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The dinitrosyliron complex $[Fe_4(\mu_3-S)_2-(\mu_2-NO)_2(NO)_6]^{2-}$ containing bridging nitroxyls: ¹⁵N (NO) NMR analysis of the bridging and terminal NO-coordinate ligands[†]

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The fluxional terminal and semibridging NO-coordinate ligands of DNIC $[Fe_4(\mu_3-S)_2(\mu_2-NO)_2(NO)_6]^{2-}$, a precursor of Roussin's black salt (RBS), are characterized by IR ν (NO), ¹⁵N (NO) NMR and single-crystal X-ray diffraction.

Nitric oxide has been identified as a signaling molecule participating in diverse physiological functions through interaction with NO-responsive targets.¹ Iron-sulfur clusters [Fe-S] were known to be the pivotal prosthetic groups targeted by NO.² The reported nuclear resonance vibrational spectroscopy (NRVS) and EPR-spectroscopic studies reveal that the major products in nitrosylating specific [Fe-S] proteins are the diamagnetic species, e.g. Roussin's red ester (RRE), Roussin's red salt (RRS) or Roussin's black salt (RBS), in addition to the dinitrosyliron complex (DNIC) with a characteristic EPR signal $g_{av} = 2.03$ ³ Also, RBS was characterized as the predominant product upon adding NO to a mutant [4Fe-4S] ferredoxin from Pyrococcus furiosus by using NRVS.^{3b} Recently, on the basis of resonance Raman and low-temperature photolysis FTIR data, the diferrous site of an FMN-free FDP (flavodiiron protein) from Thermotoga maritima (Tm deflavo-FDP) triggering the turnover of 2NO to N₂O via a NO-semibridging Fe^{II}(µ-NO)Fe^{III} intermediate was proposed.⁴ In the synthetic model, {Fe- $(NO)_2$ ⁹ thiolate-containing DNICs converted back to [4Fe4S] clusters via reassembling processes (DNIC \rightarrow RBS \rightarrow $[Fe_4S_4(NO)_4]^{2-} \rightarrow [4Fe-4S]$ cluster) and the transformation of ${Fe(NO)_2}^9$ DNICs into [2Fe2S] clusters mediated by RRS were demonstrated.⁵ In contrast to the inertness of $[Fe_2(\mu_2-S)_2 (NO)_4$ ²⁻ (RRS) toward alkaline medium, RRS readily transforms into the various polynuclear clusters ($[Fe_4(\mu_3-S)_3(NO)_7]^-$ (RBS), $[Fe_5(\mu_3-S)_4(NO)_8]^-$, and $[Fe_7(\mu_3-S)_6(NO)_{10}]^-$) via the proposed protonated intermediate $[Fe_2(\mu_2-SH)_2(NO)_4]$ under acidic

conditions.^{1b} In this report, the complex $[Fe_4(\mu_3-S)_2(\mu_2-NO)_2(NO)_6]^{2-}$ (1) with semi-bridging nitroxyls acting as a key intermediate in the transformation of RRS into RBS *via* the assembling process RRS \rightarrow complex 1 \rightarrow RBS was reported. The IR $\nu(NO)$ and ¹⁵N (NO) NMR spectra implicate that complex 1 is fluxional, scrambling terminal and bridging NO ligands at 320 K. In particular, the ¹⁵N (NO) NMR chemical shift serving as an efficient tool to discriminate terminal and bridging NO-coordinate ligands was demonstrated.

