Simultaneous nitrosylation and N-nitrosation of a Ni-thiolate model complex of Ni-containing SOD†

Phan T. Truong, a Ellen P. Broering, a Stephen P. Dzul, b Indranil Chakraborty, c *a Timothy L. Stemmler b and Todd C. Harrop c,b,a

Nitric oxide (NO) is used as a substrate analogue/spectroscopic probe of metal sites that bind and activate oxygen and its derivatives. To assess the interaction of superoxide with the Ni center in Ni-containing superoxide dismutase (NiSOD), we studied the reaction of NO† and NO with the model complex, \(\text{Et}_4\text{N}[^\text{Ni(nmp)}][\text{SPh-}o-\text{NH}_2-p-\text{CF}_3] \) (1; nmp\(^2^–\) = dianion of \(N\)-2-mercaptoethyl)picolinamide; \(\text{SPh-}o-\text{NH}_2-p-\text{CF}_3 = 2\)-amino-4-(trifluoromethyl)benzenethiolate) and its oxidized analogue \(1^\text{o}x\), respectively. The ultimate products of these reactions are the disulfide of \(\text{SPh-}o-\text{NH}_2-p-\text{CF}_3\) and the \(S,S\)-bridged tetrameric complex \([\text{Ni}_4(\text{nmp})_4]\), a result of \(S\)-based redox activity. However, introduction of NO to 1 affords the green dimeric \((\text{NiNO})^{10}\) complex \((\text{Et}_4\text{N})_2[\text{Ni}(\kappa^2-\text{SPh-}o-\text{NNO-}p-\text{CF}_3)(\text{NO})]_2 \) (2) via NO-induced loss of nmp\(^2^–\) as the disulfide and N-nitrosation of the aromatic thiolate. Complex 2 was characterized by X-ray crystallography and several spectroscopies. These measurements are in-line with other tetrahedral complexes in the \((\text{NiNO})^{10}\) class. In contrast to the established stability of this metal-nitrosyl class, the Ni–NO bond of 2 is labile and release of NO from this unit was quantified by trapping the NO with a Co\(^{11}\)-porphyrin (70–80% yield). In the process, the Ni ends up coordinated by two o-nitrosaminobenzenethiolato ligands to result in the structurally characterized trans-(\(\text{Et}_4\text{N})_2[\text{NiSPh-}o-\text{NNO-}p-\text{CF}_3] \) (3), likely by a disproportionation mechanism. The isolation and characterization of 2 and 3 suggest that: (i) the strongly donating thiolates dominate the electronic structure of Ni-nitrosyls that result in less covalent Ni–NO bonds, and (ii) superoxide undergoes disproportionation via an outer-sphere mechanism in NiSOD as complexes in the \((\text{NiNO})^{9/8}\) state have yet to be isolated.

Introduction

Nitric oxide (NO) and its derivatives (termed reactive nitrogen species or RNS) play a vital role in a variety of mammalian (and in some cases bacterial) physiological and pathological processes.\(^*\)\(^\dagger\) Additionally, this gaseous free radical has applications in fundamental research, especially in bioorganic chemistry, where it is utilized as a structural/spectroscopic probe of O\(_2\) (and other reactive oxygen species, e.g., O\(_2\)^{–} and H\(_2\)O\(_2\)) binding/activating metalloenzymes.\(^*\)\(^\dagger\) In general, this approach is employed because metal-nitrosyl (MNO) bonds are highly covalent, and hence more stable, than metal–dioxygen (M–O\(_2\)) adducts.\(^*\)\(^\dagger\) The use of NO as an O\(_2\) analogue is based on similar electronic structures between these diatoms and their reduced derivatives.\(^*\)\(^\dagger\) For example, "NO" (termed the nitrosyl anion), the one electron reduced analogue of NO, is isoelectronic with O\(_2\) with two unpaired \(\pi^*\) electrons in the HOMO. Additionally, NO, while not isoelectronic with O\(_2\)^{–}, has the same ground state electronic structure with a singly occupied \(\pi^*\) MO. Thus, NO interactions with the active sites of O\(_2\)-activating/ROS-breakdown enzymes report coordination (inner-sphere substrate binding) and the extent of substrate bond activation from vibrational spectroscopic measurements of the N–O and M–NO stretching frequencies.

