Published in final edited form as:

Dalton Trans. 2009 February 7; (5): 777–786. doi:10.1039/b810230a.

Neutral and reduced Roussin's red salt ester $[\text{Fe}_2(\mu\text{-RS})_2(\text{NO})_4]$ ($\text{R} = n\text{-Pr}$, $t\text{-Bu}$, 6-methyl-2-pyridyl and 4,6-dimethyl-2-pyrimidyl): synthesis, X-ray crystal structures, spectroscopic, electrochemical and density functional theoretical investigations[†]

Rongming Wang, Miguel A. Camacho-Fernandez, Wei Xu, Jian Zhang, and Lijuan Li

Department of Chemistry and Biochemistry, California State University, Long Beach 1250 Bellflower Blvd., Long Beach, CA, 90840, USA

Rongming Wang: ; Miguel A. Camacho-Fernandez: ; Wei Xu: ; Jian Zhang: ; Lijuan Li: lli@csulb.edu

Abstract

A series of Roussin's red salt esters $[\text{Fe}_2(\mu\text{-RS})_2(\text{NO})_4]$ ($\text{R} = n\text{-Pr}$ (**1**), $t\text{-Bu}$ (**2**), 6-methyl-2-pyridyl (**3**) and 4,6-dimethyl-2-pyrimidyl (**4**)) were synthesized by the reaction of $\text{Fe}(\text{NO})_2(\text{CO})_2$ with thiols or thiolates. Complexes **1–4** were characterized by IR, UV-vis, ^1H -NMR, electrochemistry, and single-crystal X-ray diffraction analysis. The IR spectra of complexes **1–4** display one weak and two strong NO stretching frequencies (ν_{NO}) in solution, but only two strong ν_{NO} in the solid. Density functional theoretical (DFT) calculations using complex **1** as model suggest that two spatial isomers of these complexes bear a 3 kcal energy difference in solution. Frequency calculations of the two isomers provide insight on the origin of the vibrational bands and explain the IR observation of complexes **1–4** in the solid state and in solution. Cyclic voltammetry shows two quasi-reversible, one-electron reductions for complexes **1–2** and one quasi-reversible, one-electron reduction for complexes **3–4**. The paramagnetic complexes $[\text{Fe}_2(\mu\text{-RS})_2(\text{NO})_4]^-$ (**1⁻–4⁻**), which are prepared by the chemical reduction of neutral complexes $[\text{Fe}_2(\mu\text{-RS})_2(\text{NO})_4]$ (**1–4**), have also been investigated by EPR spectroscopy. Interestingly, the EPR spectra of complexes $[\text{Fe}_2(\mu\text{-RS})_2(\text{NO})_4]^-$ (**1⁻–4⁻**) exhibit an isotropic signal of $g = 1.998\text{--}2.004$ without hyperfine splitting in the temperature range 180–298 K. The observations are consistent with the results of the calculations, which reveal that the unpaired electron is dominantly delocalized over the two sulfur and two iron atoms. The difference of the g values between the reduced form of Roussin's red ester and the typical dinitrosyl iron complexes is explained, for the first time, by the difference in unpaired electron distributions between the two types of complexes, which provides the theoretical bases for the use of g values as a spectroscopic tool to differentiate these biologically active complexes.

Introduction

A number of investigations have shown that nitric oxide (NO) performs important functions in different biological processes.¹ NO is synthesized by a family of enzymes called NO synthases (NOS).² Once produced, NO can react with thiols and metal centers in proteins to

[†]Electronic supplementary information (ESI) available: Absorption spectra and ^1H -NMR spectra for $[\text{Fe}_2(\mu\text{-RS})_2(\text{NO})_4]$ ($\text{R} = n\text{-Pr}$ (**1**), 6-methyl-2-pyridyl (**3**) and 4,6-dimethyl-2-pyrimidyl (**4**)), the Cartesian coordinates for all the optimized structures of **1–4**, **1⁻–4⁻**, and $\text{Fe}(\text{NO})_2(\text{CO})_2^+$, and the SOMO of $\text{Fe}(\text{NO})_2(\text{CO})_2^+$. CCDC reference numbers 691873–691875.

Correspondence to: Lijuan Li, lli@csulb.edu.

regulate a variety of physiological processes, including controlling blood pressure, preventing platelet aggregation, modulating vasodilation, smoothing muscle proliferation and acting as biological messengers.^{3–4} For example, NO was found to play a regulatory role in the metalloenzyme nitrile hydratase (NHase) by reversibly binding to its iron active site.⁵ Dinitrosyl iron complexes (DNICs) and *S*-nitrosothiols (RSNOs) are thought to be two possible forms for storage and transport of NO in biological systems. At present, researchers have identified that DNICs serve as products of the biosynthetic evolution of NO *in vitro*, intermediates of the iron-catalyzed degradation, and formation of RSNOs.^{4e–f,6} These DNICs have been extensively investigated by EPR and other spectroscopic techniques in biological systems, and exhibit characteristic isotropic EPR signals at $g = 2.03$.⁷ Studies also indicate that the immune system utilizes NO to combat intracellular pathogens and the process produces the dinitrosyl iron complex $\text{Cys}_2\text{Fe}(\text{NO})_2$.⁸ Recently, experimental results also showed that the interaction of NO with Fe-Fur (Ferric uptake regulation protein) produces two dinitrosyl iron species: a major one with an $\{\text{Fe}(\text{NO})_2\}^9$ ($S = 1/2$) electronic structure and a minor one with an $\{\text{Fe}(\text{NO})_2\}^8$ ($S = 0$) electronic structure.⁹ Therefore, there is considerable interest in developing different molecular models of biologically correlative dinitrosyl iron complexes.¹⁰ These models help elucidate the dinitrosyl iron electronic structure, while serving as spectroscopic references and potential NO delivery systems.¹¹

Roussin's red salt esters (RREs), the dinuclear form of DNICs, are diamagnetic and EPR silent due to the antiferromagnetic coupling between the dinuclear irons. It may be prepared by alkylation of Roussin's red salt (RRS) with an alkyl halide or by other methods.¹² It is known that RREs act as a promoter for the carcinogenic properties of other substances for a long period of time. The bactericidal effect of $[\text{Fe}_2(\text{HOCH}_2\text{CH}_2\text{S})_2(\text{NO})_4]$, a water-soluble RRE, on the food-spoilage bacterium *Clostridium sporogenes* has also been investigated and was found to be effective in the millimolar range. In comparison to the experimental results, it is proposed that NO plays an important role in the above courses.^{11b,13} IR, ¹H-NMR and electrochemical properties of $[\text{Fe}_2(\mu\text{-RS})_2(\text{NO})_4]$ ($\text{R} = \text{alkyl}$) and the EPR of the reduction products, $[\text{Fe}_2(\mu\text{-RS})_2(\text{NO})_4]^-$, have been reported by Liaw, Glidewell and Wojcicki.^{12g,14} Over the past several years, Ford and co-workers^{6e,15} have also investigated the photochemical NO release of RREs and made significant progress. They improved the light harvesting ability and enhanced the photochemical response to light with longer wavelengths by varying the R group of the compounds. In this contribution, a series of Roussin's red salt esters $[\text{Fe}_2(\mu\text{-RS})_2(\text{NO})_4]$ ($\text{R} = n\text{-Pr}$, *t*-Bu, 4,6-dimethyl-2-pyrimidyl and 6-methyl-2-pyridyl) were isolated and characterized by IR, UV-vis, ¹H-NMR, electrochemistry and single-crystal X-ray diffraction analysis, and their reduced species, $[\text{Fe}_2(\mu\text{-RS})_2(\text{NO})_4]^-$, were also characterized by IR and EPR spectroscopy. Theoretical calculations using density functional theory (DFT) that were related to IR, EPR, electrochemistry, and some structural parameters, were also performed and the results were compared with the experimental data.

