteins, electron carriers. For example, ferredoxin in green plants (chloroplasts) participates in the electron transfer during photosynthesis.

The binuclear iron cluster with the sulfur bridges [2Fe—2S] is believed to be the active center of ferredoxins,[4] in which it is coordinated with the cysteine ligands, and that of some Fe—S proteins where it is bound to a nitrogen or oxygen atom.[5] The study of the role of nitrogen monoxide and its derivatives in various physiological processes[6] have shown that precisely the nitrosyl Fe—S proteins are relatively long-lived reservoirs of bioactive NO. The main difficulty in studying the mechanisms of biochemical reactions of NO *in vivo* is a deficiency of synthetic complexes that could serve as adequate models of the active moieties of the nitrosyl complexes of Fe—S proteins. The mechanisms of further transformations of these intermediates have been studied only in few works,[7,8] which is related to the instability of the real inclusion NO complexes. The crystal structure of the model binuclear Fe—S nitrosyls $[Me_4N]_2[Fe_2S_2(NO)_4]$ and $[Et_4N]_2[Fe_2S_2(NO)_4]$ has been studied first in Refs. 9 and 10. We have shown[11] for the $Cs_2[Fe_2S_2(NO)_4] \cdot 2H_2O$ single crystals that the cation substantially affects the dianion structure.

In this work, we studied the regularities of changing the structural parameters of the binuclear dianion on the cation geometry in the complexes $[Q_4N]_2Fe_2S_2(NO)_4$, where Q = Me, Et, Pr^n, and Bu^n, on the basis of the X-ray diffraction data.

Results and Discussion

The iron—sulfur nitrosyl complexes $[Q_4N]_2Fe_2S_2(NO)_4$ with Q = Me (**1**), Et (**2**), Pr^n (**3**), and Bu^n (**4**) were synthesized by the exchange reactions of the $Na_2Fe_2S_2(NO)_4$ complex and tetraalkylammonium bromides in an aqueous solution. Complexes **1—3** are stable in storage for one year in an inert atmosphere at −8 °C. Unlike compounds **1—3**, complex **4** is unstable. It decomposes in storage for one month under similar conditions, and in air it decomposes within 1—3 h.

Comparison of the crystallographic parameters of salts **1—4** with the same anion $[Fe_2S_2(NO)_4]^{2-}$ showed that crystals of complexes **2** and **3** belong to the same structural class ($P2_1/n$, $Z = 2$) of the monoclinic system. The density in the series of complexes with the organic cation regularly decreases from 1.509 g cm^{-3} for the salt with the Me$^+$ cation to 1.246 g cm^{-3} for the salt with the Pr^{n+} cation. The general view of complex **3** is presented in Fig. 1. In the $[Fe_2S_2(NO)_4]^{2-}$ anion, both S atoms are bridges that bind the Fe atoms to form a centrosymmetric dimer characterized in all three complexes by a similar structure with a higher local symmetry D_{2h}. The monoclinic cell of structure **1** contains two independent anions. A similar structure

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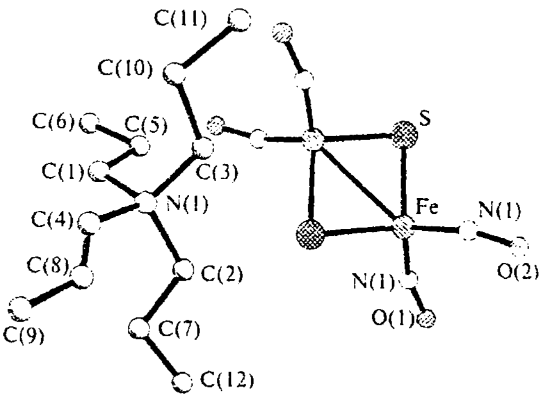

Fig. 1. General view of the cation and anion of the $[Pr^n_4N]_2[Fe_2S_2(NO)_4]$ complex.