Since 2009, our lab has designed and constructed numerous low molecular weight models of the active site of Ni-containing superoxide dismutase (NiSOD).\(^*\)\(^\dagger\) NiSOD is an unprecedented SOD due to Ni\(^{II/III}\)-coordination to cysteinato-S (CysS) and peptido-N donors (Chart 1), the former of which is susceptible to oxidative modification by the substrate (O\(_2\)^{–}) and products (O\(_2\) and H\(_2\)O\(_2\)) of the SOD catalyzed reaction.\(^*\)\(^\dagger\) Few models employ ligands with the correct spatial disposition and...
electronic nature of the unique \( N_2S_2 \) donor set found in the active site.\(^\text{21-23} \) Moreover, fewer report reversible electrochemical and/or spectroscopic evidence for the \( \text{Ni}^{\text{III}} \) oxidation state due to redox associated with the coordinated thiolates. One model from our lab, namely \( \text{Et}_4\text{N}[\text{Ni(nmp)}\text{(SPh-NO-\( \text{CF}_3 \))]} \) (1; nmp\(^{2-} \) = diamin of the \( N_2S \) ligand \( N-(2\text{-mercaptoethyl})\text{picolinanamide} \), and the anion of the \( \{\text{NiNO}\}^{10} \) complex \( \{\text{Ni}^{2-}\text{SPh-\( \text{NO}-\text{NNO-p-CF}_3\}}\text{[NO]}\}^{2-} \) (2).

Results and discussion

In the anticipation of isolating a Ni-nitrosyl as an analogue of a potential Ni-superoxeno/peroxo catalytic intermediate of NiSOD, we examined the reaction of 1 with NOBF\(_4 \) and \textit{in situ} prepared \( \text{Ni}^{\text{III}} \) with NO. In general, NO does not react with square-planar \( \{\text{Ni(nmp)}\text{[SR]}\} \) (R = simple aryl or alkyl groups) complexes due to their diamagnetic nature. However, when R contains a potentially bidentate chelate, as in 1, a different course takes place. For instance, exposing a DMF solution of 1 with NO(g) for 30 s resulted in a gradual change of the solution from dark-red to green over several minutes. Workup of this reaction indicated a Ni-nitrosyl based on the strong double-humped peak in the \( \text{N-O} \) stretching (\( \nu_{\text{NO}} \)) region of the IR spectrum (\( \nu_{\text{infra}} \)). Subsequent crystallization of the bulk material from MeCN/\( \text{Et}_2\text{O} \) at \(-20^\circ\text{C} \) resulted in green crystals of a dinuclear thiolate-bridged \( \{\text{NiNO}\}^{10} \) complex \( \{\text{Et}_4\text{N})\text{[Ni}^{2-}\text{SPh-\( \text{NO}-\text{NNO-p-CF}_3\}}\text{[NO]}\}^{2-} \) (2) as depicted in Fig. 1 with selected metric parameters listed in Table 1. The Ni centers in 2 are distorted tetrahedral (\( \tau_4 = 0.73 \) (ref. 29)) resulting from \( \text{N}_2\text{S}_2 \) coordination of the thiolato-S/deprotonated amine-N of the \( S \)-bridged o-nitrosaminobenzenethiolate and a terminal nitrosyl. To our knowledge, complex 2 represents the first example of a structurally characterized first-row metal complex with both a coordinated nitrosyl and amine-N-bound nitrosamine. In accord with other tetrahedral \( \{\text{NiNO}\}^{10} \) complexes,\(^\text{28} \) the Ni-N(O)
However, the structure is more biased towards the nitrosamino
similar metric parameters. The coordinated nitrosamine is bent
2-coordinate/S-bound Ni-nitrosyls,
30 distances/angles in similar ranges. Even neutral/cationic P-
contain Ni
1.683 Å.
X-ray crystal structure of
1.683 Å,
0
versus
O distances of 1.299 and 1.269 Å, respectively. These values
N: 1.971(2) 1.974 Å,
N: 1.299(3) 1.32 Å,
N: 1.269(3) 1.254 Å,
N: 96.66(2) 90.05 Å,
N: 86.21(6) 86.67 Å,
N: 99.10(6) 98.40 Å,
N: 121.8(5) 125.92 Å,
N: 109.8(6) 113.43 Å,
N: 133.6(5) 132.15 Å,
N: 167.8(12) 171.42 Å,
N: 114.2(2) 115.80 Å,
N: 0.73 0.72 Å.
Table 1 Selected bond distances (Å) and bond angles (deg) from the
X-ray crystal structure of 2, compared with the DFT-optimized model
2

