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# A new trend in iron–dithiocarbamate complexes: as an endogenous NO trapping agent

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**Contents**



**Abstract**

Iron complexes with dithiocarbamates, Fe(DTC), and their nitrosyl complexes had been studied extensively until the 1970s because of their unique magnetic and electronic properties. In the 1990s, however, Fe(DTC) are commanding attention from a different point of view. In virtue of their high reactivity toward nitric oxide (NO) and the high stability of the

*Abbreviations:* DETC, *N*,*N*-diethyldithiocarbamate; DTC, dithiocarbamate; DTCMP, *N*-dithiocarboxy-4-trans-methoxymethyl-L-proline; DTCS, sarcosine dithiocarbamate (*N*-(dithiocarboxy)sarcosine); EPR, electron paramagnetic resonance; EPR-CT, electron paramagnetic resonance-computed tomography; ESI MS, electrospray ionization mass spectroscopy; HPLC, high performance liquid chromatography; MGD, *N*-methyl-D-glucamine dithiocarbamate; MSD, *N*-methyl-L-serine dithiocarbamate; NO, nitric oxide; NOC-5, 3-[2-hydroxy-1-(1-methylethyl)-2-nitrosohyrazino]-1-propanamine; NOS, nitric oxide synthase; PDTC, pyrrolidine dithiocarbamate; ProDTC, L-proline dithiocarbamate.

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resultant nitrosyl complexes which exhibit a characteristic electron paramagnetic resonance signal, Fe(DTC) have been used for the detection and analysis of biological NO produced endogenously from NO synthases. We have studied the chemical basis of this detection method and its application. In spite of the method's widespread use, the chemical basis seems to be very poor. We, therefore, review the fundamental data on Fe(DTC) species and their reaction with NO, including the novel reductive nitrosylation mechanism realized in this system. 

*Keywords:* Nitric oxide; Iron complex; Dithiocarbamate; Detection method; Reductive nitrosylation

## 1. Introduction

Ferric–dithiocarbamate complexes, Fe(DTC), and ferrous nitrosyl complexes, $Fe(NO)(DTC)_2$, had attracted much attention from 1960s to 1970s because of their anomalous magnetic and electronic properties first reported by Cambi and co-workers in 1931 [1,2]. As the first and representative compounds that exhibit a spin equilibrium, the magnetic behavior of the Fe(DTC) complexes were thoroughly studied. The electronic structures of the $Fe(NO)(DTC)_2$ complexes were also investigated as representative of transition metal–nitrosyl complexes. These vigorous studies revealed that the anomalous magnetic and electronic properties can be attributed mainly to the characteristic resonance structure of the ligand, which is induced by the coordination to metal centers. These early studies on the structure, magnetism and electronic states of $Fe(DTC)_3$ and $Fe(NO)(DTC)_2$ have been reviewed [3–7]. As a result of the maturity of the chemistry, studies on $Fe(DTC)_3$ and $Fe(NO)(DTC)_2$ complexes were less common in the 1980s; of course, DTC itself has been used as a masking agent in absorption spectrophotometry, as agricultural insecticides, herbicides, and fungicides, and as a therapeutic agent for various diseases.

In 1991, these old-fashioned complexes reappeared on the stage with a different role. Vanin and co-workers used the Fe(DETC) complex as a trapping agent for NO and succeeded in detecting NO produced in biological samples [8]. Since the discovery of the physiological role of NO [9,10], the development of analytical methods for endogenously produced cellular NO became an important subject. Most of conventional methods for NO detection were developed for environmental analysis of atmospheric NO and were not suitable for biological samples. Among the several analytical methods newly developed for endogenous NO detection, this spin-trapping technique combined with EPR spectroscopy is a powerful approach by virtue of its facility and wide applicability [11,12]. In particular, the availability of in vivo invasive measurement is a unique feature of this method. The in vivo in situ detection of NO has been achieved by using this technique with a low frequency EPR spectrometer [12–14]. Further employing an EPR-CT imaging system, we first succeeded in obtaining in vivo EPR images of NO synthesized in a living lipopolysaccharide-treated mouse [15].