Results and discussion

Synthesis of the complexes

The carbonyl groups of $\text{Fe}(\text{NO})_2(\text{CO})_2$ may be replaced by the nitrogen containing and phosphorus containing ligands to yield the stable dinitrosyl complexes as reported in a previous study.¹⁶ In order to study the effects of different ligands on the properties, the Roussin's red salt esters $[\text{Fe}_2(\mu\text{-RS})_2(\text{NO})_4]$ ($\text{R} = n\text{-Pr}$ (**1**), *t*-Bu (**2**), 6-methyl-2-pyridyl (**3**) and 4,6-dimethyl-2-pyrimidyl (**4**)) were prepared, as shown in Scheme 1, by the reaction of $\text{Fe}(\text{NO})_2(\text{CO})_2$ with the relevant thiols or thiolates in the methylene chloride or methanol. All the reactions were performed under a nitrogen atmosphere according to Schlenk techniques or in a glove box and were monitored by IR spectroscopy. Upon substitution, the carbonyl stretching frequencies disappeared, and the characteristic IR absorptions of nitrosyl groups (ν_{NO}) shifted

to lower frequencies. Meanwhile, the red or green reaction solution gradually turned to dark brown. The observations are consistent with the formation of dinuclear iron complexes as characterized by IR, $^1\text{H-NMR}$, electrochemistry, and single-crystal X-ray diffraction. These complexes were soluble in common organic solvents such as CH_2Cl_2 , THF and acetone. The reduced species, $[\text{Fe}_2(\mu\text{-RS})_2(\text{NO})_4]^-$, were prepared by the reaction of neutral $[\text{Fe}_2(\mu\text{-RS})_2(\text{NO})_4]$ with slightly excess cobaltocene or $\text{Li}(\text{BHEt}_3)$ in THF. The dark brown solution turned to dark green after reduction. The EPR spectra of these complexes exhibit an isotropic signal without hyperfine splitting all the way down to 180 K. It is noteworthy that complex **4** slowly decomposes during the course of the reduction reaction.

Spectroscopic characterization

The infrared spectra of **1–4** were recorded as KBr pellets and in THF solution. When comparing with the starting material, $\text{Fe}(\text{NO})_2(\text{CO})_2$, the characteristic carbonyl stretching frequencies (ν_{CO} , 2087 and 2037 cm^{-1}) for these compounds were not present, indicating that both carbonyl groups were replaced by the sulfur containing ligands, while the typical IR absorptions of nitrosyl groups (ν_{NO}) shift from 1807, 1760 cm^{-1} to 1805–1823, 1770–1793 and 1743–1759 cm^{-1} , suggesting that these sulfur containing ligands only act as weak electron donors. IR spectra of the monoanion complexes $[\text{Fe}_2(\mu\text{-RS})_2(\text{NO})_4]^-$ (**1**[−]–**4**[−]) exhibit the characteristic ν_{NO} stretching frequencies at 1673, 1655 (**1**[−]); 1670, 1650 (**2**[−]); 1690, 1670 (**3**[−]) and 1693, 1674 cm^{-1} (**4**[−]) in THF. As shown in Fig. 1, the corresponding ν_{NO} bands are shifted by *ca.* 100 cm^{-1} to lower energy in comparison with the neutral species due to their negative charge. Interestingly, complexes **1–4** display one weak and two strong NO stretching frequencies in solution, but only two strong NO stretching frequencies in the solid state.

Such a phenomenon had been observed by Liaw^{12g} and Ford.^{15a} Moreover, Gidwell and co-workers reported the existence of *cis* and *trans* spatial isomers in solution by variable-temperature NMR.^{14a–c} In order to understand the differences between the solution and solid state IR spectra, geometry optimizations using density functional theory (DFT) were performed on the *cis* and *trans* isomers of complex **1**. The calculation showed that they only exhibit *ca.* 3 kcal mol^{-1} energy difference. To further explain the vibrational modes of the *cis* and *trans* isomers, the frequency calculations were carried out for both isomers using complex **1** as a model, and the results may be extrapolated for complexes **2–4**. The geometry optimization of the *cis* complex was calculated using the optimized structure of the *trans* complex by changing the R groups to *cis* position and optimizing from this point. Frequency calculations for both isomers were carried out using the optimized structures and applying the same level of theory. It is worth mentioning that although the results of the experimental and calculated frequencies differ quantitatively, the intention of these calculations was not to obtain the exact values, but to find out the vibrational modes of the NO moieties for both conformations. Table 1 lists the experimental and calculated results for the *cis* and *trans* isomers of complex **1**. The *cis* isomer can be considered to possess a C_{2v} symmetry and the *trans* isomer, C_{2h} , if the conformation of the R groups are not considered explicitly. The calculated results for the *cis* isomer show four different vibrational modes named a, b, c and d, which correspond to the two symmetric and two anti-symmetric vibrational modes related to the nitrosyl moieties as shown in Scheme 2. Furthermore, all the modes are IR active, whereas the *trans* isomer results in only two vibrational modes (b and c) with the other two not being IR active (a and d) as shown in Scheme 3. Thus, it only shows two different frequencies derived from two anti-symmetric vibrational modes in the IR spectrum.

It should be pointed out that the IR spectra for the mixture of *cis* and *trans* isomers should have displayed six NO vibration frequencies. However, it can be seen from Table 1 that the *trans* and *cis* isomer produce two identical vibrational frequencies derived from anti-symmetric vibrational modes at *ca.* 1730 and 1704 cm^{-1} . In addition, the *cis* isomer shows two additional

vibrational frequencies derived from symmetric vibrational modes at 1770 and 1694 cm^{-1} , but the latter is very close to the anti-symmetric vibrational frequency at 1704 cm^{-1} . Fig. 2 shows the IR spectra of the *cis* isomer simulated with the Amsterdam density functional (ADF) software and plotted using different peak widths. The result displayed was that the peak width and intensity overlap of the *cis* and *trans* isomers make the vibrational band at 1704 cm^{-1} unresolved in the IR spectrum. It is also worth noting that the calculations reproduce the separation between adjacent bands very well. The calculated results, 40 and 26(23) cm^{-1} , are very close to the experimental values of 35 and 27 cm^{-1} for the Δ_{ab} and Δ_{bc} , so it can be concluded that the calculated value is also consistent with the experimental value for the Δ_{cd} . The bands at 1775 and 1748 cm^{-1} are the result of the overlap of those bands derived from symmetric and anti-symmetric vibration modes of the *cis* and *trans* isomers, but the band at 1810 cm^{-1} is only derived from one of symmetric vibration modes of *cis* isomer. Hence, these complexes actually show only three vibrational bands for the NO moieties in the experimental solution IR spectra. In solution, the small energy difference of two spatial isomers is supplied by the solvent, which allows both isomers to co-exist. In fact, in both THF and CH_2Cl_2 solution, with the increase of spatial hindrance of the R group from complex **1–4**, the intensity of the weak absorption band at $\sim 1810 \text{ cm}^{-1}$, derived from the *cis* isomer, gradually decreases in comparison with two strong ones. In the solid state, since the absence of solvent provides insufficient energy to make the *cis* isomer exist, complexes **1–4** only contain the *trans* isomer.^{12a} Hence, their IR spectra only display two strong NO stretching frequencies.