| Bonded pair | X-ray structure 2 | DFT (BP86/def2-TZVPP) optimized structure 2
|------------|------------------|---------------------------------------------------------------|
| Ni–S1      | 2.3169(7)        | 2.294 Å                                                      |
| Ni–S1’     | 2.3355(6)        | 2.344 Å                                                      |
| Ni–N1      | 1.659(7)         | 1.648 Å                                                      |
| Ni–N1’     | 1.971(2)         | 1.974 Å                                                      |
| N2–O1      | 1.182(8)         | 1.191 Å                                                      |
| N1–N3      | 1.299(3)         | 1.32 Å                                                       |
| N3–O2      | 1.269(3)         | 1.254 Å                                                      |
| N2–O1’     | 96.66(2)         | 90.05 Å                                                      |
| N1–N1’     | 86.21(6)         | 86.67 Å                                                      |
| S1–Ni–S1’ | 99.10(6)         | 98.40 Å                                                      |
| S1–Ni–N1  | 121.8(5)         | 125.92 Å                                                     |
| N2–Ni–S1’ | 109.8(6)         | 113.43 Å                                                     |
| N1–Ni–N2  | 133.6(5)         | 132.15 Å                                                     |
| N1–N2–O1  | 167.8(12)        | 171.42 Å                                                     |
| N1–N3–O3  | 114.2(2)         | 115.80 Å                                                     |
| r4         | 0.73             | 0.72 Å                                                       |

distance is short (1.659 Å), the N–O bond (1.182 Å) is inter-
mediate between free NO’ (1.15 Å) and 1HNO (1.21 Å),39 and the
Ni–N–O bond angle is close to linear albeit slightly bent (167.8°)
(see Table 1). Complex 2 is analogous to the limited number of
four-coordinate/S-bound Ni-nitrosyls,30–34 fewer of which contain
Ni–Sthiolate bonds,11,33 which display Ni–N(O) (1.663–1.683 Å),
N–O (1.131–1.173 Å), and Ni–N–O (156.6–173.9°) distances/angles in similar ranges. Even neutral/cationic P,35–40
and N-bound,41–43 L,
Ni–NO/L,
Ni–NO complexes exhibit similar metric parameters. The coordinated nitrosamine is bent
(N–N–O: 115.4°), i.e., sp2-hybridized nitroso-N, with N–N and
N–O distances of 1.299 and 1.269 Å, respectively. These values
suggest a small degree of delocalization in the R–N–N–O unit.
However, the structure is more biased towards the nitrosamino
R–N–N–O versus diazoate R–N–N–O– resonance form. To
compare, the structure of syn-methanediazoate (N–N: 1.246 Å,
N–O: 1.306 Å) reflects the true double bond character in an
authentic R–N==N–O unit.44 These values are somewhat
comparable to other N-bound nitrosamine complexes,45–46
especially [CpNi[PPh3][ON(Me)2-p-NO2]] (1)’ (N–N: 1.327 Å, N–O:
1.249 Å, N–N–O: 113.1°). Structures of coordinated nitroso-N-
metal complexes (vs. amine-N as in 2) also afford similar structural parameters in the RNNO.47 In contrast, O-bound
nitrosamine complexes appear to favor more of a resonance
delocalized structure as the N–N (1.275–1.288 Å) and N–O
(1.251–1.275 Å) distances in a series of [FeIII(P)(ONR2)]2+ (P =
porphyrin) complexes are nearly identical and result in a single
15N-sensitive peak in the IR due to overlapping\(\rho_{\text{NO}}\)/\(\rho_{\text{NO}}\) modes.49–51