has been established for the same anion in the compound $Cs_2[Fe_2S_2(NO)_4] \cdot 2H_2O$ (**5**).[11] Each Fe atom is tetrahedrally coordinated with two S atoms and two NO groups, the angles in the tetrahedron are equal to 105.2—111.5°, the centrosymmetrically arranged Fe atom lies in the plane of the FeSFe*S tetragon, and the Fe—Fe* bond crosses the middle of the S—S* edge. In this isostructural series, we can follow the influence of the dimensional factor of the cation. In each crystallographically independent pair of the Fe—N and Fe—S distances, in all anions **1**—**3** and in a similar anion of the cesium salt,[11] the distances are equal within experimental accuracy, and the local symmetry of the anion is higher — D_{2h}. In anion **3**, the Fe—Fe distance equal to 2.704(2) Å is comparable to the similar distance in the structure described[11] and by 0.01 Å shorter than the Fe—Fe distances in structures **1** and **2**. The single-type interatomic distances and angles in anion **3** are equal within the accuracy and differ from similar distances and angles in **1** and **2** by at most 0.01 Å (Table 1). The difference between the analogous distance in the dimeric anions $[Fe_2S_2(NO)_4]^{2-}$ of structures **1** and **2** also amounts to 0.01 Å. Also note the high values of some Fe—N—O angles in **1** and **2**: 168—166° as compared to 163—164° in complex **3**.

Table 1. Main interatomic distances (*d*) and bond angles (ω) in structure **3**

Bond	*d*/Å
Fe—N(1)	1.650(6)
Fe—N(2)	1.655(7)
Fe—S	2.224(2)
Fe—S	2.226(2)
Fe—Fe	2.704(2)
O(1)—N(1)	1.176(7)
O(2)—N(2)	1.179(8)
N(3)—C(3)	1.501(10)
N(3)—C(4)	1.51(1)
N(3)—C(1)	1.514(9)
N(3)—C(2)	1.52(1)
C(1)—C(5)	1.49(1)
C(2)—C(7)	1.53(2)
C(2)—C(71)	1.42(2)
C(3)—C(10)	1.48(2)
C(4)—C(8)	1.39(2)
C(5)—C(6)	1.50(1)
C(8)—C(9)	1.65(3)
C(10)—C(11)	1.52(2)
C(71)—C(12)	1.54(3)
C(7)—C(121)	1.58(3)
Angle	**ω/deg**
N(1)—Fe—N(2)	111.5(3)
N(2)—Fe—S	111.0(2)
N(2)—Fe—S	109.0(2)
N(1)—Fe—Fe(1)*	124.3(2)

Angle	ω/deg
S(1)—Fe—Fe(1)	52.62(6)
Fe(1)—S—Fe	74.82(7)
O(2)—N(2)—Fe	163.2(6)
C(3)—N(3)—C(1)	110.8(6)
C(3)—N(3)—C(2)	109.2(6)
C(1)—N(3)—C(2)	109.7(6)
C(7)—C(2)—N(3)	117(1)
N(3)—C(2)—C(71)	118(1)
C(8)—C(4)—N(3)	124(1)
C(12)—C(7)—C(2)	110(2)
C(4)—C(8)—C(9)	105(2)
N(1)—Fe—S	110.7(2)
N(1)—Fe—S	109.4(2)
S(1)—Fe—S	105.2(1)
N(2)—Fe—Fe(1)	124.2(2)
S—Fe—Fe(1)	52.56(6)
O(1)—N(1)—Fe	163.5(6)
C(3)—N(3)—C(4)	114.5(7)
C(4)—N(3)—C(1)	104.3(6)
C(4)—N(3)—C(2)	108.2(6)
C(5)—C(1)—N(3)	116.3(6)
C(7)—C(2)—C(71)	108(1)
C(10)—C(3)—N(3)	116.1(9)
C(1)—C(5)—C(6)	109.6(9)
C(121)—C(71)—C(2)	110(2)
C(3)—C(10)—C(11)	109(1)

* Fe(1) is the atom related to the initial inversion center.

Table 2. Parameters of ^{57}Fe Mössbauer spectra of the binuclear iron—sulfur nitrosyl complexes at 78 K

Compound	δ [a]	ΔE_Q [b]	Γ [c]
	mm s^{-1}		
$(Me_4N)_2[Fe_2(\mu_2\text{-}S)_2(NO)_4]$	0.092(1)	0.303(2)	0.29
$(Et_4N)_2[Fe_2(\mu_2\text{-}S)_2(NO)_4]$	0.080(1)	0.245(2)	0.30
$(Pr^n{}_4N)_2[Fe_2(\mu_2\text{-}S)_2(NO)_4]$	0.076(1)	0.252(2)	0.29
$(Bu^n{}_4N)_2[Fe_2(\mu_2\text{-}S)_2(NO)_4]$	0.065(1)	0.267(2)	0.28

Note. Coordination of iron is $\{S_2(NO)_2\}$.