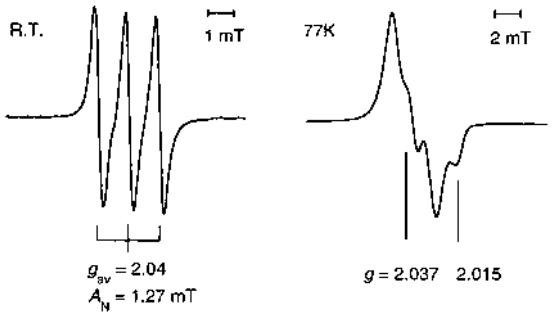


Fig. 1. EPR spectra of $Fe(NO)(DTCS)_2$ in aqueous solution at X-band; (left) at room temperature and (right) at 77 K.

Despite this method's wide application, the chemical fundamentals have not yet been established. In this review, we try to summarize our present knowledge about the chemical aspects of this NO detection method, especially on the chemistry of the Fe(DTC) complexes as an NO trapping agent.

## 2. Dithiocarbamates used for NO trapping

DTC derivatives form various complexes with iron ion. Planar $Fe(II)(DTC)_2$ [16,17], octahedral $Fe(II)(DTC)_3$ [18], $Fe(III)(DTC)_3$ [19], and $Fe(IV)(DTC)_3$ [20] were reported, where the total charge of the complexes is omitted. The synthesis and structure of these complexes have been reviewed [4,5]. The detection of NO by employing Fe(DTC) complexes as an NO trap is based on the formation of a stable $Fe(II)(NO)(DTC)_2$ complex, which exhibits a characteristic three-line EPR spectrum ($g_{av} = 2.04$) at room temperature and a spectrum with axial symmetry ($g_{\perp} = 2.037$, $g_{//} = 2.015$) at low temperature (Fig. 1). Both $Fe(II)(DTC)_2$ and $Fe(III)(DTC)_3$ can react with NO directly to produce $Fe(II)(NO)(DTC)_2$ even in the presence of oxygen (details are discussed in Section 4).

Table 1 lists the DTC derivatives used for NO detection. These DTC derivatives can be classified into two groups by the solubility of its iron complex in water.

Table 1
Dithiocarbamate derivatives used for NO trapping

| Solubility in $H_2O$ | DTC | Charge of NO complex | References |
|---|---|---|---|
| Insoluble | DETC | 0 | [8,12,21,22] |
| | PDTC | 0 | [23] |
| Soluble | MGD | 0 | [11,12,14,24] |
| | DTCS | −2 | [12,15,25,26] |
| | ProDTC | −2 | [26–28] |
| | MSD | −2 | [28] |

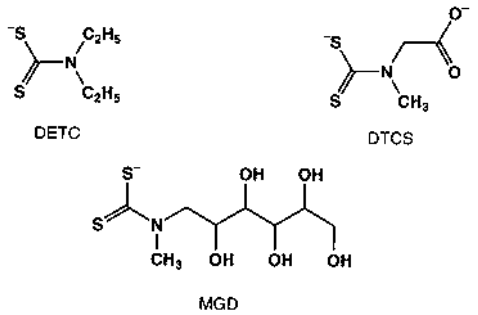


Fig. 2. Dithiocarbamate derivatives used as NO trapping agents.