Complex 2 was characterized by a variety of spectroscopic
methods. The solid-state IR spectrum (KBr matrix) of 2 exhibits
two closely spaced, but well-resolved, \(\rho_{\text{NO}}\) at 1759 and 1743 cm\(^{-1}\)
(1724, 1708 cm\(^{-1}\) for 2–\(15\)NO; \(\rho_{\text{NO}}\): 35 cm\(^{-1}\); see Fig. 2). These
values fall in the range of known tetrahedral, neutral, and
anionic \(\{\text{NiNO}\}\) complexes.28 Because 2 is of \(C_2\) symmetry (cis
NO, syn bridging thiolates), two IR-active N–O vibrational
modes are expected. The other feasible isomer of 2 would be of
\(C_1\) symmetry (trans NO, anti bridging thiolates) and would
display one IR-active N–O stretch. Indeed, the IR spectrum of 2 in
DMSO exhibits one \(\rho_{\text{NO}}\) at 1784 cm\(^{-1}\) suggesting possible cis/
trans-NO conversion in solution (or an averaged \(\rho_{\text{NO}}\) value due to
rapid tumbling) or thiolate-bridge splitting to yield a four-

Fig. 1 X-ray structure of the anionic portion of 2 with the atom
labeling scheme (50% thermal probability). H atoms and Et4N+
ion are omitted for clarity.

![Image](https://via.placeholder.com/150)

**Fig. 2** (Top) Solid-state IR of the \(\rho_{\text{NO}}\) region for 2 (black) and 2–\(15\)NO (blue) in a KBr matrix. (Bottom) High resolution ESI-MS(–) of 2 with the theoretical isotopic distribution.
coordinate mononuclear $\{\text{NiNO}\}^{10}$ with DMSO as the fourth ligand, i.e., $[\text{Ni}(\text{SPh-o-NNO-p-CF}_3)\{\text{DMSO}\}(\text{NO})]$. The $^1H$ NMR spectrum of 2 in CD$_3$CN (Fig. S6f) or DMSO-d$_6$ (not shown) are similar and thus do not distinguish any of the proposed structures. Comparable IR spectral changes in the opposite direction are observed for the other thiolate-supported anionic dinuclear $[\text{NiNO}]^{10}$, (Et$_4N$)$_2[\text{Ni}_2(\text{NO})_2(\mu$-$\text{SPh})_2(\text{SPh})_2] \text{(II)}$, with trans NO ligands ($\delta_{\text{FNN}}$: 1709 cm$^{-1}$ in KBr; 1751, 1721 cm$^{-1}$ in THF). A similar situation is described for a pyrazolated bridged anionic dinuclear $[\text{NiNO}]^{10}$ complex. IR peaks arising from the nitrosamine were not as obvious due to multiple overlapping peaks in the region (Fig. S5f). However, $^{15}N$-sensitive peaks in the IR of 2 at 1342 and 1258 cm$^{-1}$ (1326, 1249 cm$^{-1}$ in 2-$^{15}$NO) are assigned as $\nu_{\text{FNO}}$ and $\nu_{\text{NN}}$, respectively. In comparison, a series of secondary nitrosoamines display $\nu_{\text{FNO}}$: 1428–1463 cm$^{-1}$ and $\nu_{\text{FNN}}$: 1035–1154 cm$^{-1}$ in CCl$_4$.$^{44}$ Therefore, a significant degree of delocalization occurs in the RNNO unit of 2 to cause the corresponding downshift in $\nu_{\text{FNO}}$/upshift in $\nu_{\text{FNN}}$. While no paramagnetically shifted resonances are observed in the $^1H$ NMR (CD$_3$CN) of 2, several species are indicated in freshly prepared solutions (Fig. S6f) that are likely caused by the lability of the Ni–NO bond and presence of nmpS$_2$ (vide infra).

