

Theoretical analysis of the mechanism of nitrous oxide release upon the UV irradiation of binuclear sulfur-containing nitrosyl iron complexes

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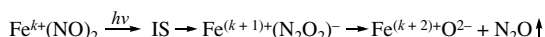
The B3LYP calculations of binuclear sulfur-containing nitrosyl iron complexes reveal the possibility of photochemical NO ligand ‘coupling’, which results in the N–N bond formation followed by N₂O release in subsequent transformations.

Previously,¹ we found that the UV irradiation of crystalline binuclear dinitrosyl iron complexes yields nitrous oxide. It is well known² that nitrous oxide is one of the photolysis products of iron–sulfur–nitrosyl complexes in inert solutions. The formation of dinitrosyl complexes of non-heme iron [Fe(NO)₂(SR)₂]^{2–} with various anionic ligands in unirradiated aqueous solutions is also accompanied by the release of nitrous oxide.³ If protons and an appropriate reducing agent are available in the solution, the NO groups of the complex are readily converted into nitroxyl, which disproportionates to yield nitrous oxide and water:



Vanin⁴ explained the formation of N₂O in the absence of a reducing agent by the initial mutual oxidation–reduction of the NO groups (due to their coordination to the iron atom) and the further interaction of NO[–] with a proton. However, this scheme is hardly applicable for explaining the photoreaction in a solid state: because of the remoteness of crystallization water from the coordination sphere of the iron atoms, the proton cannot participate in such a reaction. Besides, this reaction was also observed¹ for {Pr₄N}₂[Fe₂(μ₂-S₂O₃)₂(NO)₄] complex with no proton donating groups. Therefore, an alternative mechanism should be assumed for the solid-phase formation of nitrous oxide, which can occur in the presence of crystallization water.

Previously,¹ an assumption was made that, upon the irradiation of solid Na₂[Fe₂(μ₂-S₂O₃)₂(NO)₄]·2H₂O and {Pr₄N}₂[Fe₂(μ₂-S₂O₃)₂(NO)₄] complexes, the formation of N₂O occurs via an intermediate state (IS):



To understand the possibility of N₂O formation inside the coordination sphere, we used the density functional method to perform calculations of the energies of intermediate structures upon the transformation of two nitrosyl ligands into nitrous oxide for the simplest binuclear complex [Fe₂(NO)₄(μ₂-S₂)₂]^{2–} **1** (Figure 1).

The geometry of stationary points was optimised at the B3LYP/LANL2DZ level using the GAUSSIAN-98 program.⁵ The type of the structure, *i.e.*, the minimum on the potential energy surface, was confirmed by calculating the frequencies in an harmonic approximation. Based on the geometry obtained, the system energy was then calculated in the extended 6-311++G(*d,p*) basis set, which included diffusion and polarization functions for all atoms, taking into account zero-point energies at the B3LYP/LANL2DZ level. For some cases, the 6-31G* basis set was used for geometry optimization, and the results were similar.

The geometry obtained for **1** is consistent with experimental data (Table 1). The optimization of **1** in the 6-31G* basis set yields the structure of C_{2v} symmetry, as distinct from D_{2h} symmetry in the LANL2DZ basis set, the latter being more consistent with the geometry from the X-ray data.⁶ When studying possible intermediate products in the formation of nitrous oxide, in order to decrease a number of possible structures, the coordination spheres of both iron atoms were changed symmetrically. Therefore, the obtained energy change is assumed to be about twice as much as that upon the corresponding transformation of one centre.