DETC is a representative which forms a water-insoluble complex, and MGD and DTCS are ones which form a water-soluble complex (Fig. 2). The solubility in water simply depends on the charge of the complex formed; therefore, the relative solubility of the Fe complex is in the order; DTCS > MGD ≫ DETC ≈ 0. As an index of hydrophobicity, $R_f$ values of several Fe(DTC) complexes were determined by reverse-phase thin layer chromatography [28]. This trend is more remarkable in $Fe(NO)(DTC)_2$ complexes. In fact, the solubility of neutral $Fe(NO)(MGD)_2$ is less than 1 mM, whereas dianionic $Fe(NO)(DTCS)_2$ is more than 100 mM (unpublished results). The solubility of Fe(DTC) complex is an important factor in its practical use. For example, procedures for the preparation of the trapping complex [13] and the distribution of the complex administered in biological samples [28–31] are dependent on solubility.

All the DTC derivatives can be also used as an NO trapping agent. Novel functions such as accumulation in specific organs may be realized by modifying a functional DTC group. Nakagawa et al. reported that $Fe(DTCMP)_2$ has a unique property to give the nitric oxide adduct only in the blood [28]. However, DTC derivatives and Fe(DTC) complexes are exogenous substances in biological systems. Special attention should be given to their physiological action and toxicity. DTC derivatives are known to exert pro-oxidant and antioxidant effects in both cell-free and biological systems. For example, some DTC derivatives which form water-insoluble iron complexes prevent the induction of inducible NOS through the inhibition of nuclear factor $\kappa_B$ by functioning as an antioxidant [32]. DTC derivatives also have a metal-chelating property; hence, they have been used in the analysis of trace metals and in the treatment of nickel and copper poisoning [33–35]. In relation to the chelating properties, DETC is known to inhibit the Cu/Zn-superoxide dismutase activity through the withdrawal of copper ion [36], although DTC derivatives which form water soluble metal complexes did not withdraw copper ion [30]. These characteristics of DTC derivatives may affect the states and levels of endogenous NO, of which details remain to be explored.

## 3. Reactivity toward NO and stability of NO complexes

The chemical properties of Fe(II)(NO)$(DTC)_2$, a key compound of this detection method, have been extensively studied. Nitrosyl iron complexes with many kinds of DTC derivatives have been synthesized [4,5]. According to the notation of Enemark and Feltham [6], the electronic configuration of these five-coordinate complexes can be defined as $\{FeNO\}^7$, where the superscript 7 corresponds to the number of electrons on the metal-d and NO-$\pi^*$ orbitals. Fe(II)(NO)$(DTC)_2$ complexes are paramagnetic and have square-pyramidal geometry with a slight displacement of iron out of the basal plane, and with a nearly linear NO group ($\angle$ Fe–N–O = 170–179°) in the apical position [5,6]. Various spectroscopic investigations have shown that an unpaired electron on the complex is in an antibonding orbital which is predominantly $d_{z^2}$ (Fe) and $\sigma^*$ (NO). These earlier studies revealed that the structure, magnetism, and electronic states of Fe(II)(NO)$(DTC)_2$ are modulated mainly by the substituents on amine nitrogen of DTC. These static properties have been well reviewed [4–6].

As an NO trapping agent, the dynamic properties of Fe(DTC) and Fe(II)(NO)$(DTC)_2$ complexes such as reactivity toward NO and stability of NO complexes are also important factors, because the detection is accompanied by a dynamic process and the sensitivity is influenced by these properties. Interestingly, NO trapping efficiency (% yield) of Fe(III)$(DTC)_3$ complex depends on the substituents of the ligand [26]. The difference of the trapping efficiency was clearly shown by tracing the changes in EPR spectra of three water-soluble Fe(II)(NO)$(DTC)_2$ complexes, which are formed from the reaction of Fe$(DTC)_3$ with NO generated from the NOC-5, an NO donor ($t_{1/2}$ = 7.0 min at pH 7.4, 37°C) (Fig. 3) [26,37]. The ligands tested were DTCS, MGD, and ProDTC. In addition, trapping efficiency also depends on the medium. NO trapping efficiency in some media and some other spectral data are summarized in Table 2. The difference in trapping efficiency seems mainly to reflect the difference in stability constant of each complex in media. Steric accessibility of NO to Fe(III)$(DTC)_3$ complex may also affect the efficiency.