The reaction of $[Fe_2(\mu_2-S)_2(NO)_4]^{2-}$ with two equiv. of {Fe- $(NO)_2$ ¹⁰ DNIC [(TMEDA)Fe(NO)_2] (TMEDA = tetramethylethylenediamine) in CH₃CN afforded $[Fe_4(\mu_3-S)_2(\mu_2-NO)_2(NO)_6]^{2-}$ (1) bearing bridging and terminal NO ligands, characterized by IR, UV-vis, SQUID, ¹⁵N NMR and single-crystal X-ray diffraction (Scheme 1a). The reaction is presumed to proceed via coordinative association of [(TMEDA)Fe(NO)2] and RRS accompanied by release of the labile TMEDA ligand. The straightforward conversion of RRS into complex 1 was monitored by the IR $\nu_{\rm NO}$ (1742 w, 1701 s and 1668 m cm⁻¹ (CH₃CN)). With the aid of isotopic labeling experiments, the reaction of CH₃CN solutions of $[(TMEDA)Fe(^{15}NO)_2]$ and $[Fe_2(\mu_2-S)_2(^{14}NO)_4]^{2-1}$ in a 2:1 molar ratio yielded semi-enriched $[Fe_4(\mu_3-S)_2 ({}^{14}NO)_4({}^{15}NO)_4]^{2-}$ (1- ${}^{15}NO$) identified by the characteristic IR ν_{NO} spectrum (ν_{NO} : 1721 br, 1685 sh, 1657 vs, 1638 sh, 1510 w and 1483 m cm⁻¹ (KBr)), compared to $\nu_{\rm NO}$ (1739 w, 1702 sh, 1685 vs, 1668 s and 1510 m cm⁻¹ (KBr)) for complex 1 (ESI Fig. S1^{\dagger}). The magnitude of ~27 cm⁻¹ of the isotopic shift



Scheme 1 Conversion pathway from RRS to RBS *via* complex **1**.

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Fig. 1 $\,$ ^{15}N NMR spectra of complex 1 in d_6-acetone at (a) 320 K, (b) 300 K, (c) 250 K and (d) 220 K, respectively.

from 1510 cm⁻¹ (μ -NO) to 1483 cm⁻¹ (μ -¹⁵NO) is consistent with the calculated position, based only on the difference in mass between ¹⁴NO and ¹⁵NO.^{5c} The IR ν (NO) spectra suggest that complex 1 is fluxional, scrambling terminal and bridging NO ligands at room temperature. This point has received further support from the study of temperature-varied ¹⁵N NMR of complex 1. As shown in Fig. 1a, the ¹⁵N (NO) NMR spectra showing one broad signal (δ 58.3 ppm vs. MeNO₂) in the NO region also support that complex 1 is fluxional, scrambling terminal and bridging NO ligands in d₆-acetone at 320 K. Interestingly, complex 1 exhibits a diagnostic ¹⁵N (NO) NMR spectrum with bridging NO resonances (δ 200.8 and 200.1 ppm vs. MeNO₂) well-removed from the terminal NO resonances (\$\delta\$ 79.7, 73.5, 43.9, 30.3, 27.1 and 21.9 ppm) at 220 K (Fig. 1d). As elucidated by Mason and co-workers, the bent nitrosyl possessing a lower $n_N - \pi^*$ excitation energy and a greater imbalance of charge in the valence shell giving a much larger deshielding displays the downfield chemical shift (in the range of 300-900 ppm) in the ¹⁵N NMR, compared to that of the linear nitrosyl (in the range of 20–200 ppm).⁶ The presence of two sets of 15 N (NO) NMR peaks (δ 200.8, 79.7, 43.9, 21.9 ppm and δ 200.1, 73.5, 30.3, 27.1 ppm with a 3 : 1 ratio, which are integrated on the basis of the similar environments of individual ¹⁵NO displaying similar relaxation mechanisms in the ladder and boat forms) in complex 1 might be interpreted either as equilibrium isotope effects or as two isomeric forms (ladder-form and, presumably, boat-form (inset of Fig. 3)).⁶ The latter is preferred due to the significant difference in ¹⁵N chemical shift of the two species. It is noticed that the ¹⁵N NMR spectrum of complex 1 at 220 K displays δ 79.7, 73.5, 43.9, 30.3, 27.1 and 21.9 ppm (terminal ¹⁵NO) in d₆acetone falling within the range of δ –7.8 to 25.0 ppm and δ 23.1-76.1 ppm, the characteristic ¹⁵N NMR chemical shifts of ${\rm Fe(NO)_2}^{10}$ and ${\rm Fe(NO)_2}^9$ DNICs, respectively.⁷ Compared to RRS displaying two absorption bands at 264 and 378 nm in the UV-vis spectrum,^{5b} complex 1 shows absorption bands at 273, 343 and 478 nm.