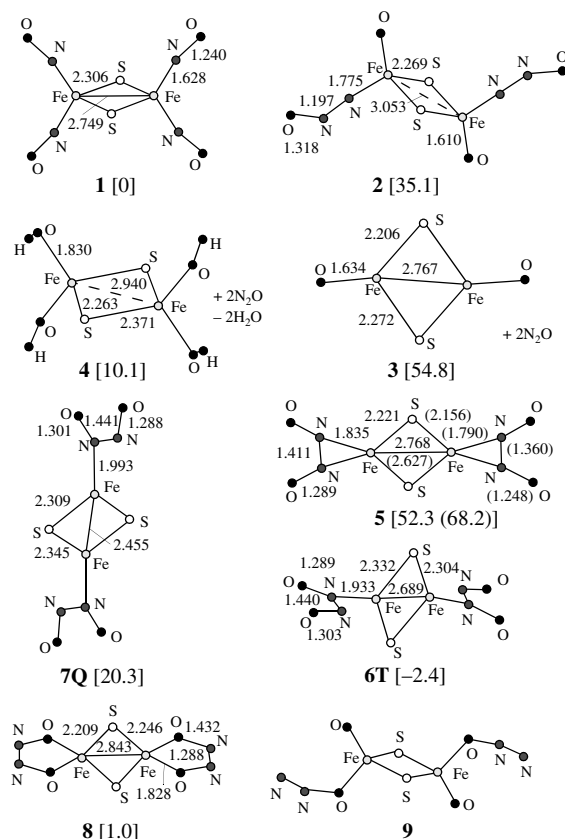


Figure 1 Isomeric structures of the [Fe₂(NO)₄(μ₂-S)₂]^{2–} complex and the structures of [Fe₂(OH)₄(μ₂-S)₂]^{2–} and [Fe₂(O)₂(μ₂-S)₂]^{2–} complexes. Relative energies (in brackets) are in kcal mol^{–1}, and distances are in Å. The values in parentheses were obtained by optimization in the 6-31G* basis set.

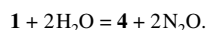
The energies of nitrous oxide complex **2** and initial complex **1** differ by 35.1 kcal mol^{–1}, and this value is permissible for a photochemical process. Essentially non-linear NNO fragments (N–N–O angle of 140.3°) and an elongated N–O bond (1.318 Å) indicate that **2** is the complex of [Fe₂O₂S₂] with two N₂O-species, which have an angular geometry in the isolated form: N–N–O = 133° and N–O = 1.369 Å.⁷ Indeed, the total charge on the NNO fragment, –0.61, is twice as much as that on the NO fragment in complex **1**, –0.31. However, the average energy of the Fe–N₂O bond cleavage in complex **2** appears to be unexpectedly small (9.8 kcal mol^{–1}). Taking into account the translational entropy of N₂O, the free energy does almost not change when **2** transforms to **3**. We assume that such a low dissociation energy for such a short distance (Fe–N = 1.775 Å) is due to the fact that Fe atoms in the reaction product (complex **3**) form a linkage, which does not occur in **2**. Its length of 2.767 Å is noticeably shorter than the Fe–Fe distance in **2** (3.053 Å). A small elongation of the Fe–O bond from 1.610 Å in **2** to 1.634 Å in **3** also indicates a strong Fe–Fe interaction, which partially compensates the energy of the Fe–N₂O bond cleavage. Apparently, the possibility of changing the Fe–Fe

Table 1 Distances (Å) and angles (degree) in the $[\text{Fe}_2(\text{NO})_4(\mu_2\text{-S})_2]^{2-}$ complex obtained by the B3LYP method and experimental data.

Distances and angles	Calculation in the LANL2DZ basis set	Calculation in the 6-31G* basis set	Experiment ⁶
Fe–S	2.306	2.231	2.235, 2.243, 2.230, 2.240
Fe–N	1.628	1.600, 1.649	1.665, 1.654, 1.66, 1.675
N–O	1.240	1.200, 1.211	1.155, 1.17, 1.175, 1.148
Fe–Fe	2.749	2.601	2.703
Fe–N–O	165.8	176.9, 143.9	165.4, 166.6, 167.9, 163.8
N–Fe–N	116.7	110.3	112.3, 144.9

bond length in binuclear nitrosyl iron complexes upon their photoexcitation is important for N_2O formation. In any case, we found recently that, in related mononuclear iron complexes, UV irradiation does not yield detectable amounts of nitrous oxide. The data on the comparative mass-spectrometric analysis of gas release upon the irradiation of mono- and binuclear complexes will be published elsewhere.