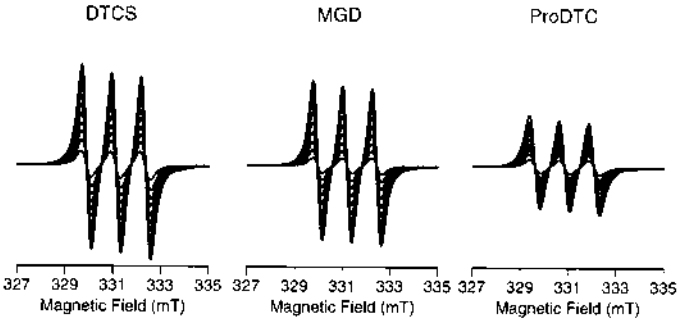


Fig. 3. EPR spectral change of Fe$(DTC)_3$ complexes in Krebs bicarbonate buffer (pH 7.40) in the presence of NOC-5. Successive scans begin 10 min after addition of NOC-5 and are 10 min apart.

Table 2
NO trapping efficiency of water-soluble iron dithiocarbamates and the chemical properties of iron complex with DTC [26]

| DTC | NO trapping efficiency (% yield) [a] | | | | IR (KBr, $cm^{-1}$) | | EPR [b] | |
|---|---|---|---|---|---|---|---|---|
| | Krebs [c] | PBS [d] | HBSS [e] | Tris/HCl [f] | $\nu_{N-O}$ | $\nu_{C-N}$ | $g_{av}$ | $A_N$ |
| DTCS | 60 | 40 | 48 | 95 | 1693 | 1529 | 2.038 | 1.278 |
| MGD | 55 | 35 | 56 | 95 | 1708 | 1519 | 2.039 | 1.274 |
| ProDTC | 30 | 5 | 49 | 82 | 1714 | 1497 | 2.040 | 1.265 |

[a] Calculated from the EPR signal at two hours after addition of NOC-5 solution. Data are means from $n = 3$. S.E. was $<10\%$ in all cases.
[b] Parameters obtained from the spectra of DMSO solution.
[c] Krebs bicarbonate buffer, pH 7.40.
[d] Phosphate buffered solution, 0.1 M, pH 7.40.
[e] Hanks' balanced salt solution, pH 7.20.
[f] pH 7.40.

Practically, the trapping efficiency is useful for quantification of NO produced in biological samples. The amount of NO generated in a sample is calculated from the observed EPR signal intensity. Since only the NO trapped by the complex is evaluated, the actual amount of NO in a sample is often underestimated. The absolute amount of NO can be estimated by considering both the observed EPR signal intensity and the carefully determined trapping efficiency of the complex. The values of trapping efficiency listed in Table 2 will change if the ratio of NO to $Fe(DTC)_3$ complexes deviates significantly from the original ratio of 1:5. A choice of DTC and medium sometimes can bring us a good result. As shown in Table 2, the trapping efficiencies of each DTC derivative and their order differ with media; therefore, it is expected that the detection limit is lowered by an appropriate choice of DTC and media. Improvement in signal-to-noise ratio is effective, especially for the measurement of small amounts of NO such as from endothelial NOS [38,39].

Another interesting property of $Fe(II)(NO)(DTC)_2$ complexes is their stability in ambient air. In general, metal nitrosyl complexes are very air-sensitive. If once they are exposed to the air, oxidative degradation occurs. For $Fe(II)(NO)(DTC)_2$ complexes, it is reported that an analytically pure crystal cannot be prepared under aerobic condition [40]. In practical use as a probe, however, $Fe(II)(NO)(DTC)_2$ complexes are fairly stable to air even in solution. The time profile of the EPR signal intensity shows that more than 70% of the NO complex still remains EPR active at 120 min after introduction of the air [13].