The single-crystal X-ray structure of the $[Fe_4(\mu_3 \cdot S)_2 \cdot (\mu_2 \cdot NO)_2(NO)_6]^{2-}$ unit in K⁺-18-crown-6-ether salt is depicted in



Fig. 2 Molecular structure of complex 1. Selected bond distances (Å) and angles (°): Fe(1)…Fe(2) 2.573(1); Fe(1)…Fe(1)¹ 2.740(1); K(1)…O(2) 2.777(3); Fe(1)–N(1) 1.660(3); Fe(1)–N(2) 1.761(3); Fe(2)–N(2) 1.967(3); Fe(2)–N(3) 1.676(4); N(1)–O(1) 1.184(4); N(2)–O(2) 1.224(4); N(3)–O(3) 1.182(5); N(4)–O(4) 1.181(4); Fe(1)–N(1)–O(1) 170.2(3); Fe(1)–N(2)–O(2) 138.8(3); Fe(2)–N(2)–O(2) 131.0(3).

Fig. 2 and selected bond dimensions are presented in the figure caption. The molecule is symmetrical because of a crystallographically imposed inversion center. The unique laddershaped structure is constructed from one RRS $[Fe_2(\mu-S)_2(NO)_4]$ moiety coordinated by two $[Fe(NO)_2]$ motifs. The Fe(1)... $Fe(1^i)$ distance of 2.740(1) Å is longer than the Fe…Fe bond distance of RRS (2.678 Å), and the relatively short Fe(1)…Fe(2) distance of 2.573(1) Å suggests stronger Fe---Fe interaction. The bridging N(2)–O(2) bond length of 1.224(4) Å (the bond angles Fe(1)-N(2)-O(2) 138.8(3)° and Fe(2)-N(2)-O(2) 131.0(3)°) is comparable to the N-O bond distance of 1.26 Å in NO⁻ and the N–O distance of 1.330(12) Å (the bent Fe–N–O) in $[Fe(NO)_4]^{-.8}$ Of importance, the difference in bond distance between Fe(1)-N(2) (1.761(3) Å) and Fe(2)–N(2) (1.967(3) Å) suggests that the Fe(1) center in complex 1 would retain a ${Fe(NO)_2}^9$ core and Fe(2) permit a semibridging interaction of N(2)O(2) within the $[(NO)Fe(\mu-NO)Fe(NO)_2]$ unit. This N(2)O(2) polarization may be promoted by a semi-bridging electrostatic interaction with the immediate vicinity ${Fe(NO)_2}^{10}$ motif. This type of interaction may increase the nucleophilicity of semi-bridging NO, as is evidenced by site-selective interaction of K^+ at the bridging nitroxyl oxygen (Fig. 2). The 150 cm⁻¹ decrease in ν (NO) (RRS vs. semi-bridging NO of complex 1) is believed to reflect the strong electron donation from the electron-rich ${Fe(NO)_2}^{10}$ motif to N(2)-O(2), thereby weakening both Fe(1)-N(2) and N(2)-O(2) bonds and lowering the corresponding stretching frequency. Interestingly, the semi-bridging-NO stretching frequency (1510 cm^{-1} (KBr)) of complex **1** is comparable to that of a semi-bridging interaction of NO within the [Fe^{II}-{Fe(NO)}⁷] unit, observed in Hr(NO) (mononitrosyl adduct of the nonheme diiron protein hemerythrin) (1658 cm^{-1} (H₂O)) and FDP(NO) (1681 cm⁻¹ (H₂O)).⁴ In addition, the terminal N-O bond lengths (N(1)-O(1) 1.184(4), N(3)-O(3) 1.182(5) and N(4)-O(4) 1.181(4)) of complex 1 are comparable to the range [1.184(2)-1.187(3) Å] of the $\{Fe(NO)_2\}^{10}-\{Fe(NO)_2\}^9$ reducedform dinuclear DNICs.9 Therefore, the electronic structure of complex 1 may be best described as a coordinative assembly of two fully delocalized $[{Fe(NO)_2}^9 - {Fe(NO)_2}^{10}]$ motifs. As is evidenced by the IR $\nu_{\rm NO}$ spectrum (1510 cm⁻¹), the bent Fe-N-O bond angle (Fe(1)-N(2)-O(2) 138.8(3)° and Fe(2)-N(2)-O(2) 131.0(3)°) as well as the relatively long N–O bond distance