Because of the presence of a free coordination site after nitrous oxide elimination, ligands available in the system can be coordinated, thus making nitrous oxide release much more favourable. Hydroxo complex **4** formed upon the addition of two water molecules to **3** was calculated as a model. In this case, 10 kcal mol^{−1} (or 5 kcal mol^{−1} in average per N_2O molecule) is lost in the reaction



For the formation of the N–N bond, a change in the N–Fe–N angle in complex **1** is sufficient. Singlet complex **5** exists as an equilibrium structure, and an average of 26 kcal mol^{−1} per site is necessary for its formation. Thus, from the thermodynamical point of view, we expected such a ‘coupling’ of the NO ligands in photochemical processes. The transition **1** → **5** is accompanied by electron density transfer (0.2e) to the ONNO fragment, and its charge becomes −0.80. Structure **5** can be considered as a di-*N*-oxo π -complex of molecular nitrogen or a hyponitrite complex with an unusual coordination of the hyponitrite ligand via two N atoms. The transition to a typical coordination of hyponitrite (structure **8**) is accompanied by an energy gain of 51 kcal mol^{−1}. The N–N bond in this case is shortened from 1.411 to 1.288 Å, while the N–O bond is elongated from 1.289 to 1.432 Å, with a small increase in the negative charge to −0.90. This means that the geometry of the ONNO fragment becomes close to the geometry of the free dianion ONNO^{2-} with the N–N and N–O distances calculated to be 1.318 and 1.411 Å, respectively.⁷

For triplet and quintet states of **5**, the coordination of the ONNO ligand is monodentate with a considerable decrease in the energy, and the corresponding structures **6T** and **7Q** are 2.4 kcal mol^{−1} lower and 20.3 kcal mol^{−1} higher than initial complex **1**, respectively. For the states with open shells, the transition to an unrestricted approximation results in an additional small decrease of the energy. However, in the case under consideration, the difference between occupied shell orbitals with opposite spins is much bigger because of a drastic change in the electron structure. For example, in complex **7Q**, the parallel orientation of three unpaired electrons on each iron

atom, with a spin density equal to 2.87, and the anti-parallel orientation of one unpaired electron on each ONNO ligand, with a spin density of −0.90, occur. For other complexes with zero spin, each metal atom also has a non-zero local spin density. For example, in **4** the Fe^{III} site in a tetrahedral surrounding certainly has a non-zero spin. Therefore, its real electron structure corresponds to the superposition of electron configurations for the two possible variants of localised spins orientations: $\text{Fe}\uparrow\text{Fe}\uparrow$ and $\text{Fe}\uparrow\text{Fe}\downarrow$. In a one-configuration approximation, this effect cannot be reproduced adequately, thus leading to increasing the energy of states with $S=0$ as compared to the energy of states with a non-zero spin. This can be seen while calculating the energies of vertical singlet–triplet transitions in **1** and **5** (Table 2), which actually should be small since they correspond to weak exchange interactions in the system with two magnetic centres. Table 2 summarises the electron structure characteristics of the excited triplet state with different spin structures.

Thus, we can assume that the energies of complexes **5**, **6T** and **7Q** are much closer than it follows from a one-configuration approach. Therefore, we suppose that initially formed complex **5** transforms first into **6T** or **7Q** and then into **2**. The first process occurs due to a soft deformation mode of ONNO rotation in the Fe coordination sphere, so it must have a low activation energy in thermal reactions. The further process is similar to the α -elimination of a hydrogen atom, which readily occurs in the coordination sphere. On the other hand, the formation of hyponitrite complex **8** is also possible, with its further conversion, by breaking the elongated N–O bond, into **9**, the complex of nitrous oxide with N_2O coordination over the oxygen atom.

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Table 2 Electron structure characteristics of complexes **1** and **5** obtained in the B3LYP/LANL2DZ approach.

Complex	Relative energy/ kcal mol ^{−1}	Charges on the atoms and groups			Spin densities on the atoms and groups		
		Fe	NO	ONNO	Fe	NO	ONNO
1 $S=0$	0	0.07	−0.30	—	—	—	—
1 $S=1$	−9.4	0.07	−0.35	—	2.59	−1.01	—
1 $S=1^a$	21.8	0.03	−0.31	—	−0.12	0.55	—
5 $S=0$	0	0.04	—	−0.80	—	—	—
5 $S=1$	−6.1	0.13	—	−1.19	1.31	—	0.20

^aExcited state with a different spin structure, which can be found using a less accurate convergence criterion.

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