The $^{15}N$ NMR spectrum of 2-$^{15}$NO confirms multiple solution speciation with four major peaks in the range for nitrosoamines and linearly coordinated NO ($\delta$: 40–190 ppm in CD$_3$CN, vs. CH$_3$NO$_2$, Fig. S7f).$^{34}$–$^{37}$ Moreover, the $^1H$ NMR of thiolate-bridged dinuclear complex I displays broadened aryl-$H$ resonances caused by rapid exchange of PhS$_2$ ligands because of disproportionation to the mononuclear (Et$_4N$)$_2[\text{Ni(NO)(SPh)}]$ \text{(II)} and an uncharacterized $[\text{Ni(NO)(SPh)}]$ species.\textsuperscript{33} However, high-resolution electrospray ionization mass spectrometry (HR-ESI-MS; negative mode) displays one dominant compound with the formula and isotopic distribution consistent with the diahronic portion of 2 ($m/z$: 307.926, $z = 2$, Fig. 2, S8 and S9f) and 2-$^{15}$NO ($m/z$: 309.920, $z = 2$, Fig. S10 and S11f), although this measurement does not discriminate against cis and trans NO conformers. Another minor peak in the HR-ESI-MS($-$) is centered at $m/z$: 248.960 ($z = 2$, Fig. S8f) that suggests a new $[\text{Ni}(\text{N}_2\text{S}_2)]^{12}$ species through loss of the Ni-coordinated NO and one Ni (vide infra).

Solutions of 2, especially in donor solvents such as MeCN or DMSO, gradually lose their green color to give red-brown solutions more reminiscent of square-planar Ni$^{II}$-N$_2$S$_2$ complexes.$^{35}$–$^{38}$ Even freshly prepared CD$_3$CN solutions of 2 exhibit multiple peaks in the $^1H$/$^{15}N$ NMR, and ESI-MS shows a new species with a Ni isotopic pattern at $m/z$: ~249 (vide supra). This change is enhanced when vacuum is applied and FTIR spectra of these reaction mixtures lack any $\nu_{\text{FNO}}$ suggesting the loss of coordinated NO from 2 to generate a new Ni species. Slow diffusion of Et$_2$O into MeCN solutions of 2 that have been left standing for several weeks result in crystals (10–20% isolated yield from crystallization) of a square-planar ($\tau_4 = 0.12$) Ni$^{II}$ compound where two N,S-chelating o-nitrosoaminobenzothiolate ligands bind to Ni in a trans configuration, viz. trans-([Et$_4N$]$_2[\text{Ni}(\text{SPh-o-NNO-p-CF}_3)]_2$) (3) (Fig. 3). The bond lengths (Ni–S: 2.072 Å, Ni–N: 1.896 Å) and angles (Table S3f) are similar to other planar Ni$^{II}$-N$_2$S$_2$ complexes that contain $\kappa^2$-N,S-0-aminobenzothioliligands.$^{39}$–$^{41}$ The Ni–N distance in 3 is shorter than the typical Ni–N$_2$amine bond and reflects the enhanced donor strength of the deprotonated nitrosamino-N, which is comparable to, although weaker than, a Ni–N$_2$carbamido (~1.86 Å).$^{53,55}$ No evidence for a coordinated ligand radical is evident from the X-ray structure (i.e., short C–S, C–N distances of the coordinated o-aminobenzothioligand) and confirm the N,S-ligand is a closed-shell dianion. The R–N–O–N linkage in 3 (avg. of two crystallographically distinct molecules, N–N: 1.309 Å, N–O: 1.264 Å; avg. N–N–O: 115.2°) is unremarkable from 2. $^1H$ and $^{15}N$ NMR (RN$^{15}$O, 6: 194 ppm vs. CH$_3$NO$_2$) of crystals of 3 are consistent with the X-ray structure and analogous to other nitrosamines (Fig. S13 and S14f).$^{55,57}$ As expected, the IR of 3 lacks the intense $\rho_{\text{FNO}}$ from the NiNO of 2 (although IR and ESI-MS show that some 2 remains even in crystals of 3, Fig. S12f) and the $\rho_{\text{FNO}}$ and $\rho_{\text{NN}}$ of the R–N–O–N unit is similar. HR-ESI-MS($-$) confirms this formulation with peaks corresponding to [M–2Et$_4N$]$^{2+}$ ($m/z$: 248.960, $z = 2$, for 3; $m/z$: 249.957, $z = 2$, for 3-$^{15}$NO) as the prominent peak (Fig. S15–S18f).