It is interesting and important to know what factors make the NO complex so stable in air. Oxidation of various nitrosyl complexes by $NO_2$ or $X_2$ ($X = I$, Br, Cl, SCN) proceeds readily and results in the six-coordinate $\{FeNO\}^6$ products of $Fe(II)(NO)(DTC)_2X$ [40]. However, there have been few systematic investigations of the reaction of the NO complex and oxygen [41,42]. Oxidative degradation is presumably caused by a reaction of oxygen with the unpaired electron on the $Fe(II)(NO)(DTC)_2$ complex. The electronic state of the unpaired electron is mainly

modulated by substituents on the amine nitrogen of DTC [43]; therefore, a careful scrutiny of correlation between the reactivity toward oxygen and the other chemical parameters such as N–O and C–N stretching frequencies, *g*-values and hyperfine coupling constant of N [26,43] may reveal the factors which stabilize the NO complexes.

## 4. Mechanisms of the reaction of NO with $Fe(III)(DTC)_3$ complex

NO reacts with the $Fe(II)(DTC)_2$ complex as a simple addition, i.e.

$$NO + Fe(II)(DTC)_2 \rightarrow Fe(II)(NO)(DTC)_2 \quad (1)$$

The rate constant of the reaction of NO with $Fe(II)(ProDTC)_2$ was reported to be $(1.1 \pm 0.3) \times 10^8\ M^{-1}\cdot s^{-1}$ [27]. The HPLC profile of the reaction mixture of NO with $Fe(II)(DTCS)_2$ showed that $Fe(II)(NO)(DTCS)_2$ is the only product [44].

Interestingly, NO also reacts directly with $Fe(III)(DTC)_3$ complex to produce NO–$Fe(II)(DTC)_2$ complex [26], indicating that the reaction occurs via reductive nitrosylation. Reductive nitrosylation is well known in heme protein and iron porphyrin complexes [45–50]. Although the detailed mechanism has not been established yet, the overall reaction is formulated by Eq. (2):

$$Fe(III)\text{–}L + 2NO \rightarrow Fe(II)(NO)\text{–}L + NO^+ \quad (2)$$

where L means the remaining ligands such as porphyrins and an axial ligand. Recent quantitative studies of ferriheme protein reductive nitrosylation suggested that the first nitrosyl ligand is eliminated by a nucleophilic attack of $OH^-$ to give the ferrohemeproteins and nitrite ion [50]. The resultant ferrohemeproteins can react further with NO to give the nitrosyl complex.

Studies on the reaction mechanism of NO with $Fe(III)(DTC)_3$, however, are inconsistent with the conventional reductive nitrosylation (Eq. (2)) [44]. The results of HPLC and LC-ESI MS clearly showed that the products of the reaction of NO with $Fe(III)(DTCS)_3$ are $Fe(II)(NO)(DTCS)_2$ and the dimer of DTCS in which two DTCS binds through a disulfide bond (DTCS–disulfide) (Fig. 4). On pulse radiolysis of deaerated aqueous solution of $Fe(III)(DTCS)_3$ in the presence of $NaNO_2$ (NO source), the absorption changes consisted in three phases, as judged from kinetic difference spectra. In the faster phase, radiolytically generated NO reacted with $Fe(III)(DTCS)_3$ with a second-order rate constant of $4.8 \times 10^8\ M^{-1}\cdot s^{-1}$. Subsequently, a transient intermediate with an absorption maximum at 460 nm was formed. In the third step, the species was found to decay on a time scale of seconds to form the resulting final product of $Fe(II)(NO)(DTCS)_2$. Similar spectral changes were observed in the reaction of $Fe(IV)(DETC)_3$ with free DETC ligand. Interestingly, the decay process of the intermediate as well as its formation process was accelerated with increasing the concentration of $Fe(III)(DTCS)_3$. These data suggest that the unreacted $Fe(III)(DTCS)_3$ is concerned with the decay process of the intermediate.