(1.224(4) Å), the electronic structure of the bridging NO closely approaches the nitroxyl anion (NO⁻).⁸

In order to gain more information about possible isomers of complex 1, density functional theory (DFT) computations with the BP86 functional¹⁰ and a mixed basis set of SDD ECP¹¹ on Fe and $6-311++G(d,p)^{12}$ on all other atoms were employed on ladder-form A and boat-form B (inset of Fig. 3).¹³ On the basis of the experimental and computational parameters summarized in Table S1,† the geometric parameters and nitroxyl vibrational frequencies of ladder-form A are well comparable to those of complex 1. The boat-form B is unstable compared to the ladder-form **A** by 1.7 kcal mol^{-1} (1.8 kcal mol^{-1}) in the gas phase at 220 K (298 K). The ¹⁵NO-enriched boat-form B-¹⁵NO is found to be slightly unstable than the ¹⁵NO-enriched ladder-form A-¹⁵NO by only 0.6 kcal mol⁻¹ (0.7 kcal mol⁻¹) in the solvation of acetone at 220 K (298 K), which corresponds to an equilibrium constant $K_{B/A} \sim 0.36$ (0.31). Interestingly, this value is consistent with the 3:1 ratio of two isomeric 1-15NO observed in ¹⁵N NMR spectra (Fig. 1 and inset of Fig. 3). The calculated IR spectrum of conformation A displays four active NO vibrational frequencies at 1696, 1682, 1645 and 1533 cm^{-1} , which mainly correspond to the anti-symmetric stretching vibrations of two central Fe-terminal NO motifs (Chart 1a), the two anti-symmetric stretching vibrations of two $\{Fe(NO)_2\}$ motifs (Chart 1b and c), and the anti-symmetric stretching



Fig. 3 The calculated vibrational spectra for ladder-form A (blue line), boat-form B (green line), and the combination of forms A and B (3:1 ratio) (red line).



Chart 1 NO vibrational modes of ladder-form A.

vibrations of two Fe₂-semi-bridging NO motifs (Chart 1d), respectively. In boat-form **B**, the seven active NO vibrational frequencies were calculated to be 1726, 1682, 1678, 1667, 1645, 1540 and 1538 cm⁻¹. The detailed vibrational modes are delineated in ESI Chart S1.† As shown in Fig. 3, the combined calculated spectrum of forms **A** and **B** (3 : 1 ratio), displaying a similar pattern to the experimental IR spectrum of complex 1 (ESI Fig. S1†), also supports two different isomers of complex 1 with a 3 : 1 ratio in the ¹⁵N NMR at 220 K.

