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Structure of the neutral mononuclear dinitrosyl iron complex with 1,2,4-triazole-3-thione $[Fe(SC_2H_3N_3)(SC_2H_2N_3)(NO)_2]{\cdot}0.5H_2O$

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The mononuclear complex $[Fe(SC_2H_3N_3)(SC_2H_2N_3)(NO)_2]{\cdot}0.5H_2O$ 1 of the '$g = 2.03$ family' with protonated and deprotonated ligands, which provide a neutral structure and are connected *via* the sulfur atom in a monodentate way, has been synthesised and characterised by X-ray diffraction, IR, EPR and Mössbauer spectroscopy.

Mononuclear dinitrosyl iron complexes (DNIC) with sulfur ligands are analogous to nitrosyl [Fe–2S] non-heme iron complexes, and they are identified in solutions by a characteristic EPR signal of $g = 2.03$.[1,2] Their molecular and crystal structure is being actively discussed. Unfortunately, their crystallization is difficult because of their instability *in vivo* and *in vitro*. The first DNIC was assumed to have the anionic structure $[NEt_4][Fe(NO)_2(SR)_2]$ **2**, where R = Ph.[3] Neutral DNIC $[Fe(NO)_2(R)_2]$ with a nitrogen-containing ligand (R = metylimidazole) was also referred to the '$g = 2.03$ family',[4] though the EPR signal with $g = 2.015$ was only detected in solution for the $[Fe(NO)_2(R)_2]^+$ form of the complex.

In this work, a neutral DNIC with a sulfur-containing ligand has been first synthesised and investigated by X-ray analysis,[†] IR,[‡] EPR[§] and Mössbauer[¶] spectroscopy and magnetochemistry.[††] Complex **1** was synthesised by the reaction of 3-mercapto-1,2,4-triazole with $[Na_2Fe_2(S_2O_3)_2(NO)_4]{\cdot}2H_2O$ and $Na_2S_2O_3{\cdot}5H_2O$ in a molar ratio of 10:1:2 in an aqueous alkaline solution, with the subsequent recrystallization from MeOH. The yield is 30%, and the decomposition temperature is 160 °C. The complex is soluble in methanol, ethanol, dimethyl sulfoxide and dimethylformamide. Polycrystalline powder of **1** is stable on storage in dry air in the dark at 16–18 °C.

There are several ways of the monodentate coordination of an iron atom to heterocyclic thiols because of their prototropic tautomerism[5] (Figure 1). Thiols containing the μ-N–C–S thioamide group are mainly coordinated in a thio ketone form (**b**), with the C=S bond length of 1.671(8)–1.732(5) Å,[6] while the C–S bond length is 1.719 Å when the metal atom is coordinated with an anionic deprotoned ligand in form (**c**).[7]

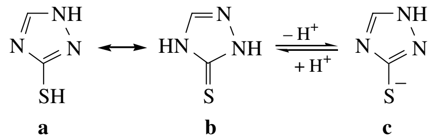

Figure 1 Tautomeric forms of 1,2,4-triazole-3-thione.