To confirm that NO(g) is released from 2 (forming 3 among other products), solutions of 2 were mixed with the NO(g) trap [Co(T(–OMe)PP)] (T(–OMe)PP = 5,10,15,20-tetrakis(4-methoxyphenyl)-21H,23H-porphine).$^{61}$ For example, mixing 2 and the Co$^{III}$-P (1 : 2) in CH$_2$Cl$_2$ at RT for 24 h resulted in the (CoNO)$_8$ complex [Co(T(–OMe)PP)](NO) in ~70% avg. yield as quantified by $^1H$ NMR (CD$_3$Cl$_2$) and further verified by IR spectroscopy using 2-$^{15}$NO (Fig. S21–S23f). Notably, the reaction mixture becomes red over the course of the reaction. Workup of this solution after separating the Co–P compounds (MeOH-insoluble) reveals the presence of 3 (MeOH-soluble) via $^1H$ NMR to confirm the fate of the (NiNO)$_{10}$ complex 2. To eliminate bimolecular NO-transfer via a putative Co···NO···Ni intermediate, NO(g) release was further verified by vial-to-vial trapping reactions wherein a CH$_2$Cl$_2$ solution of the Co$^{III}$-P was separated from an MeCN solution of 2 (Co$^{III}$-P in excess, see the ESI†). Carrying out this reaction confirmed that NO(g) is indeed released from 2 (or 2-$^{15}$NO) to generate the (CoNO)$_8$ porphyrin complex (80% avg. yield) as shown by $^1H$ NMR and IR measurements (Fig. S24f). In contrast, no reaction takes place between THF solutions of 2 with [Fe(TPP)Cl] (1 : 2; TPP = 5,10,15,20-tetraphenylporphyrin), a common HNO (or NO$^*$) trap.$^{64}$ Although [NiNO]$^{10}$ has not been characterized as

Fig. 3 X-ray structure of the dianion of 3 with the atom-labeling scheme (50% thermal probability). One of two crystallographically distinct molecules shown. H atoms, Et$_4N$ counterions, and solvent of crystallization (Et$_2$O) are omitted for clarity.
a particularly labile EF notation, we note that the majority of these complexes are cationic or neutral without coordinated thiolate ligands.28 Indeed, the thiolate-ligated {Ni(NO)}10 complex III photochemically releases NO to [Co(TPP)] in MeCN suggesting some lability in the Ni–NO bond. Furthermore, the RN–NO bond is quite stable (as noted by formation of some lability in the NiIII–NO bond). The formation of the frontier MOs of 2* show that, much like other {Ni(NO)}10 systems with Tp ligands (Fig. S25†). On the other hand, the HOMO (Fig. 4) and HOMO–1 have little contribution from NO, but large contributions from Ni-dπ (38.0%) and S-pτ (19.3%) orbitals of the Ni(μ-SR)2Ni core. The HOMO is antibonding in nature and suggests a thermally unstable structure. As expected from analogous {Fe(NO)}7 systems, based on the increased donor strength of the anionic nitrosamine-N/thiolate-S supporting ligands in 2*, the covalency in the Ni–N–O unit is less than in TpNi–NO complexes and rationalizes the observed lability of the Ni–NO bond and the Ni(μ-SR)2Ni core in 2.