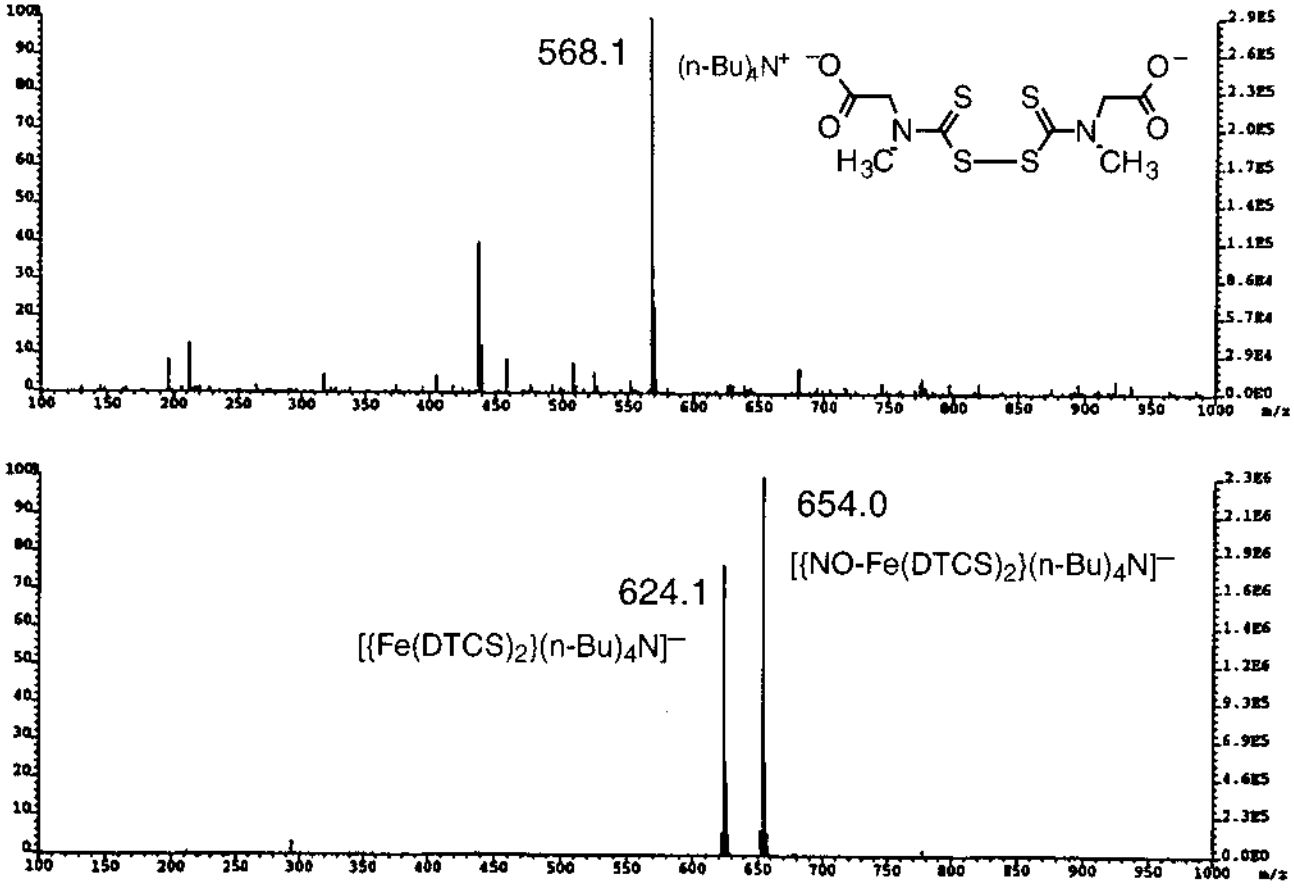


Fig. 4. LC-ESI mass spectra of (upper) DTCS-disulfide and (lower) $[\{Fe(NO)(DTCS)_2\}(n\text{-}Bu)_4N]^-$. Tetra-*n*-butylammonium salt was used as an ion pair reagent. Spectra were measured in the negative mode [44].