[a] δ_{Fe} is the isomeric shift.

[b] ΔE_Q is the quadrupole splitting.

[c] Γ is the linewidth.

The Mössbauer spectra of complexes **1**—**4** are single doublets, which indicates that the Fe atoms in the anions of these complexes are structurally equivalent, *i.e.*, the nearest coordination sphere of the Fe atoms consists of identical atoms. It is seen from the data in Table 2 that the isomeric shift (δ) increases substantially with an increase in the cation size, indicating an increase in the s-electron density on the ^{57}Fe nuclei. A decrease in the Fe—N—O bond angle should favor the weakening of the back donation dπ(Fe)→π*(NO) and, correspondingly, a decrease in the isomeric shift and the absorption frequency of NO (see Table 2), which was observed in the study of these complexes by IR and Mössbauer spectroscopy. The value of quadrupole splitting (ΔE_Q) changes irregularly, but reflects, as a whole, a tendency to a more symmetrical overall distribution of charges in the valence shell of iron and surrounding atoms with an increase in the cation size.

Examination of the interatomic distances in structure **3** shows that alkyl substituents in the ammonium cation can be divided into two nonequivalent pairs by the type of coordination with the anion. The first pair includes the secondary carbon atoms C(1) and C(4) that have close contacts with the NO groups with the distances O(1)...C(1) 3.44 Å, N(1)...C(1) 3.43 Å, O(2)...C(4) 3.80 Å, and N(2)...C(4) 3.61 Å. The second pair of alkyl substituents is characterized by the absence of contacts with the NO groups and higher thermal vibrations, which correlates with the mobility of the terminal groups and disordering of one of the propyl groups (see Fig. 1). The alkylammonium cations are localized in the channel cavities, which are staggered with the channels filled with the anions. Disordering of one of four propyl groups in structure **3** correlates with the enlargement of the alkylammonium cation in the homological series Me_4N, Et_4N, Pr_4N, $Bu^n{}_4N$. It can be assumed, by analogy to salt **3**, that disordering is also observed in complex **4** containing the larger cation $[Bu^n{}_4N]^+$ due to an increase in the degree of incommensurability of the cationic and anionic fragments and results in the instability of structure **4** under standard conditions of investigation.

Thus, the nature of the cation in the homological series Me_4N, Et_4N, Pr_4N, $Bu^n{}_4N$ affects the properties of the binuclear nitrosyl complexes with the dianion $[Fe_2S_2(NO)_4]^{2-}$: the stability of the compounds in the solid state substantially decreases with an increase in the cation size and the rate of solid phase spontaneous transformation of the complexes into the thermodynamically more stable tetranuclear clusters with the $[Fe_4S_3(NO)_7]^-$ anion, as we have shown previously.[11]

The coordinates of atoms, bond lengths, and bond angles of the complex $[Pr^n_4N]_2Fe_2S_2(NO)_4$ were deposited in the Cambridge Structural Data Bank.

Experimental

Synthesis. The freshly prepared salt $NH_4[Fe_4S_3(NO)_7] \cdot H_2O$ synthesized previously[11] was used as the initial compound for the preparation of a series of binuclear complexes with the $[Fe_2S_2(NO)_4]^{2-}$ anion. A weighed sample of this salt was treated with the calculated amount of a 22% solution of NaOH (analytical purity grade) and heated on a water bath for 2.5 h at 85 °C. Then $Fe(OH)_3$ that formed was filtered off, and an aqueous solution of the corresponding cation was added to the filtrate, which is a solution of the binuclear complex $Na_2Fe_2S_2(NO)_4$. Tetraalkyl ammonium bromides, Me_4NBr, Et_4NBr, Pr_4NBr, and $Bu^n{}_4NBr$ (Fluka), were used as cations. The mixture was stored in a vacuum desiccator above calcined $CaCl_2$ for one day. The single crystals that formed were separated from the mother liquor by filtration, washed with diethyl ether (5—30 mL), and dried for 6 h $CaCl_2$ *in vacuo*. The yields of the products were 70—85%.