DFT computations on 3* were performed in the same fashion as for 2*. Geometry optimized 3* is square-planar (τd = 0.09) with metric parameters on-par with the X-ray structure of 3* and within the error of the DFT method (Table S9†). Unlike 2*, the π* HOMO of 3* is comprised primarily of Ni(dπ)/S(pτ) contributions (Fig. S26†), typical of planar NiIII–N2S2 complexes with strong-field ligands and suggests a highly covalent Ni–SR bond.15

The formation of 2 likely follows a mechanistic path analogous to those observed in the reductive nitrosylation of Cu-ammine systems, where one-equiv. of NO reacts with CuIII–NR2 complexes to yield R2N–NO and deligated CuI.76,77 The difference here is that the nitrosated ligand remains coordinated and the resulting paramagnetic Ni binds NO radical. Our working model is depicted in Scheme 2. Complex

![Scheme 2 Working model for the formation of (Ni(NO))10 complex 2 and NiIII–N2S2 complex 3 starting from NiII–N2S2 monomer 1. RSSR: disulfide of nmp2 –, i.e., N-(2-mercaptoethyl)picolinamide. Intermediates represented in brackets have not been spectroscopically identified. The py-N of RSSR is a possible H+ receptor.](image)

**Fig. 4** DFT (OLYP/def2-TZVPP) optimized structure of 2* (left) with natural population analysis charges in blue and HOMO (right).
1 is likely in resonance with a distorted tetrahedral species which places the anilido-N in the coordination sphere. This proposal is supported by the presence of low intensity peaks in the $^{1}H$ NMR spectrum of 1 and may explain the difficulty in crystallizing this complex.\textsuperscript{46} On the other hand, X-ray absorption spectroscopic (XAS) characterization of 1, not reported previously, suggests a four-coordinate planar Ni\textsuperscript{II} center (XANES analysis, see Fig. S3\textsuperscript{t}) with two O/N- and S-ligands at 1.90 Å and 2.17 Å (EXAFS, Fig. S3, Table S4\textsuperscript{t}), respectively. Thus, 1 is structurally analogous to other [Ni(nmp)]\textsuperscript{2} complexes at least in the solid-state. Introduction of NO(g) can then result in either: (i) reduction of Ni\textsuperscript{II} to Ni\textsuperscript{I} and formation of NO\textsuperscript{+} that nitrosates the coordinated amine, or (ii) nitrosylation of Ni to yield [Ni(NO)]\textsuperscript{10} with the electron originating from the coordinated thiolate of nmp\textsuperscript{2}− to result in the disulfide. Our results do not differentiate either of these transformations, but the disulfide of nmp\textsuperscript{2}− (i.e., nmpS\textsubscript{2}−/H NMR and IR of the reaction mixture, see Fig. S19 and S20\textsuperscript{t}) is spectroscopically observed in the reaction mixture and checked against independently synthesized nmpS\textsubscript{2}. Thus, the fate of one proton and one electron is reasonably confirmed. At this point these intermediates can react with another equiv. of NO to yield the three-coordinate precursor to 2. Compound 3 forms through either disproportionation (shown in Scheme 2) to yield a Ni\textsuperscript{II} species or ligand rearrangement \textit{via} the loss of a Ni\textsuperscript{I}–NO fragment (not shown). In ligand rearrangement, the products would be a Ni\textsuperscript{I}–S\textsubscript{2}S\textsuperscript{2} precursor to 3 (3-PC), an L–Ni\textsuperscript{I}–NO species (L = solvent), and free NO. Ultimately this Ni\textsuperscript{I} intermediate oxidizes 3-PC to generate Ni\textsuperscript{II} complex 3 and an L–Ni\textsuperscript{II}–NO complex that would presumably release NO(g) as evidenced by the NO(g) trap experiments (\textit{vide supra}). While the reaction mechanism for the conversion of 2-to-3 is likely more complex, similar chemistry has been proposed for Heterocyclic carbene (NHC) Ni-nitrosyls.\textsuperscript{30,78} The details of this mechanism are still under investigation.