The electronic absorption spectra of complexes **1–4** were measured in THF. Complexes **1** and **2** show one strong band at 239 and 241 nm and two medium bands at 312, 313 and 363, 358 nm, respectively. These spectra are analogous to the spectra of aqueous RRS, which shows bands at 242, 314 and 374 nm.^{15a} Complex **3** only displays a medium band at 389 nm and no obvious absorption band is observed at higher energy. Complex **4** displays a strong shoulder at 237 nm, but only a medium band at 363 nm. These results show that the absorption spectra of the esters are related to their R group to some extent.

Roussin's red salt esters are diamagnetic and EPR silent due to the antiferromagnetic coupling between the dinuclear irons, which is demonstrated by good NMR spectra. EPR spectra of the reduced species, $[\text{Fe}_2(\mu\text{-RS})_2(\text{NO})_4]^-$, exhibits an isotropic signal at $g = 1.998\text{--}2.004$ (Table 2) without hyperfine splitting in the temperature range 180–298 K. At even lower temperatures, such as 110K, complex **1** displays an axial EPR signal at $g_{\perp} = 2.007$ and $g_{\parallel} = 1.916$, as shown in Fig. 3. There appears to be a slight shoulder at higher fields, which could be due to the rhombic local symmetry rather than the axial symmetry because of the interaction with neighbouring atoms. It is known that the main EPR characteristics of DNICs are g values close to 2.03 and the hyperfine structures arising from the coupling between the unpaired electron and the nitrogen of the NO.¹⁷ In the case of the four anionic RREs (**1–4**[−]), the EPR spectra reveal no hyperfine structures and the g values are in the range of 1.998–2.004, which is close to the free radical. Similar phenomena have also been observed by others.^{12g} In order to interpret the difference, single point calculations on the four optimized structures of the anionic complexes were carried out by including all electrons. The spin density distributions of the singly occupied molecular orbit (SOMO) for the complexes **1–4**[−] are shown in Fig. 4. From the calculations, one can see that there are 60–63% of the electron delocalized on two iron atoms, 25.0–25.8% of the electron delocalized on two sulfur atoms, and only 2–6% of the electron delocalized on four NOs. Because most of the unpaired electron is delocalized over the Fe and S atoms and the most natural abundance of isotopes of these are ⁵⁶Fe and ³²S, whose nuclear spins (I) are zero, the lack of hyperfine splitting in the EPR spectra of these complexes can be understood. The differences between the g values for **1–4**[−] (~ 2.000) and the typical DNICs (2.03) can also be explained by the amount of electron density delocalized on Fe and NO, which dictates the g value. The distribution of electron density on the SOMO of complex $[\text{Fe}(\text{NO})_2(\text{CO})_2]^+$ was calculated by using DFT calculations as well, and the results showed

that Fe and NO moiety possessed 54.4 and 41.8% of the electron density of the SOMO, respectively. It has been noted that the calculated distribution of electrons on the iron in DNICs (54%) is lower than the values obtained by ^{57}Fe -enriched EPR experiments on other $g = 2.03$ species.^{17b} However, it is well known that it is quite common to obtain an over-delocalized distribution of the charge by DFT. Nonetheless, for complex **1**[−]–**4**[−], the amount of electron density on the each iron is in the range of 30–32%, and the total percentage of the electrons on the NO moieties is only 2–6%. Therefore, the difference between the EPR g values and the lack of hyperfine couplings from the NO group in complexes **1**[−]–**4**[−], compared with the typical DNICs, can be well explained by the calculated percentage of the electrons on the metal and NO moiety using DFT method.

To further validate the above mentioned results, additional calculations were carried out to obtain the g values by using complex **2**[−] as an example. The calculated isotropic g value is 1.995, which is very close to the experimental data of 1.999. The calculated anisotropic parameters, $g_{\perp} = 2.014$ and $g_{\parallel} = 1.958$ are in agreement with the experimental data $g_{\perp} = 2.009$ and $g_{\parallel} = 1.965$, reported for this complex.^{12g} These theoretical results explain clearly why hyperfine structures were not observed and corroborate that the electron density of the SOMO is mostly delocalized on the Fe and S atoms.

Electrochemical properties

The redox behaviour of complexes **1**–**4** was studied by cyclic voltammetry (CV) in CH_2Cl_2 . The experiments were performed with the supporting electrolyte tetrabutylammonium hexafluoro-phosphate. All the complexes exhibited irreversible oxidations. In fact, these complexes are very unstable in air. As shown in Fig. 5, complexes **1**–**2** exhibit two quasi-reversible one-electron reductions at -1.16 , -1.84 and -1.20 , -1.81 V, respectively, but complexes **3**–**4** only show one quasi-reversible one-electron reduction at -0.99 and -0.91 V, respectively, even when more negative scan potentials were applied. Complexes **1** and **4** were also investigated at various scan rates up to 2 V s^{-1} . At higher scan rates, complexes **1** and **4** remained quasi-reversible, which indicates that the large peak-to-peak separation is indeed due to the electrochemical quasi-reversibility rather than from the presence of possible coupled chemical complications. All of these reductions can be attributed to iron–sulfur-based redox processes. The half-wave potentials for the first reduction peak clearly turn to more positive values in the order of complex **2**, **1**, **3** and **4**, showing these complexes are easier to reduce along the sequence. This is consistent with the less electron donor effect of the R group in this order. These results indicate that the electronic property of the R group of RREs significantly influences the electrochemical properties of the relevant complexes. The reduction potentials for this series of iron–sulfur nitrosyl complexes were also calculated using DFT. It has been proven that the use of DFT is a reasonably accurate tool for the prediction of reduction potentials.¹⁸ It has been shown to reproduce experimental results satisfactorily on organic compounds and also on metal complexes. In order to calculate the reduction potentials, a thermodynamic cycle depicted in Scheme 4 was used. Considering the expression $\Delta G^{\circ} = -nFE^{\circ}$, the value for the reduction potential *versus* NHE can be calculated from $\Delta G^{\circ}_{\text{red}}(\text{A}/\text{A}^{-}) = \Delta G^{\circ}_{\text{red}}(\text{IV}) + \Delta G^{\circ}_{\text{ox}}$ (Where A represents the neutral complex, and A[−] represents the reduced complex). $\Delta G^{\circ}_{\text{red}}(\text{IV})$ can also be expressed as $\Delta G^{\circ}_{\text{red}}(\text{IV}) = \Delta G^{\circ}_{\text{red}}(\text{I}) + \Delta G^{\circ}_{\text{solv}}(\text{III}) - \Delta G^{\circ}_{\text{solv}}(\text{II})$, where $\Delta G^{\circ}_{\text{red}}(\text{I})$ is calculated by using $\text{EA}_{(\text{g})}$ and the difference in thermal functions to the Gibbs energy of $[\text{Fe}(\text{NO})_2\text{SR}]_2$ due to changes in the electronic, vibrational and rotational partition functions under reduction.^{18c} The terms $\Delta G^{\circ}_{\text{solv}}(\text{III})$ and $\Delta G^{\circ}_{\text{solv}}(\text{II})$ represent the Gibbs energies of solvation in dichloromethane for the anion and neutral species, respectively. The free-energy ($\Delta G^{\circ}_{\text{ox}}$) associated with the reference electrode process $1/2\text{H}_2 \rightarrow \text{H}^{+} + \text{e}^{-}$ has been estimated to be 4.28 eV.^{18a} The calculated results are summarized in Table 3 together with the experimental data. When comparing with the experimental data of the first

reduction potentials for **1–4**, the calculated values are more negative, a similar trend had been noticed by Cramer, Truhlar *et al.*^{18a,18e}