The paramagnetic broadening of the ¹⁵N NMR peak of NO groups at 300 K (or 250 K) (Fig. 1) suggests that the singletground-state complex 1 has a low-lying triplet excited state with a small thermal population. In order to estimate the singlet/triplet energy splitting ($\Delta_{S/T}$), the magnetic susceptibility measurement of a powdered sample of complex 1 was collected in the temperature range of 2-300 K at 0.5 T. The temperature-dependent effective magnetic moment decreases from $0.666\mu_B$ at 300 K to $0.201\mu_B$ at 2 K (ESI Fig. S2[†]). The best fit to the data indicates that the low-lying triplet excited state is higher than the singlet ground state by about 1843 \pm 2 cm⁻¹ with the g value for $[{Fe(NO)_2}^9 - {Fe(NO)_2}^{10}]$ fixed at 1.997 $(R^2 = 0.991 \text{ and TIP} = (141.6 \pm 3.3) \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1})$ (ESI Fig. S3[†]). Complex 1, measured in CH_3CN with 0.1 M [^{*n*}Bu₄N]- $[PF_6]$ as a supporting electrolyte at room temperature (scan rate 0.5 V s⁻¹), displays a reversible redox wave at $E_{1/2} = -1.72$ V (vs. Cp_2Fe/Cp_2Fe^+) with $\Delta E_p = 150$ mV and $i_{pa}/i_{pc} = 0.92$ (ESI Fig. S4[†]). The redox potential of -1.72 V (vs. Cp₂Fe/Cp₂Fe⁺) for complex 1 lies between that of RRS ($-2.26 \text{ V} \nu s. \text{ Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+$) and that of RRE $[(NO)_4Fe_2(\mu-SEt)_2](-0.95 \text{ V} \nu s. \text{ Cp}_2Fe/\text{Cp}_2Fe^+).^{5b}$

In contrast to the inertness of RRS toward HSCPh₃, the addition of 1 equiv. of $[Cp_2Fe][BF_4]$ and HSCPh₃ into a CH₃CN solution of complex **1** generates the known $[{Fe(NO)}^{7}-({Fe(NO)}^{9})_3]$ $[Fe_4(\mu_3-S)_3(NO)_7]^-$ (RBS) characterized by IR (ν_{NO}) stretching frequencies shifting from (1742 w, 1701 s and 1668 m cm⁻¹) to (1796 w, 1741 s, 1706 w cm⁻¹), and nitric oxide trapped by $[PPN]_2[S_5Fe(\mu-S)_2FeS_5]$ producing the known complex $[PPN][S_5Fe(NO)_2]$ (Scheme 1b).¹⁴ The conversion of complex **1** into RBS triggered by one equiv. of S-donor species HSCPh₃ and oxidant $[Cp_2Fe][BF_4]$ provided a facile pathway for the transformation of RRS into RBS *via* complex **1**.^{1b}

In summary, the assembly of RRS and ${Fe(NO)_2}^{10}$ DNIC $[(TMEDA)Fe(NO)_2]$ generating the iron-sulfur nitrosyl cluster 1, a precursor of Roussin's black salt (RBS), was discovered. Compared to the {Fe(NO)₂}⁹ and {Fe(NO)₂}¹⁰ DNICs/RREs displaying 15 N (NO) NMR chemical shifts (δ 23–76 ppm) and (δ –7.8 to 25 ppm),⁷ respectively, the first semibridging nitroxyl of complex 1 exhibits the distinct 15 N (NO) NMR chemical shift (δ 200.8 and 200.1 ppm vs. MeNO₂). That is, the 15 N (NO) NMR chemical shift may serve as an efficient tool to discriminate the binding forms of NO (terminal NO vs. semibridging NO and straight M–NO vs. bent M–NO terminal links),⁶ in addition to IR ν (NO) spectroscopy (e.g. observed in the diferrous site of an FMN-free FDP (flavodiiron protein) triggering the turnover of 2NO to N₂O via a NO-semibridging Fe^{II}(µ-NO)Fe^{III} intermediate).⁴ In this study, we further showed how the electronic structure of the coordinated NO groups of RRS is modulated

by the electronic richness of the immediate vicinity ${Fe(NO)_2}^{10}$ motifs.

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