The results are best explained by assuming an NO-triggered intercomplex electron transfer, followed by the formation of $Fe(II)(NO)(DTCS)_2$ and DTCS–disulfide (Fig. 5) [44]. Formation of DTC–disulfide from the reaction of $Fe(IV)(DTC)_3$ complex with free DTC ligand has been reported by Chant et al. [51]. The proposed mechanism (Fig. 5) suggests that NO serves as a modulator of redox potential by ligating to the metal center. The role of NO in $Fe(DTC)_3$ system is different from that in ferriheme protein where NO serves as a reducing agent in reductive nitrosylation (Eq. (2)). Another important difference in mechanisms between $Fe(DTC)_3$ system and the ferriheme protein system is the number of NO molecule to reduce the ferric ion. NO reacts with the ferric ion in a ratio of 1:1 in the former case, but in a ratio of 2:1 in the latter case. In that sense, the reaction of NO with $Fe(III)(DTC)_3$ is not strictly reductive nitrosylation. However, it can be said that the proposed mechanism is a novel category of reductive nitrosylation, because Fe(III) ion is actually reduced by the action of NO.

## 5. Summary

This review summarizes the chemical aspects of an NO detection method using Fe(DTC) complexes, especially those of reactivity toward nitric oxide of iron complexes, and its reaction mechanism. The most convincing mechanism of the reaction of NO with $Fe(III)(DTC)_3$ is explained by a novel reductive nitrosylation. The proposed mechanism involving intercomplex electron transfer triggered by NO and concomitant conformational change will provide insights into the interaction of NO with iron-sulfur proteins, which is a major physiological action of NO.

Although many application studies using some DTC derivatives have been reported, little is known about the chemical properties and the reactivity of

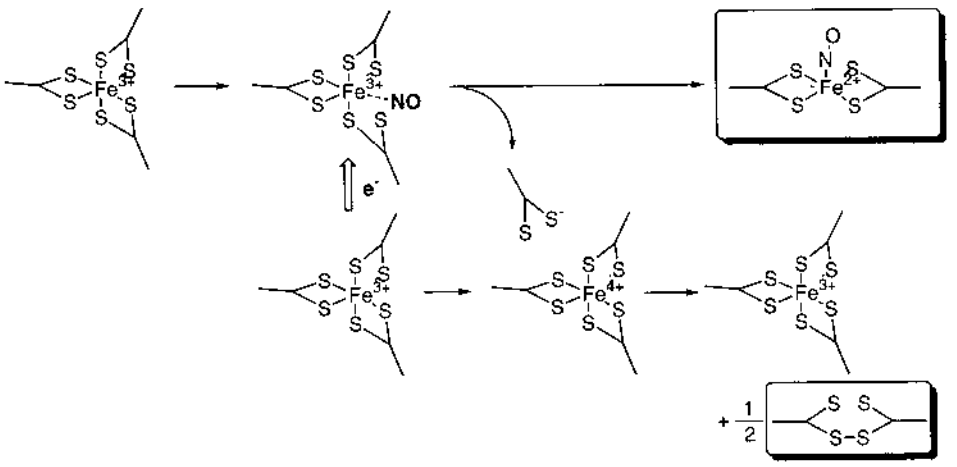


Fig. 5. Proposed mechanism for reductive nitrosylation.

Fe(DTC) complexes, especially of water-soluble ones. How the substituents of the ligand affects the reactivity of Fe(DTC) complexes is an important question to answer. Understanding how the stability of the NO complex is modulated by the substituents will afford useful information on how to design excellent ligands for new NO trapping agent. Systematic investigations should provide answers to these questions.

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