The iron atom in complex **1** is coordinated by two triazolethionato rings (**A**, **B**, Figure 2) and two NO groups. The N(3) and N(6) nitrogen atoms of the triazole rings are *syn*-oriented to the iron atom, and intramolecular hydrogen bonds form between triazole rings: N(6)–H···N(3) 1.817(3) Å, N(6)···N(3) 2.715(3) Å, the N(6)–H···N(3) angle is 169.2(2)°. The torsion angles FeS(1)C(1)N(3) and FeS(2)C(3)N(6) are decreased to 28.6° and –7.1° as compared to FeS(1)C(1)N(4) and FeS(2)C(3)N(7) (–153.0 and 176.3°, respectively). The intramolecular distances Fe···N(3) 3.439(2) Å and Fe···N(6) 3.446(2) Å point to the absence of additional coordination of the iron atoms by the nitrogen atoms of the rings. Heterocyclic ligands coordinate the iron atom in two different ways: (1) as an anionic ligand, by the thionato group (**c**, Figure 1); therefore, heterocycle **B** contains two hydrogen atoms; (2) as a neutral ligand, in the thione form (**b**, Figure 1), and heterocycle **A** has three hydrogen atoms. Two different types of coordination are proved by differences in the bond lengths C(3)–S(2) 1.703(2) Å and C(1)–S(1) 1.725(2) Å, as well as of the bonds Fe–S(1) 2.298(1) Å and Fe–S(2) 2.318(1) Å. Moreover, the bond lengths and angles at the C(3) and C(1) carbon atoms of two triazole rings are noticeably different: C(3)–N(7) 1.353(3) Å, C(3)–N(6) 1.322(3) Å and C(1)–N(3) 1.333(3) Å, C(1)–N(4) 1.334(3) Å, N(7)C(3)N(6) 105.4° and N(3)C(1)N(4) 108.5°. The increase of the bond length N(6)–N(8) 1.375(2) Å as compared to that in ring **B** N(4)–N(5) 1.359(3) Å can also be due to the intramolecular hydrogen bond N(6)–H···N(3) 1.817(3) Å. Moreover, geometrical differences of heterocycles **A** and **B** might result from the three types of intermolecular hydrogen bonds (Figure 2): (i) N(5)···H–N(7) 1.998(3) Å, N(5)···N(7) 2.776(3) Å, N(5)···H–N(7) 174.9(2)°; (ii) N(4)–H···O(3) 2.045 Å, O(3)···N(4) 2.876 Å, O(3)···H–N(4) 160.6° and (iii) N(8)···H–O(3) 2.207 Å, O(3)···N(8) 2.938 Å, O(3)–H···N(8) 172.5°.

The IR spectra of the ligand in the thione form exhibit characteristic 'thioamide' bands at 1570–1395 (band I), 1420–1260 (band II), 1140–940 (band III) and 800–700 cm^{-1} (band IV).[6] The bands are mainly caused by N=C stretching vibrations and N–H deformation vibrations. The C=S stretching

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[†] *Crystal data*: $C_4H_6FeN_8O_{2.5}S_2$, $M = 326.14$, monoclinic, space group $C2/c$, $a = 18.789(4)$ Å, $b = 9.528(2)$ Å, $c = 13.623(3)$ Å, $\beta = 99.73(3)°$, $V = 2403.7(9)$ Å^3, $d_{\mathrm{calc}} = 1.802$ g cm^{-3}, $Z = 8$, $\mu = 1.611$ mm^{-1}, $T = 293$ K; $N = 3525$, $N_0[I > 2\sigma(I)] = 1964$, $R = 0.0304$, $R_w = 0.0806$, GOF = 0.929. The experimental array of reflections was obtained on a KM-4 KUMA DIFRACTION automated four–circle diffractometer (MoKα radiation; $\lambda = 0.70926$ Å). The crystal structure was solved by the direct method (SHELXS 86)[10] and refined by the full-matrix least-squares method in an anisotropic approximation using the SHELX-97 program package.[11] The hydrogen atoms were revealed from the difference Fourier synthesis.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 188638. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2004.

[‡] IR spectra were recorded on a Perkin Elmer 1720X Fourier transform spectrometer at ~20 °C. The samples were prepared as pellets with KBr (1 mg of a compound in 300 mg of KBr). IR (ν/cm^{-1}): 3116 (m), 1807 (vs), 1749 (vs), 1586 (s), 1505 (m), 1457 (s), 1280 (m), 1225 (m), 1094 (m), 1030 (m), 998 (s), 954 (m), 899 (m), 856 (m), 702 (m).

[§] The EPR spectra in a 3-cm range were recorded on a SE/X 2544 spectrometer (Radiopan, Poznan) under conditions excluding spectra distortion. The number of spins in a sample was determined by comparing the second integrals of the EPR spectra of the test sample and $CuSO_4{\cdot}5H_2O$ powder.

[¶] The Mössbauer absorption spectra were recorded on a WissEl Unit (Germany) operating under conditions of a constant acceleration; ^{57}Co in the Rh matrix served as a radiation source. Low-temperature spectra were measured using a CF-506 flow-type helium cryostat (Oxford Instruments) with controllable temperature. The Mössbauer spectra were processed by the least-squares method assuming the individual spectral components to be of a Lorentzian shape.

