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Precision X-ray study of mononuclear dinitrosyl iron complex $[Fe(SC_2H_3N_3)(SC_2H_2N_3)(NO)_2]{\cdot}0.5H_2O$ at low temperatures

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Abstract

X-ray analysis of mononuclear dinitrosyl iron complex $[Fe(SC_2H_3N_3)(SC_2H_2N_3)(NO)_2]{\cdot}0.5H_2O$ (**1**) has been performed at 100 K (the crystallographic data are: $a = 18.5006(3)$ Å, $b = 9.5207(1)$ Å, $c = 13.5719(2)$ Å, $\beta = 99.8860(7)°$, $V = 2355.04(6)$ Å^3, space group $C2/c$, $Z = 8$). From precision study of **1**, distribution maps of deformation electron density (DED) have been obtained. Both DED and topological parameters clearly indicate that Fe–S bonds in **1** are similar, though originally one of the molecules of ligand 1,2,3-triazole-3-thione coordinates the Fe atom in a thiol form (A), while the other in a thione form (B). These bonds can be described as interatomic interactions of a peak–peak type. The geometry and bond lengths in 5-membered cycles for A and B forms are rather similar. Fe–NO bonds can be described as interactions of a peak–hole type. The thermal motion of NO groups (even at 100 K) is highly anisotropic (this being an intrinsic feature of NO groups), thus suggesting mobility of the Fe–NO bond.

Keywords: Dinitrosyl iron complex; 1,2,4-Triazole-3-thione; Electron density distribution; X-ray structure; Chemical bond

1. Introduction

Natural iron complexes with nitrosyl groups involve a class of dinitrosyl complexes of the iron atom coordinated by NO groups and thiol-containing ligands in a tetrahedral mode (DNIC) [1,2]. The complexes are expected to form by the interaction of endogenic NO molecules with active centers of non-heme [Fe–S] proteins [3,4]. There is mounting evidence that DNICs play important biochemical roles in bacterial cells, plants and mammal organisms. Hence the mechanism of their formation, their structure and properties are of considerable interest. DNIC are supposed to be the alternative to nitrosothiols as natural NO-reservoirs for storage and transportation of nitrogen monoxide. Similar to RSNO, they may be sources of NO that stimulate vasodilatation [5]. Furthermore they are possibly responsible for NO cytotoxicity [6] as intermediates in reactions of decomposition and formation of natural *S*-nitrosothiols, which are catalyzed by free cellular iron [7]. Hence the preparation and study of synthetic analogs modeling DNIC reactivity and structure is an important fundamental and applied problem [8–10]. The crystalline structure of such synthetic models has not been investigated frequently so far [11–15]. The use of various azaheterocyclic thiols is quite promising for synthesis of such structures. We have recently synthesized a neutral paramagnetic mononuclear dinitrosyl iron complex $[Fe(SC_2H_3N_3)(SC_2H_2N_3)(NO)_2]{\cdot}0.5H_2O$ (**1**) with 1,2,4-triazole-3-thione as a ligand, and performed its X-ray analysis at room temperature [16]. The 1,2,3-triazole-3-thione ligand was shown to coordinate the iron atom both in thiol and thione forms to produce a covalent coordinated Fe–S bond with one molecule and a donor–acceptor Fe ← S bond with the other ligand. These results are important for the target synthesis and for understanding of the structure of neutral mononuclear nitrosyl iron complexes with paramagnetic

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properties. To comprehend the molecular structure and, in particular, the character of Fe–S and Fe–NO bonds in complex **1**, a low temperature X-ray study was necessary. This provides precision distribution of the electron density in the crystal, and, hence, deformation electron density (DED) in the molecule, i.e., the difference of the total electron density and electron density of the "pro-molecule" (superposition of electron densities of spherically symmetrical non-interacting atoms located in the same positions as in the real molecule). Thus, DED map shows re-distribution of the electron density induced by overlapping of the orbitals upon the chemical bond formation.

In the article, we present the results of precision X-ray study of complex **1** at low temperature (100 K), which are the basis for plotting the maps of deformation density and provide a more detailed information on the electron structure of complex **1**.

2. Experimental

The details of the X-ray data collection at SMART APEX II CCD diffractometer and conventional full-matrix anisotropic–isotropic refinement are listed in Table 3. The experimental electron density in the crystal was obtained by the multipole refinement based on Hansen–Coppens formalism [17] using XD program [18] package. The static molecular charge density in this model is described as a sum of rigid pseudoatoms [19] at the nuclear positions (R_j), $\rho\ (r) = \sum_j \rho_j(r - R_j)$.

Each pseudoatom electron density has form

$$\rho_j(r_j) = P_{\rm core}\rho_{\rm core}(r_j) + \kappa'^3 P_{\rm val}\rho_{\rm val}(\kappa'^3 r_j) + \sum_{l=0}^{l_{\max}} \sum_{m=-l}^{m=+1} \kappa''^3 P_{\rm lm} R_l(\kappa'' r_j) d_{\rm lmp}(\theta_j, \phi_j)$$

where $r_j = r - R_j$. Both $\rho_{\rm core}$ and $\rho_{\rm val}$ are derived from wave functions fitted to a relativist Dirac–Fock solution [19] and describe the frozen core with fixed population ($P_{\rm core}$), and spherical valence density with population $P_{\rm val}$ is varied to allow charge transfer between atoms. The k' variable allows concentration or expansion of the charge cloud of the pseudoatom. The last term in the expansion expression describes the asphericity of the valence density by a set of deformation functions composed by the spherical harmonics ($d_{\rm lmp}$) and radial Slater-type functions with expansion–contraction coefficient k''.

