

Dinitrosyl–iron complexes with thiol-containing ligands: Spatial and electronic structures

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Abstract

Parameters of the EPR signals of monomeric dinitrosyl–iron complexes with 1*H*-1,2,4-triazole-3-thiol (DNIC–MT), obtained by treating MT + ferrous iron in DMSO solution with gaseous NO, have been compared with those of the crystalline monomeric DNIC–MT with tetrahedral structure. Dissolved DNIC–MT were characterized by the isotropic EPR signal centered at $g = 2.03$ with half-width of 0.7 mT and quintet hyperfine structure when recorded at ambient temperature or the anisotropic EPR signal with $g_{\perp} = 2.045$, $g_{\parallel} = 2.014$ from frozen solution at 77 K. DNIC–MT in crystalline state showed the structure-less symmetrical singlet EPR signal centered at $g = 2.03$ and half-width of 1.7 mT at both room and liquid nitrogen temperature. The Lorentz shape of this signal indicates the strong exchange interaction between these complexes in the DNIC–MT crystal. Being dissolved in DMSO the crystalline sample of DNIC–MT demonstrated the EPR signal typical for DNIC–MT, obtained by treating MT + ferrous iron in DMSO solution with gaseous NO. Low spin ($S = 1/2$) d^9 electron configuration of DNIC–MT with tetrahedral structure (formula $\{(\text{MT-S})_2\text{Fe}^{-1}(\text{NO}^+)_2\}^+$) was suggested to be responsible for the signal of DNIC–MT in crystalline state. Dissolving of the crystals of DNIC–MT may result in the change of their spatial and electronic structure, namely, tetrahedral structure of the complexes characterized by low spin d^9 electronic configuration transforms into a plane-square structure with d^7 electronic configuration and low spin $S = 1/2$ state (formula $\{(\text{MT-S})_2\text{Fe}^+(\text{NO})_2\}^+$). The latter was suggested to be characteristic of other DNICs with various thiol-containing ligands in the solutions. The proposed mechanism of these DNICs formation from ferrous iron, thiol and NO shows that the process could be accompanied by the ionization of NO molecules to NO^+ and NO^- ions in the complexes. Detailed analysis of the shape of the EPR signals of these complexes provided additional information about the exchange interaction typical for DNIC–MT in crystals.

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Dinitrosyl–iron complexes (DNIC)¹ with thiol-containing ligands are endogenous nitroso compounds, which provide, together with *S*-nitrosothiols, the stabilization,

storage and transport of NO molecules in human and animal organisms [1–4]. DNICs were detected almost 40 years ago due to a characteristic EPR signal at $g_{\text{av}} = 2.03$ (2.03 signal), which was first observed in yeast cells [5,6] and then in animal tissues [7,8]. Work [9], in which formation of water soluble paramagnetic DNICs with various anionic ligands (both of thiol and non-thiol nature) had been shown, was determining for the identification of these complexes. As follows from the hyperfine structure (HFS) typical for these signals, which is due to the interaction of the

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¹ Abbreviations used: DNIC, dinitrosyl–iron complex; DMFA, dimethyl formamide; DMSO, dimethyl sulfoxide; EPR, electron paramagnetic resonance; HFS, hyperfine structure; MNIC, mononitrosyl iron complex; MT, mercaptotriazole (1*H*-1,2,4-triazole-3-thione); NO, nitric oxide.

unpaired electron with the nitrogen nuclei of NO ligands and magnetic nuclei of atoms involved in anionic ligands, as well as the nucleus of iron isotope ^{57}Fe introduced in DNIC, DNICs are mononuclear iron complexes coordinated with two NO ligands hypothetically in the form of nitrosonium ion (NO^+) and two anionic ligands. The unpaired electron is mainly localized on the iron atom hypothetically in d^7 electron configuration [9].

Freezing of DNIC aqueous solutions results in considerable broadening of EPR signals due to g -factor and HFS anisotropy. DNIC with low-molecular thiol-containing ligands, cysteine or glutathione, appeared to give, after the solution freezing, the EPR signal, whose shape coincides with signal 2.03 registered in biologic objects [8,10]. The further studies have shown that this coincidence is non-random, and that signal 2.03 is actually due to DNIC containing not low-molecular thiols, but mainly cysteine residues of proteins as anionic ligands [8,11–14]. Participation of the protein in these complexes formation appears in keeping of signal 2.03 anisotropy while increasing the temperature of its recording from low (77 K) to ambient. This can be due to a low mobility of protein DNICs at room temperature: it is insufficient for averaging the anisotropy of g -factor and HFS, this being true for DNICs with low-molecular ligands.