[††] Magnetic susceptibility was determined by the comparative Faraday method[12] in the temperature range 78–300 K at applied magnetic fields of $-1\ \mathrm{T} \le H \le 1$ T. $Hg[Co(CNS)_4]$ was used as a standard for the calibration.

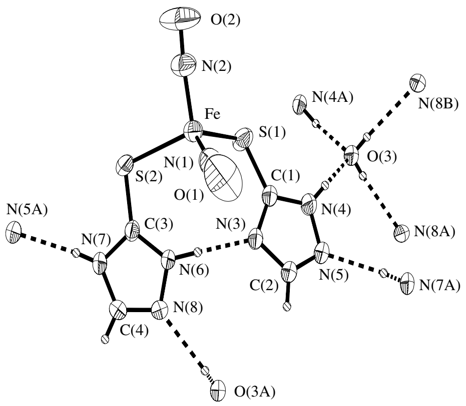

Figure 2 A fragment of the crystal structure of complex **1** with atom indexes. In the text, the heterocyclic ring C(3)N(7)C(4)N(8)N(6) is marked as **A** and the ring C(1)N(3)C(2)N(5)N(4) is marked as **B**. Selected bond lengths (Å): Fe–N(1) 1.669(2), S(1)–C(1) 1.725(2), C(3)–N(7) 1.353(3), Fe–N(2) 1.677(2), S(2)–C(3) 1.703(2), C(4)–N(8) 1.298(3), Fe–S(1) 2.298(1), C(1)–N(4) 1.334(3), C(4)–N(7) 1.343(3), Fe–S(2) 2.318(1), C(1)–N(3) 1.333(3), C(3)–N(6) 1.322(3), N(1)–O(1) 1.157(3), N(5)–C(2) 1.301(3), N(3)–C(2) 1.348(3), N(2)–O(2) 1.150(3), N(5)–N(4) 1.359(3), N(6)–N(8) 1.375(2); selected bond angles (°): O(1)–N(1)–Fe 168.2(3), C(1)–S(1)–Fe 105.2(1), N(7)–C(3)–S(2) 123.7(2), O(2)–N(2)–Fe 171.5(3), C(3)–S(2)–Fe 106.3(1), N(8)–C(4)–N(7) 112.1(2), N(1)–Fe–N(2) 118.7(1), N(4)–C(1)–N(3) 108.5(2), C(1)–N(3)–C(2) 103.7(2), S(1)–Fe–S(2) 112.0(1), N(4)–C(1)–S(1) 123.6(2), C(1)–N(4)–N(5) 110.4(2), N(1)–Fe–S(1) 111.2(1), N(3)–C(1)–S(1) 127.9(2), N(5)–C(2)–N(3) 114.6(3), N(2)–Fe–S(1) 103.2(1), C(2)–N(5)–N(4) 102.7(2), C(3)–N(6)–N(8) 111.7(2), N(1)–Fe–S(2) 108.1(1), N(6)–C(3)–N(7) 105.4(2), C(4)–N(7)–C(3) 107.2(2), N(2)–Fe–S(2) 103.2(1), N(6)–C(3)–S(2) 130.8(2), C(4)–N(8)–N(6) 103.6(2).

vibrations also contribute considerably to the intensity of these bands. There are several absorption bands in I–III regions of the IR spectrum of complex **1** (Figure 3), and one band at 702 cm^{-1} in region IV. In the initial 1,2,4-triazole-3-thione (**b**), this band is observed at 750 or 745 cm^{-1}.[8] A considerable shift of band IV during the complex formation implies a significant weakening of the C=S bond and, hence, the high stability of the S→Fe bond. This is consistent with the fact that the lengths of S→Fe and S–Fe bonds are close. Thus, the sulfur atom S(1) is supposed to be negatively charged as a result of deprotonation, and the bond with the iron atom is covalent; this is typical of the compounds described previously;[7] the other sulfur atom S(2) is formally neutral and forms a donor–acceptor bond with the iron atom.[8] The NO group charge is close to zero. According to IR spectroscopy, the most intense absorption bands in complex **1** are related to NO group vibrations (1807 and 1749 cm^{-1}). Note that there is a structural 'non-equivalency' of the Fe–N–O groups in complex **1**, similar to that we observed earlier.[9,10] Slight differences in the structures of the Fe–N–O fragments (within 3σ for N–O and 5σ for Fe–N) can be explained by differences in the electron density transfer from the iron atom to the NO due to the dative interaction $d_\pi(\mathrm{Fe}) \rightarrow p\pi^*(\mathrm{NO})$.