Structural studies

The molecular structures of complexes **1–4** were determined by X-ray diffraction analysis and the structural parameters of complex **2** resemble the reported one.^{12a,d} Single crystals of these complexes were obtained by slow diffusion of MeOH into the corresponding CH₂Cl₂ solutions at ambient temperature. All these complexes show a “chair-shape” structure. Two R groups are almost parallel to each other along opposite directions and form an angle of ~110° with the 2Fe–2S plane. Fig. 6–8 shows the molecular structures of compounds **1**, **3** and **4** viewed from the upper side of the “chair”. The Fe(1)–Fe(1a) distance of *ca.* 2.70 Å suggests that there is a fairly strong interaction between the two iron centers. The average Fe–N(NO) bond distance for complex **1–4** is ~1.670 Å, which is significantly longer than the reported value in the dinuclear complex Fe₂(μ-L)₂(NO)₄ (L = Ph₂PCH₂PPh₂ and Ph₂PC ≡ CPPH₂) (average values: 1.644 and 1.656 Å),^{16a} clearly shorter than the reported value in the dinuclear complex [(N₂C₅H₇)Fe(NO)₂]₂ (N₂C₅H₇ = 3,5-dimethylpyrazolyl) (average value: 1.696 Å)¹⁹ and the tetramer [Fe(NO)₂(Im)]₄ (Im = imidazole) (average value: 1.694 Å),^{16b} but only slightly shorter than the value found in the complex Fe(NO)₂[(SC₆H₄-*o*-NHC(O)CH₃)₂][–] (average value: 1.681 Å).^{10e} The Fe–Fe distance and the average Fe–S bond length for complex **4** are 2.741 and 2.278 Å, respectively, which are longer than the corresponding values (2.698, 2.708, 2.708 and 2.257, 2.257, 2.270 Å) for complexes **1–3**, indicating that complex **4** is essentially more unstable. The observations are in accordance with the results of the electrochemical studies where complex **4** possessed the most positive reduction potential amongst the four complexes.

DFT geometry optimization

Optimizations were carried out for neutral and negatively charged complexes; the spin-unrestricted method was employed for all the complexes. Frequency calculations were also carried out, which show no negative frequencies, proving that the optimized structures are at a minimum. The selected bond distances and angles are listed in the Table 4 along with the calculated values and the single-crystal X-ray diffraction data. All the bond distances are well reproduced by the calculations. The main difference between the X-ray data and the calculated data is that the FeN–O angle is underestimated by an average of 2.5° in calculation. This difference is usually very common for metal nitrosyls and it is thought to have an electronic origin,²⁰ and thus cannot be attributed to packing forces, bearing in mind that calculations were carried out in the gas phase. Even when using very large basis sets, this structural characteristic of metal nitrosyls is difficult to calculate accurately.¹⁷ Therefore, the calculated results using the TZ2P basis set are in fairly good agreement with the experimental data. Optimization using the same level of theory on charged complexes was also performed and the results are shown in the Table 4 as well. Comparing the structural parameters of the charged and neutral species in all four complexes, most of the bond lengths and angles remain with no obvious change but with the exception of the Fe–Fe distance, which exhibited an increase ranged from 0.298–0.382 Å. These results and the single-point calculations show that the extra electron goes mainly onto the Fe atoms. This increase in the electron density on the iron atoms will effect the back-donation from the Fe to the NO moieties by showing larger electron back-donation from Fe to NO for the anion than for the neutral complex, therefore shifting the NO stretching bands to lower frequencies. This is also reflected by the NO distances. The NO distances for the neutral complexes are very close to the X-ray data, only 0.010–0.015 Å longer, but in the anionic complexes, the bond distances are about 0.027–0.036 Å longer than the X-ray data, clearly indicating that the increased electron density on the Fe centers enhances the back-donation to the π*-orbital of the NO moiety, thus weakening the NO bond. In addition, the single point calculations also explain why adding electrons causes weakening the bond between two irons.

The molecular orbital characters of the SOMOs in Fig. 3 are clearly anti-bonding; thus adding electrons into the SOMO actually increases electron–electron repulsion between the iron atoms and contributes to the weakening of the Fe–Fe bond. The composition of the SOMO mainly comes from the d orbital of the metal but also has some 3p character, although in a very small amount for all four complexes, while the sulfur contribution is solely from its p orbital.

Conclusion

In summary, a series of Roussin's red salt esters $[\text{Fe}_2(\mu\text{-RS})_2(\text{NO})_4]$ with different R groups (R = *n*-Pr (**1**), *t*-Bu (**2**), 6-methyl-2-pyridyl (**3**) and 4,6-dimethyl-2-pyrimidyl (**4**)) were prepared. The structures of these complexes have been fully characterized by single-crystal X-ray diffraction. The reduced complexes $[\text{Fe}_2(\mu\text{-RS})_2(\text{NO})_4]^-$ (**1**[−]–**4**[−]) were also prepared by the chemical reduction of the neutral complexes $[\text{Fe}_2(\mu\text{-RS})_2(\text{NO})_4]$ (**1**–**4**). The neutral and reduced species were studied by IR, EPR and electrochemistry. Density functional theory was used for theoretical calculations and the results were compared with experimental parameters generated from IR, EPR, electrochemistry and X-ray crystal analysis. DFT calculations show that *cis* and *trans* isomers of complexes **1** exhibit *ca.* 3 kcal energy difference in solution. Frequency calculations for both isomers were carried out using the optimized structures. In the solution IR spectrum, the bands at 1775 and 1748 cm^{-1} are the result of the overlap of other bands derived from symmetric and anti-symmetric vibration modes of the *cis* and *trans* isomers, but the band at 1810 cm^{-1} was only derived from one of the symmetric vibration modes of the *cis* isomer. In the solid state, these complexes only contain the *trans* isomers and hence their IR spectra only display two strong NO stretching frequencies at 1727 and 1704 cm^{-1} , derived from the two anti-symmetric vibrations. Cyclic voltammetry shows two quasi-reversible, one-electron reductions for complexes **1–2** at −1.16, −1.84 and −1.20, −1.81 V and one quasi-reversible, one-electron reduction for complexes **3–4** at −0.99 and −0.91 V. The calculated values of the first reduction potentials for complexes **1–4** are more negative, but considered to be in a reasonable agreement with the experimental data. The EPR spectra of complexes $[\text{Fe}_2(\mu\text{-RS})_2(\text{NO})_4]^-$ (**1**[−]–**4**[−]) exhibit an isotropic signal at $g = 1.998\text{--}2.004$ without hyperfine splitting even at low temperatures. These observations are consistent with the results of the DFT calculations, which reveal that the SOMO is mostly of metal character with an anti-bonding π^* -orbital and the unpaired electron is dominantly delocalized between the Fe and S atoms. This provides, for the first time, an explanation on the differences in the EPR g values and hyperfine couplings compared with the typical $g = 2.03$ dinitrosyl iron complexes. These theoretical and experimental results enhance the understanding on the properties and possible NO release mechanism of this class of nitrosyl iron complexes.