Prior to the refinement, all the C–H bond distances were normalized to the ideal value of 1.08 Å [20]. The refinement for **1** was carried out with electroneutrality constraints. The level of the multipole expansion was hexadecopole for the Fe atom and octopole for the carbon atoms. The dipole D_{10} and the hexadecapole H_{40} were refined for all hydrogen atoms for a more accurate description of hydrogen bonds according to Ref. [18]. The scattering factors of the hydrogen atoms were calculated from the contracted radial density functions ($k = 1.2$). All bonded pairs of atoms satisfy the Hirshfeld rigid-bond criteria (difference of the mean square displacement amplitude was 8×10^{-4} Å^2). The residual electron density was below 0.17 eÅ^{-3}. The refinement was carried out against F. The results of the multipole refinement are listed in Table 3.

The values of the kinetic energy density $g(\mathbf{r})$ and the electron energy density $h_e(r)$ in CP $(3, -1)$ for the experimental $\rho(\mathbf{r})$ function were evaluated through the semiquantitative approximation proposed by Kirzhnits [21]. According to Ref. [22,23], the $g(\mathbf{r})$ function is described as $(3/10)(3\pi^2)^{2/3}[\rho(\mathbf{r})]^{5/3}+(1/72)|\nabla\rho(\mathbf{r})|^2/\rho(\mathbf{r})+1/6\nabla^2\rho(\mathbf{r})]$, thus leading, in conjunction with the virial theorem $(2g(\mathbf{r}) + v(\mathbf{r}) = 1/4\nabla^2\rho(\mathbf{r}))$, to the expression for potential energy density $v(\mathbf{r})$ and finally to the $h_e(\mathbf{r})$ – the sum of potential and kinetic energy densities.

Analysis of the deformation electron density and topology of $\rho(\mathbf{r})$ was carried out using the WINXPRO program package [24].

3. Results and discussion

The previous X-ray diffraction analysis of **1** at room temperature has revealed the significant non-equivalence of Fe–S bonds in the complex, which was attributed to different types of chemical bonding, namely covalent of an exchange type and of a dative type [16]. The same tendency is preserved in the case of low temperature X-ray diffraction data, i.e., the difference for Fe–S and C–S bond is equal to 0.02 Å (Table 1).

It should be noted that in spite of crystal cooling from 298 to 100 K the thermal motion of NO groups is still highly anisotropic. In particular, for the oxygen atoms of the NO group the mean square atomic displacement in the direction perpendicular to the N–O bond is three times

Table 1
Selected bond lengths (Å) and angles (°)

Bond lengths (Å)			
Fe–N(1)	1.6861(6)	Fe–N(2)	1.6903(6)
O(1)–N(1)	1.1641(8)	O(2)–N(2)	1.1626(8)
Fe–S(1)	2.3015(2)	Fe–S(2)	2.3219(2)
S(1)–C(1)	1.7308(6)	S(2)–C(3)	1.7072(6)
N(3)–C(1)	1.3416(8)	N(7)–C(3)	1.3590(7)
N(3)–C(2)	1.3561(8)	N(7)–C(4)	1.3585(8)
N(4)–C(1)	1.3405(7)	N(6)–C(3)	1.3353(7)
N(4)–N(5)	1.3656(7)	N(6)–N(8)	1.3755(7)
N(5)–C(2)	1.3190(8)	N(8)–C(4)	1.3062(7)
Bond angles (°)			
N(1)–Fe–N(2)	119.79(3)	S(1)–Fe–S(2)	112.297(7)
N(1)–Fe–S(1)	110.76(2)	N(1)–Fe–S(2)	107.86(2)
N(2)–Fe–S(1)	102.74(2)	N(2)–Fe–S(2)	103.23(2)
C(1)–S(1)–Fe	105.28(2)	C(3)–S(2)–Fe	106.110(19)
O(1)–N(1)–Fe	169.02(7)	O(2)–N(2)–Fe	172.84(6)
C(1)–N(3)–C(2)	103.98(5)	C(3)–N(6)–N(8)	111.57(5)
C(1)–N(4)–N(5)	110.20(5)	C(3)–N(7)–C(4)	107.30(5)
C(2)–N(5)–N(4)	103.01(5)	C(4)–N(8)–N(6)	104.27(5)
N(3)–C(1)–N(4)	108.78(5)	N(6)–C(3)–N(7)	105.39(5)
N(3)–C(1)–S(1)	127.73(4)	N(6)–C(3)–S(2)	130.77(4)
N(4)–C(1)–S(1)	123.50(4)	N(7)–C(3)–S(2)	123.73(4)
N(5)–C(2)–N(3)	114.02(5)	N(8)–C(4)–N(7)	111.45(5)