IR spectra for all samples were recorded on a Perkin FTIR 1600 spectrometer in KBr pellets in air at ~20 °C.

Tetramethyl- and tetraethylammonium bis(μ-thio)-bis(dinitrosylferrates) ($[Me_4N]_2[Fe_2S_2(NO)_4]$ (1) and $[Et_4N]_2[Fe_2S_2(NO)_4]$ (2)) were synthesized by the known procedures.[9,10]

Tetra(*n*-propyl)ammonium bis(μ-thio)-bis(dinitrosylferrate), $[Pr^n_4N]_2[Fe_2S_2(NO)_4]$ (3). Lustrous black-red single crystals of **3** were formed when a solution of Pr_4NBr (0.2266 g) in water (5 mL) was added to the filtrate obtained by heating of $NH_4[Fe_4S_3(NO)_7] \cdot H_2O$ (0.4058 g) in alkali (2.43 mL) and diluted with 10 mL of water. ν(NO)/cm^{-1}: 1720, 1653, 1632. Found (%): C, 42.7; H, 8.2; Fe, 16.3; N, 12.9; S, 10.3. $C_{24}H_{56}Fe_2N_6O_4S_2$. Calculated (%): C, 43.1; H, 8.3; Fe, 16.7; N, 12.2; S, 9.6.

Table 3. Crystallographic data for complex **3**

Parameter	$[NPr_4]_2[Fe_2S_2(NO)_4]$
M	452.39
System	Monoclinic
Space group	$P2_1/n$
a/Å	10.455(2)
b/Å	13.647(1)
c/Å	12.504(3)
β/deg	93.02(3)
V/Å^3	1781.6(7)
Z	2
D/g cm^{-3}	1.246

Tetra(*n*-butyl)ammonium bis(μ-thio)-bis(dinitrosylferrate), $[Bu^n_4N]_2[Fe_2S_2(NO)_4]$ (4). The finely crystalline powder of **4** was synthesized by heating of $NH_4[Fe_4S_3(NO)_7] \cdot H_2O$ (0.5358 g) in alkali (3.8 mL) followed by the treatment of the filtrate diluted with 10 mL of water with a solution of Bu_4NBr (0.6101 g) in water (5 mL). The precipitate (lustrous thin fine red needles) was separated from the mother liquor, washed, and dried for 6 h. All procedures were carried out in an inert atmosphere. The complex is very unstable and requires storage in an inert atmosphere. The lability of the structural fragments in complex **4**, which is considered below and related to the incommensurability of the anionic and cationic fragments, did not allow us to prepare single crystals appropriate for XDA. ν(NO)/cm^{-1}: 1657, 1637, 1617. Found (%): C, 49.4; H, 9.3; Fe, 14.5; N, 10.7; S, 9.5. $C_{32}H_{72}Fe_2N_6O_4S_2$. Calculated (%): C, 49.2; H, 9.2; Fe, 14.3; N, 10.7; S, 8.2.

X-ray diffraction analysis. Parameters of the monoclinic cell (Table 3) and a set of experimental data for decoding of structure **3** were obtained from the single crystal with a size of 0.20×0.10×0.20 mm^3 on a KM-4 automated four-circle diffractometer (Kuma Diffraction Co.) using MoKα radiation. The experimental set contained 1125 $I > 2\sigma(I)$. The recording method used ω/2θ scan mode in the interval of angles 2.21° < θ < 30.06°. The structure of compound **3** was solved by the direct method by the SHELX-86 complex of programs[12] and refined by the full-matrix least-squares method in the anisotropic approximation (SHELXL-93).[13] In one of four propyl substituents of the ammonium cation, the terminal CH_2Me fragment is disordered by two positions with a population of 0.5 of each position. Hydrogen atoms, except those in the disordered fragments, were revealed objectively from the difference Fourier synthesis, and only positional parameters were refined for them. The final value of the *R* factor was equal to 0.036 (ω*R* = 0.089, GooF = 0.92).

Mössbauer absorption spectra were recorded on a WissEl standard setup (Germany) working in the regime of permanent acceleration. ^{57}Co in the Rh matrix at ~20 °C was used as the ion source. Low-temperature measurements of samples were carried out on a CF-506 flow-type temperature-controlled helium cryostat (Oxford Instruments). Mössbauer spectra were processed by the least-squares method in assuming a Lorentzian shape for the individual spectral components.

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