Computational details

Ground state electronic calculations were carried out using the ADF 2006.01²¹ on the basis of DFT methods. Triple- ζ Slater type function complemented with two polarization functions (TZ2P) was employed for all atoms (Fe, N, C, O and S), except for H in which a double Slater type function was used. In addition, a frozen core approximation was also applied (3p for Fe, 2p for S, and 1s for N, O and C). The same basis set was used for complexes **1–4** and **1 cis** isomer to carry out the frequency calculations; no imaginary frequencies were found for **1–4**, indicating that they are at a minimum. DFT calculations were carried out using an unrestricted wave function with the GGA BLYP (Becke exchange with Lee, Yang, and Parr correlation) functional.²² To take into account the relativistic effects, scalar relativistic corrections to all atoms within the zero-order regular approximation (ZORA) formalism were applied.²³ This methodology was used for all the gas phase geometry optimizations and condensed phase calculations. For single-point calculations, the same TZ2P basis set including all electron (non-frozen cores) was used. Calculations in the presence of solvent were carried out using the conductor-like screening model (COSMO) implemented in ADF using a Klamt surface type,

the solvent used was dichloromethane as pre-defined in ADF.^{24a} The anisotropic and isotropic g values were calculated using the ADF EPR program with a restricted open-shell and spin-nonpolarized wavefunction incorporating spin-orbit (SO) coupling, together with SAOP^{24b} model (ADF/SAOP), ZORA formalism, and TZ2P basis set including all electrons.

Experimental

$\text{Fe}(\text{NO})_2(\text{CO})_2$ was synthesized according to the reported procedure.²⁵ Other chemicals were purchased from Aldrich Chemical Co. and were used without further purification. All solvents were purified and/or dried by standard techniques and degassed under vacuum prior to use. IR spectra were recorded on a Nicolet AVATAR 370 FTIR infrared spectrophotometer. UV-vis spectra were measured on a Varian Cary 300 Bio UV-vis spectrophotometer. EPR measurements were recorded on an X-band Bruker EMX spectrometer equipped with a variable temperature controller and internal frequency counter. The ^1H -NMR spectra were obtained on a Bruker 400 MHz NMR spectrometer, using tetramethylsilane as an internal standard.

Synthesis of complex 1

A mixture of $\text{Fe}(\text{NO})_2(\text{CO})_2$ (0.2 mL, 1.8 mmol) and 1-propanethiol (0.16 mL, 1.8 mmol) in CH_2Cl_2 (10 mL) in the presence of potassium carbonate (414 mg, 3 mmol) was stirred for 72 h at ambient temperature under a nitrogen atmosphere. The reaction was monitored by FTIR and the IR ν_{NO} stretching frequencies shifted from 1807 and 1760 cm^{-1} to 1810, 1775 and 1748 cm^{-1} . The reaction solution was filtered to remove undissolved potassium carbonate, and methanol was slowly added to the filtrate, then the mixed solution was left at $-35\text{ }^\circ\text{C}$ overnight to crystallize in a glovebox. The black crystals, suitable for X-ray crystallography, were collected by filtration and washed with methanol. The solid was dried under vacuum for several hours. Yield: 216 mg (63%). FT-IR $\nu_{\text{NO}}/\text{cm}^{-1}$: 1809, 1774, 1747 (THF); 1810, 1775, 1748 (CH_2Cl_2); 1782, 1729 (KBr). UV-vis spectrum $\lambda_{\text{max}}/\text{nm}$: 239 (sh), 312, 363 (THF). ^1H -NMR (CDCl_3) δ/ppm : 3.00 (6, 4H), 1.89 (m, 4H), 1.11 (t, 6H).

Synthesis of complex 2

Method A—Complex **2** was obtained using the 2-methyl-2-propanethiol by the same procedure as described above for **1**. Yield: 181 mg (49%). FT-IR $\nu_{\text{NO}}/\text{cm}^{-1}$: 1805, 1770, 1743 (THF); 1806, 1771, 1744 (CH_2Cl_2); 1776, 1725 (KBr). UV-vis spectrum $\lambda_{\text{max}}/\text{nm}$: 241, 313, 358 (THF). ^1H -NMR (CDCl_3) δ/ppm : 1.43 (s, 18H).

Method B— $\text{Fe}(\text{NO})_2(\text{CO})_2$ (0.2 mL, 1.8 mmol) and sodium 2-methyl-2-propanethiolate (202 mg, 1.8 mmol) were dissolved in methanol (10 mL) and stirred for 48 h at ambient temperature under a nitrogen atmosphere. The solution turned from green to dark brown. The reaction solution was filtered to remove any dissolved impurity after putting at $-35\text{ }^\circ\text{C}$ overnight. The residue was redissolved in CH_2Cl_2 and methanol was slowly added to the solution. The mixed solution was then left at $-35\text{ }^\circ\text{C}$ in a glovebox overnight to crystallize. The black crystals, suitable for X-ray crystallography, were collected by filtration and washed with methanol. The solid was dried under vacuum for several hours. Yield: 225 mg (61%).

Synthesis of complex 3

A mixture of $\text{Fe}(\text{NO})_2(\text{CO})_2$ (0.2 mL, 1.8 mmol) and 4,6-dimethyl-2-mercaptopyrimidine (252 mg, 1.8 mmol) in CH_2Cl_2 was stirred for 72 h at ambient temperature under a nitrogen atmosphere. The reaction was monitored by FT-IR and the IR ν_{NO} stretching frequencies shifted from 1807 and 1760 cm^{-1} to 1821, 1789 and 1758 cm^{-1} . Methanol was slowly added to the reaction solution, and the mixed solution was left in a glovebox at $-35\text{ }^\circ\text{C}$ overnight to crystallize. The black crystals, suitable for X-ray crystallography, were collected by filtration and washed with methanol. The solid was dried under vacuum for several hours. Yield: 225

mg (49%). FT-IR $\nu_{\text{NO}}/\text{cm}^{-1}$: 1818, 1786, 1755 (THF); 1821, 1789, 1758 (CH_2Cl_2); 1796, 1728 (KBr). UV-vis spectrum $\lambda_{\text{max}}/\text{nm}$: 389 (THF). $^1\text{H-NMR}$ (CDCl_3) δ/ppm : 7.41 (t, 2H), 7.30 (s, 3H), 6.95 (d, 1H).

Synthesis of complex 4

Complex **4** was obtained using 6-methyl-2-mercaptopyridine by the same procedure as described above for **3**. Yield: 298 mg (69%). FT-IR $\nu_{\text{NO}}/\text{cm}^{-1}$: 1823, 1793, 1759 (THF); 1827, 1797, 1763 (CH_2Cl_2); 1791, 1748 (KBr). UV-vis spectrum $\lambda_{\text{max}}/\text{nm}$: 237 (sh), 363 (THF). $^1\text{H-NMR}$ (CDCl_3) δ/ppm : 6.71 (s, 2H), 2.30 (s, 12H).