According to the formal charges of ligands in complex **1** (NO^0, S$^-$, S^0), the iron atom in this complex contains an odd number of electrons $\{\mathrm{Fe(NO)_2}\}^9$ and is isoelectronic to complex **2**. As it follows from the data of Mössbauer spectroscopy, the spectrum of complex **1** has a doublet structure with the following parameters: $\delta_{\mathrm{Fe}} = 0.188(1)$ mm s^{-1}, $\Delta E_\mathrm{Q} = 1.118(1)$ mm s^{-1} and $\Gamma = 0.258(2)$ mm s^{-1} at 296 K. In complex **2**, $\delta_{\mathrm{Fe}} = 0.08$ mm s^{-1} and $\Delta E_\mathrm{Q} = 0.78$ mm s^{-1} at 296 K. A comparison of the interatomic distances and angles in complexes **1** and **2** shows their slight difference. A considerable increase in the isomeric shift in **1**, as compared to that in **2**, can be explained by the unusual coordination of 1,2,4-triazole-3-thione (STrias) in **1**, *i.e.*, in the form of thione (**b**) and thionato (**c**) ligands. The elongation of the Fe–(STrias)$^-$ bonds in **1**, as compared to the Fe–(SPh)$^-$ in **2**, results in a decrease of 4*s* electron density on the iron atom and, consequently, in an increase of the isomer shift. Moreover, the reduction of σ-donation of the thione ligand on the iron atom (heterocycle **A**, Figure 3), which is also connected with the decrease of the 4*s* electron density on the iron atom, contributes additionally to the increase of the isomer shift. A highly asymmetric distribution of charges surrounding the iron atom in the Fe^{+1}(S^{0}S$^-$NN) chromophore in comparison with Fe^{+1}(S$^-$S$^-$NN) qualitatively accounts for the ΔE_Q increase in complex **1** as compared to the value of quadrupole splitting in **2**.

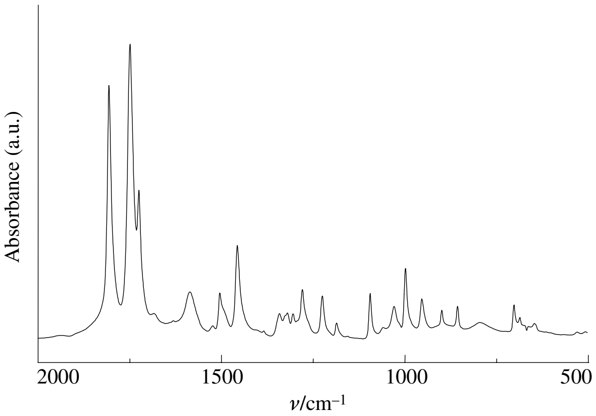

Figure 3 IR spectrum of complex **1**.

Complex **1** shows paramagnetic properties: in contrast to the diamagnetic binuclear complexes[9] with Fe–Fe distances of ~2.7 Å; the Fe···Fe′ distance is 5.225 Å. The EPR spectrum of polycrystals of **1** is typical of an axial anisotropy of *g*-factor ($g_\perp = 2.04$, $g_\parallel = 2.02$). At $T = 100$–300 K, the EPR line shape remains unchanged, the dependence of the second integral of the EPR spectrum on temperature obeys the Curie law, and no EPR spectrum is observed in the half magnetic field. A single crystal of **1** gives a single line with the *g*-factor between $g_\perp$ and $g_\parallel$, depending on the orientation of the single crystal in a magnetic field. The temperature dependence of magnetic susceptibility obeys the Curie law. The effective magnetic moment per iron atom is 1.77 μ_B. This value is near to the theoretical value for spin $s = 1/2$ ($\mu_{\mathrm{eff}} = 1.73\ \mu_\mathrm{B}$), *i.e.*, it corresponds to 0.85 spin/complex, which is consistent with EPR data.

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