As follows from analysis of the EPR signal of DNICs with thiol ligands, d^7 iron electron configuration in these complexes with effective electron spin $S=1/2$ is consistent with plane-square structure of the complexes, with unpaired electron localized on d_{z^2} iron orbital [15] (Scheme 1A). Axial symmetry of g -factor tensor ($g_{\perp}=2.04$, $g_{\parallel}=2.014$) was explained by the effect of polar water molecules, which level the differences of the electron density on the iron bonds with the nitrogen and sulfur atoms of thiol and NO^+ ligands, thus resulting in D_{4h} symmetry of the complex [14].

DNIC's redox-state characterized by the EPR signal with $g_{av}=2.03$ is not the only paramagnetic state of DNICs with thiol ligands. Apparently, two-electron reduction of the complexes transforms them into the other paramagnetic state with the iron electron configuration being hypothetically d^9 , which is characterized by the EPR signal with $g_{\perp}=2.01$, $g_{\parallel}=1.97$ [16–18]. Broadening of an EPR signal for complexes with include isotope ^{57}Fe (nuclear spin $I=1/2$)

points to preferential localization of the unpaired electron on the iron atom for reduced DNICs.

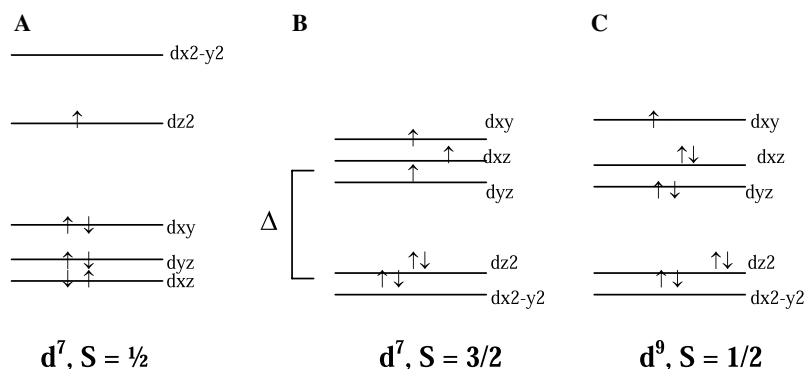
Plane-square structure suggested for explanation of d^7 iron configuration in DNICs with thiol-containing ligands is inconsistent with X-ray analysis data for single crystals of these complexes. DNICs with both thiol and other anionic ligands appeared to have tetrahedral structure in the crystalline state [19–32]. As distinguished from planar-square structure [15], in a tetrahedron with a weak separation of three higher iron d -orbitals (d_{xy} , d_{xz} , d_{yz} orbitals, t_2 manifold), a high-spin state of DNIC with $S=3/2$ should be realized for d^7 iron configuration (Scheme 1B), which is typical for mononitrosyl iron complexes (MNIC). The latter have the EPR signal with $g=4.0$, 3.95, and 2.0 at low temperature. Strong spin–lattice interaction typical for these high-spin complexes makes impossible the EPR signal registration at ambient temperature. For the iron electron configuration d^9 , the electron spin of the tetrahedral complex becomes $1/2$ (Scheme 1C), with a weaker spin–lattice interaction; therefore, registration of the EPR signal becomes possible at room temperature. Such type of the iron electron configuration in DNIC has been suggested by some researchers for interpretation of the EPR parameters and electron structure of these complexes [24,28,30,31,33].

However, no data evidencing DNIC's structure identity in the crystalline state and in the solution have been presented so far. Such identity could be confirmed by the coincidence of DNIC's EPR signals in the crystal and in the solution. Such investigation has been performed in this work, i.e., parameters of EPR signals for crystals of DNIC with 3-mercaptopotriazole (MT) [27] and its solutions as well as of DNICs with various thiol-containing ligands have been compared. Basing on these results, the suggestion on the mechanism of formation of DNICs with thiol and their electronic and spatial structure has been made.

Materials and procedure

Materials

L-Cysteine, reduced glutathione, dithiotreitol, *N*-acetylcysteine, homocysteine, sodium thiosulphate, and *N*-acetyl-



Scheme 1. Suggested electronic configuration of d orbitals for planar-square (A [15]) or tetrahedral (B and C) DNIC with thiol-containing ligands. Δ is d -orbital splitting in tetrahedral ligand field ($\Delta = E_{t_2} - E_e$).

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