Crystallography

Crystallographic data and structure refinement parameters of compounds **1**, **3**, and **4** are summarized in Table 5. The structural parameters of complex **2** were omitted from the table because they resembles the reported ones.^{12a,d} The diffraction data of compounds **1–4** were collected on a SMART CCD diffractometer with a graphite-monochromated $\text{MoK}\alpha$ sealed tube ($\lambda = 0.7103 \text{ \AA}$) at 293 K, using a ω scan mode with an increment of 0.3° . Preliminary unit cell parameters were obtained from 45 frames. Final unit cell parameters were obtained by global refinements of reflections obtained from integration of all the frame data. The collected frames were integrated using the preliminary cell-orientation matrix. The SMART software was used for collecting frames of data, indexing reflections, and determination of lattice constants; SAINT-PLUS for integration of intensity of reflections and scaling; SADABS for absorption correction; and SHELXL for space group and structure determination, refinements, graphics and structure reporting.^{26–28}

Electrochemistry

Cyclic voltammetry (CV) was carried out with a CH Instruments electrochemical analyzer 730 A. A three-electrode system consisted of a platinum working electrode, a platinum wire counter electrode and an Ag/Ag^+ reference electrode was used. The reference electrode was separated from the bulk of the solution by a fritted-glass bridge filled with the solvent-supporting electrolyte mixture. The CV data were recorded with the scan rate ranging from 100 mV s^{-1} to 2 V s^{-1} ; and all CV spectra shown in the manuscript were recorded at the scan rate of 100 mV s^{-1} . All potential values are reported vs. ferrocene/ferrocenium ion; the $E_{1/2}[\text{Fe}(\text{Cp})_2/\text{Fe}(\text{Cp})_2^+]$ under our experimental conditions are 0.22, 0.22, 0.22 and 0.20 V for complexes **1–4**, respectively.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

We wish to thank the National Institute of Health (NIH) MBRS SCORE Program (Grant #2 S06 GM 063119) for financial support.

References

1. Richter-Addo, GB.; Legzdins, P. Metal Nitrosyls. Oxford University Press; New York: 1992. (b) Traylor TG, Sharma VS. Biochemistry 1992;31:2847–2849. [PubMed: 1348002] (c) Lai TS, Hausladen A, Slaughter TF, Eu JP, Stamler JS, Greenberg CS. Biochemistry 2001;40:4904–4910. [PubMed: 11305905] (d) Huang J, Hadimani SB, Rupon JW, Ballas SK, Kim-Shapiro DB, King SB. Biochemistry 2002;41:2466–2474. [PubMed: 11841242] (e) Silaghi-Dumitrescu R, Kurtz DM Jr, Ljungdahl LG, Lanzilotta WN. Biochemistry 2005;44:6492–6501. [PubMed: 15850383]

2. (a) Moncada S, Palmerr RMJ, Higgs EA. *Pharmacol Rev* 1991;43:109–142. [PubMed: 1852778] (b) Nathan C. *FASEB J* 1992;6:3051–3064. [PubMed: 1381691] (c) Pant K, Crane BR. *Biochemistry* 2006;45:2537–2544. [PubMed: 16489746]
3. (a) Ignarro LJ, Gruetter CA. *Biochim Biophys Acta* 1980;631:221–231. [PubMed: 6105889] (b) Kelm M, Schrader J. *Circ Res* 1990;66:1561–1575. [PubMed: 2160870] (c) Culotta E, Koshland DE. *Science* 1992;258:1862–1865. [PubMed: 1361684] (d) Ludbrook SB, Scrutton MC, Joannou CL, Cammack R, Hughes MN. *Platelets* 1995;6:209–216. (e) Maes EM, Walker FA, Montfort WR, Czernuszewicz RS. *J Am Chem Soc* 2001;123:11664–11672. [PubMed: 11716723] (f) Dall'Agnoli M, Bernstein C, Bernstein H, Garewal H, Payne CM. *Proteomics* 2006;6:1654–1662. [PubMed: 16404723]
4. (a) Bredt DS, Hwang PM, Glatt CE, Lowenstein C, Reed RR, Snyder SH. *Nature* 1991;351:714–718. [PubMed: 1712077] (b) Abu-Soud H, Stuehr DJ. *Proc Natl Acad Sci U S A* 1993;90:10769–10772. [PubMed: 7504282] (c) Bredt DS, Snyder SH. *Annu Rev Biochem* 1994;63:175–195. [PubMed: 7526779] (d) Griffith OW, Stuehr DJ. *Annu Rev Physiol* 1995;57:707–736. [PubMed: 7539994] (e) Frederik AC, Wiegant IY, Malyshev IY, Kleschyov AL, van Faassen E, Vanin AF. *FEBS Lett* 1999;455:179–182. [PubMed: 10428497] (f) Heo J, Campbell SL. *Biochemistry* 2004;43:2314–2322. [PubMed: 14979728]
5. (a) Noguchi T, Hoshino M, Tsujimura M, Odaka M, Inoue Y, Endo I. *Biochemistry* 1996;35:16777–16781. [PubMed: 8988015] (b) Odaka M, Fujii K, Hoshino M, Noguchi T, Tsujimura M, Nagashima S, Yohda N, Nagamune T, Inoue I, Endo I. *J Am Chem Soc* 1997;119:3785–3791. (c) Bonnet D, Artaud I, Moali C, Pétré D, Mansuy D. *FEBS Lett* 1997;409:216–220. [PubMed: 9202148] (d) Huang W, Jia J, Cummings J, Nelson M, Schneider G, Lindqvist Y. *Structure* 1997;5:691–699. [PubMed: 9195885]
6. (a) Stamler JS, Singel DJ, Loscalzo J. *Science* 1992;258:1898–1902. [PubMed: 1281928] (b) Stamler JS. *Cell* 1994;78:931–936. [PubMed: 7923362] (c) Foster MW, Cowan JA. *J Am Chem Soc* 1999;121:4093–4100. (d) King SB. *Free Radical Biol Med* 2004;37:735–736. [PubMed: 15304248] (e) King SB. *Free Radical Biol Med* 2004;37:737–738. [PubMed: 15304249] (f) Weckslar SR, Mikhailovsky A, Korystov D, Buller F, Kannan R, Tan L, Ford PC. *Inorg Chem* 2007;46:395–402. [PubMed: 17279817]
7. (a) McDonald CC, Phillips WD, Mower HF. *J Am Chem Soc* 1965;87:3319–3326. (b) Drapier JC, Pellat C, Henry Y. *J Biol Chem* 1991;266:10162–10167. [PubMed: 1645341] (c) Lee M, Arosio P, Cozzi A, Chasteen ND. *Biochemistry* 1994;33:3679–3687. [PubMed: 8142366] (d) Boese M, Mordvintsev PI, Vanin AF, Busse R, Mulsch A. *J Biol Chem* 1995;270:29244–29249. [PubMed: 7493954] (e) Kennedy MC, Antholine WE, Beinert H. *J Biol Chem* 1997;272:20340–20347. [PubMed: 9252338]
8. (a) Vanin AF, Varich VY. *Stud Biophys* 1981;86:177–179. (b) Lancaster JR Jr, Hibbs JB Jr. *Proc Natl Acad Sci U S A* 1990;87:1223–1227. (c) Feldman PL, Griffith OW, Stuehr DJ. *Chem Eng News* 1993;71:26–38.
9. D'Autréaux B, Horner O, Oddou J, Jeandey C, Gambarelli S, Berthomieu C, Latour J, Michaud-Soret I. *J Am Chem Soc* 2004;126:6005–6016. [PubMed: 15137765]
10. (a) Ford PC, Lorkovic IM. *Chem Rev* 2002;102:993–1017. [PubMed: 11942785] (b) Wang PG, Xian M, Tang X, Wu X, Wen Z, Cai T, Janczuk AJ. *Chem Rev* 2002;102:1091–1134. [PubMed: 11942788] (c) Ueno T, Susuki Y, Fujii S, Vanin AF, Yoshimura T. *Biochem Pharmacol* 2002;63:485–493. [PubMed: 11853699] (d) Tsai ML, Chen CC, Hsu I, Ke SC, Hsieh CH, Chiang KA, Lee GH, Wang Y, Chen JM, Lee JF, Liaw WF. *Inorg Chem* 2004;43:5159–5167. [PubMed: 15285693] (e) Ford PC, Fernandez BO, Lim MD. *Chem Rev* 2005;105:2439–2455. [PubMed: 15941218] (f) Tsai FT, Chiou SJ, Tsai MC, Tsai ML, Huang HW, Chiang MH, Liaw WF. *Inorg Chem* 2005;44:5872–5881. [PubMed: 16060642]
11. (a) Bourassa JL, Ford PC. *Coord Chem Rev* 2002;200:887–900. (b) Butler AR. *Chem Rev* 2002;102:1155–1165. [PubMed: 11942790] (c) Patra AK, Rowland JM, Marlin DS, Bill E, Olmstead MM, Mascharak PK. *Inorg Chem* 2003;42:6812–6823. [PubMed: 14552634] (d) McCleverty JA. *Chem Rev* 2004;104:403–418. [PubMed: 14871130] (e) Patra AK, Rose MJ, Olmstead MM, Mascharak PK. *J Am Chem Soc* 2004;126:4780–4781. [PubMed: 15080673]
12. (a) Glidewell C, Hannan ME, Hursthouse MB, Johnson IL, Motevalli M. *J Chem Res* 1988;7:212–213. (b) Hayton TW, Legzdins P, Sharp WB. *Chem Rev* 2002;102:935–991. [PubMed: 11942784] (c) Chiang CY, Miller ML, Reibenspies JH, Darensbourg MY. *J Am Chem Soc* 2004;126:10867–10874. [PubMed: 15339171] (d) Harrop TC, Song D, Lippard SJ. *J Am Chem Soc* 2006;128:3528–

3529. [PubMed: 16536520] (e) Tsai ML, Liaw WF. *Inorg Chem* 2006;45:6583–6585. [PubMed: 16903707] (f) Tsai ML, Hsieh CH, Liaw WF. *Inorg Chem* 2007;46:5110–5117. [PubMed: 17444639] (g) Tsou CC, Lu TT, Liaw WF. *J Am Chem Soc* 2007;129:12626–12627. [PubMed: 17900121]
13. (a) Cheng SJ, Sala M, Li MH, Courtois I, Chouroulinkov I. *Carcinogenesis* 1981;2:313–319. [PubMed: 7023729] (b) Liu JG, Li MH. *Carcinogenesis* 1989;10:617–620. [PubMed: 2494003] (c) Cui XY, Joannou CL, Hughes MN, Cammack R. *FEMS Microbiol Lett* 1992;98:67–70. [PubMed: 1459420] (d) Maraj SR, Khan S, Cui XY, Cammack R, Joannou CL, Hughes MN. *Analyst* 1995;120:699–703.
14. (a) Glidewell C, Hyde AR. *Polyhedron* 1985;4:1155–1158. (b) Butler AR, Glidewell C, Johnson IL. *Polyhedron* 1987;6:1147–1148. (c) Glidewell C, Johnson IL. *Chem Scr* 1987;27:441–444. (d) Crayston JA, Glidewell C, Lambert RJ. *Polyhedron* 1990;9:1741–1746. (e) Chau CN, Wojcicki A. *Polyhedron* 1992;11:851–852.
15. (a) Conrado CL, Bourassa JL, Egler C, Wecksler SR, Ford PC. *Inorg Chem* 2003;42:2288–2293. [PubMed: 12665362] (b) Conrado CL, Wecksler SR, Egler C, Magde D, Ford PC. *Inorg Chem* 2004;43:5543–5549. [PubMed: 15332805] (c) Wecksler SR, Mikhailovsky A, Ford PC. *J Am Chem Soc* 2004;126:13566–13567. [PubMed: 15493884] (d) Wecksler SR, Hutchinson J, Ford PC. *Inorg Chem* 2006;45:1192–1200. [PubMed: 16441130]
16. (a) Hörsken A, Zheng G, Stradiotto M, McCrory CTC, Li L. *J Organomet Chem* 1998;558:1–9. (b) Reginato N, McCrory CTC, Pervitsky D, Li L. *J Am Chem Soc* 1999;121:10217–10218. (c) Li L. *Comments Inorg Chem* 2002;23:335–353. (d) Li L, Reginato N, Urschey M, Stradiotto M, Liarakos JD. *Can J Chem* 2003;81:468–475. (e) Wang X, Sundberg EB, Li L, Kantardjieff KA, Herron SR, Lim M, Ford PC. *Chem Commun* 2005:477–479.
17. (a) Dai RJ, Ke SC. *J Phys Chem B* 2007;111:2335–2346. [PubMed: 17295535] (b) Li L, Morton JR, Preston KF. *Magn Reson Chem* 1995;31:S14–S19.
18. (a) Lewis A, Bumpus JA, Truhlar DG, Cramer CJ. *J Chem Educ* 2004;81:596–604. (b) Shamsipur M, Sirouejinejad A, Abbaspour A, Sharghi H, Alizadeh K, Arshadi S. *J Electroanal Chem* 2007;600:345–358. (c) Marcaccio M, Paolucci F, Fontaseni C, Fioravanti G, Zanarini S. *Inorg Chim Acta* 2007;360:1154–1162. (d) Romo S, Fernandez JA, Maestre JM, Keita B, Nadjo L, de Graaf C, Poblet JM. *Inorg Chem* 2007;46:4022–4027. [PubMed: 17447755] (e) Patterson EV, Cramer CJ, Truhlar DG. *J Am Chem Soc* 2001;123:2025–2031. [PubMed: 11456825]
19. Chong KS, Rettig SJ, Storr A, Trotter J. *Can J Chem* 1979;57:3119–3125.
20. Hayton TW, McNeil WS, Patrick BO, Legzdins P. *J Am Chem Soc* 2003;125:12935–12944. [PubMed: 14558842]
21. (a) Guerra CF, Snijders JG, Velde GT, Baerends E. *J Theor Chem Acc* 1998;99:391–403. (b) Velde GT, Bickelhaupt FM, van Gisbergen SJA, Guerra CF, Baerends EJ, Snijders JG, Ziegler T. *J Comput Chem* 2001;22:931–967. ADF2006.01, SCM, Theoretical Chemistry. Vrije Universiteit; Amsterdam, The Netherlands: <http://www.scm.com>
22. (a) Becke AD. *J Chem Phys* 1993;98:1372–1377. (b) Lee C, Yang W, Parr RG. *Phys Rev B: Condens Matter Mater Phys* 1988;37:785–789.
23. (a) Lenthe EV, Baerends EJ, Snijders JG. *J Chem Phys* 1993;99:4597–4610. (b) Lenthe EV, Baerends EJ, Snijders JG. *J Chem Phys* 1994;101:9783–9792. (c) Lenthe EV, Ehlers AE, Baerends EJ. *J Chem Phys* 1999;110:8943–8953.
24. (a) Pye CC, Ziegler T. *Theor Chem Acc* 1999;101:396–408. (b) Schipper PRT, Gritsenko OV, van Gisbergen SJA, Baerends EJ. *J Chem Phys* 2000;112:1344–1352.
25. Heibner W, Beutner HZ. *Anorg Z Allg Chem* 1963;320:101–111.
26. SMART and SAINT for Windows NT Software Reference Manuals v. 5.0. Bruker Analytical X-Ray Instrument Inc.; Madison, WI, USA: 1997.
27. Sheldrick, GM. SADABS, Program for area detector adsorption correction. Institute for Inorganic Chemistry, University of Göttingen; Germany: 1996.
28. Sheldrick GM. *Acta Crystallogr, Sect A: Found Crystallogr* 2008;64:112.

Fig. 1. Infrared spectra of complexes in the nitrosyl stretching region: (a) **2**⁻ in tetrahydrofuran, (b) **2** in tetrahydrofuran and (c) **2** in KBr.

Fig. 2.
The calculated vibrational spectra using different peak widths for the *cis* isomer of complex 1.

Fig. 3.
(a) EPR spectra of complex 3^- at 180 K and (b) complex 1^- at 110 K.

Fig. 4. Spin density distribution of the SOMO for complexes 1^- – 4^- and the calculated composition (%) of the SOMO in terms of Fe, S and NO fragments.

Fig. 5. Cyclic voltammograms of a 2 mM solution of complex **1** (a), **2** (b), **3**(c), and **4** (d) in 0.1 M $[\text{NBu}_4][\text{PF}_6]-\text{CH}_2\text{Cl}_2$.

Fig. 6.
Molecular structure of complex **1** with thermal ellipsoids drawn at the 30% probability,
symmetry code: $a = -x, 1 - y, 1 - z$.

Fig. 7.
Molecular structure of complex **3** with thermal ellipsoids drawn at the 30% probability,
symmetry code: a = 1 -x, 1 -y, -z.

Fig. 8.
Molecular structure of complex **4** with thermal ellipsoids drawn at the 30% probability,
symmetry code: $a = 2 - x, 1 - y, -z$.

R = n-Pr (**1**), tBu(**2**), 6-methyl-2-pyridyl(**3**), 4,6-dimethyl-2-pyrimidyl(**4**)

Scheme 1.

1 CIS ISOMER C_{2V}

Scheme 2.

1 TRANS ISOMER C_{2h}

Scheme 3.

Scheme 4.

Table 1

The experimental and calculated values of vibrational frequencies for *cis* and *trans* isomers of complex **1**. Δ is the difference between adjacent bands

Vibrational frequency/cm ⁻¹							
	a	Δab	b	Δbc	c	Δcd	d
Experiment	1810	35	1775	27	1748	—	Hidden
<i>cis</i> (calcd)	1770	40	1730	26	1704	7	1697
<i>trans</i> (calcd)	—	—	1727	23	1704	—	—

Table 2

The g values of complex **1–4** at different temperatures

T/K	180	200	240	270	298
g					
1	1.9977	1.9978	1.9979	1.9984	1.9988
2	1.9988	1.9988	1.9993	1.9995	1.9988
3	2.0032	2.0030	2.0032	2.0033	2.0036
4	2.0044	2.0039	2.0039	2.0042	2.0040

Table 3

Experimental redox potentials for complexes 1–4^a determined by cyclic voltammetry and calculated theoretical values by DFT calculations

	<i>E</i> /eV	$\Delta G^\circ_{\text{solv}}$ /eV ^b	<i>E</i> [°] _{calc} / <i>N</i> (vs. NHE)	<i>E</i> [°] ₀ → -1,exp/ <i>N</i> (vs. NHE)	<i>E</i> [°] ₋₁ → -2,exp/ <i>N</i> (vs. NHE)
1	-2.04	-1.06	-1.18	-0.76	-1.44
2	-2.05	-1.24	-0.98	-0.80	-1.41
3	-2.28	-1.05	-0.95	-0.59	Not observed
4	-2.11	-1.32	-0.85	-0.51	Not observed

^aCondition: 0.2 mmol dm⁻³ CH₂ Cl₂ solution at ambient temperature, 0.1 mol dm⁻³ [Bu₄ N][PF₆], scan rate of 100 mV s⁻¹, platinum working electrode.

^b $\Delta G^\circ_{\text{solv}} = \Delta G^\circ_{\text{solv}}(\text{III}) - \Delta G^\circ_{\text{solv}}(\text{II})$.

Table 4

List of selected bond distances (Å) and angles (°) from the single-crystal X-ray diffraction data and the corresponding parameters from DFT optimized (BLYP/TZ2P) structures for complex **1–4**

		Fe–N–O/°	Fe–N/Å	N–O/Å	Fe–Fe/Å	S–S/Å	Fe–S/Å
1	X-Ray ^a	170.72	1.670	1.172	2.698	3.618	2.257
	Neutral	168.15	1.689	1.182	2.765	3.670	2.297
	Charged (–1)	169.70	1.684	1.201	3.097	3.665	2.399
2	X-Ray ^a	168.93	1.673	1.170	2.708	3.610	2.257
	Neutral	166.00	1.686	1.185	2.796	3.658	2.302
	Charged (–1)	167.45	1.679	1.206	3.176	3.547	2.381
3	X-Ray ^a	168.52	1.672	1.168	2.708	3.644	2.270
	Neutral	166.75	1.689	1.181	2.785	3.683	2.309
	Charged (–1)	166.70	1.683	1.198	3.169	3.613	2.403
4	X-Ray ^a	168.47	1.682	1.167	2.741	3.639	2.278
	Neutral	166.55	1.690	1.179	2.787	3.679	2.304
	Charged (–1)	167.25	1.684	1.195	3.085	3.697	2.408

^aData from current experimental X-ray diffraction analysis.

Table 5
Crystallographic collection and refinement parameters for **1**, **3** and **4**

	1	3	4
Formula	C ₆ H ₁₄ N ₄ O ₄ S ₂ Fe ₂	C ₁₂ H ₁₂ N ₆ O ₄ S ₂ Fe ₂	C ₁₂ H ₁₄ N ₈ O ₄ S ₂ Fe ₂
<i>M_r</i> /g mol ⁻¹	382.05	480.11	510.13
Size/mm ³	0.18 × 0.14 × 0.08	0.16 × 0.13 × 0.10	0.17 × 0.14 × 0.08
Crystal system	Triclinic	Triclinic	Tetragonal
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>I</i> 4 ₁ / <i>a</i>
<i>a</i> /Å	5.0016(5)	6.3865(7)	19.90180(10)
<i>b</i> /Å	7.9562(9)	7.0898(8)	19.90180(10)
<i>c</i> /Å	9.4709(9)	10.6042(13)	10.06270(10)
<i>α</i> /°	77.803(7)	73.929(7)	90
<i>β</i> /°	80.488(7)	87.184(7)	90
<i>γ</i> /°	79.337(7)	70.935(7)	90
<i>V</i> /Å ³	358.88(6)	435.62(9)	3985.65(5)
<i>Z</i>	1	2	8
<i>F</i> (000)	194	242	2064
<i>ρ</i> _{calcd} /g cm ⁻³	1.768	1.830	1.700
<i>μ</i> /mm ⁻¹	2.321	1.937	1.702
<i>θ</i> range/°	2.22–25.19	3.16–25.13	2.05–29.34
Reflections collected	2615	3566	17 082
Independent reflections	1263 (<i>R</i> _{int} = 0.0844)	1440 (<i>R</i> _{int} = 0.0443)	2736 (<i>R</i> _{int} = 0.0880)
Parameters	82	118	127
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0513	0.0289	0.0339
w <i>R</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.1233	0.0821	0.0770
Goodness of fit	0.943	1.097	0.917