\section*{Conclusions}

In conclusion, NiSOD model complex 1 reacts with NO(g) in the Ni\textsuperscript{II} state to form the metastable [Ni(NO)]\textsuperscript{10} dimeric complex 2 \textit{via} loss of the nmp\textsuperscript{2}− ligand as the disulfide and N-nitrosation of the o-aminobenzenethiolate ligand. Reaction of NO with 1\textsuperscript{ox}, or NO\textsuperscript{+} with 1, only yields the S,S-bridged tetrameric compound [Ni\textsubscript{4}(nmp)\textsubscript{4}]\textsuperscript{4−} \textit{via} oxidation of the aromatic thiolate ligand. While any reaction with NO (S = 1/2) is generally unexpected for square-planar (S = 0) Ni\textsuperscript{II} complexes, this Ni-nitrosyl likely forms due to an equilibrium mixture of 1 and a tetrahedral (S = 1) or five-coordinate derivative (Scheme 2). Even if NO were to result in an nmp-bound Ni–NO complex, the resulting [Ni(NO)]\textsuperscript{9} (reaction of 1 with NO) or [Ni(NO)]\textsuperscript{8} (reaction of 1\textsuperscript{ox} with NO) oxidation levels have yet to be defined and support an outer-sphere superoxide interaction in NiSOD. Although these EF notations have yet to be accessed, one would propose that NiSOD mimetics, especially with strong-field carboxamido-N and alkyl-thiolato-S donors, would surely stabilize such an electron poor species. Furthermore, the properties of complexes such as 2 extend to biology, where analogous S-bridged mononitrosyl species, \textit{i.e.}, Fe–S clusters and tetrahedral (RS)\textsubscript{3}Fe–NO complexes are proposed as intermediates in the repair of NO-damaged clusters.\textsuperscript{79–81} Complex 2 is stable in the solid-state but breaks down slowly in solution causing rupture of the Ni(μ-SR)\textsubscript{2}Ni core and release of NO that was trapped in near quantitative yield with a Co\textsuperscript{II}-porphin receptor. The resulting Ni\textsuperscript{II}–S\textsubscript{2}O\textsubscript{2} complex 3 (coordination of two o-aminobenzene-thiolate in \textit{trans} configuration) was isolated and structurally/spectroscopically characterized as the ultimate Ni breakdown product with the nitrosamine unit still intact. This release may take place through a disproportionation mechanism (or through ligand rearrangement), as has been proposed in other Ni-nitrosyls, to a yet ill-defined Ni\textsuperscript{0} complex (see Scheme 2).\textsuperscript{28,78} Hence, thiolate-supported {Ni(NO)}\textsuperscript{10} cores are reactive. While nitrosamines have been utilized as sources of NO, the RN–NO homolytic bond dissociation energy (BDE) is high (87.7 kcal mol\textsuperscript{−1} [ref. 82]) compared to more traditional small molecule sources of NO such as nitrosothiols (RSNO) that have RS–NO BDEs between 20–32 kcal mol\textsuperscript{−1}.\textsuperscript{83,84} Overall, the electronic structures of [Ni(NO)]\textsuperscript{10} complexes are modulated by the supporting ligands. Indeed, the majority are stable entities; however, a small number are reactive and result in release of NO (thiolate-supported/anionic complexes 2 and III) or generate other reactive intermediates of environmental significance such as hyponitrite (N\textsubscript{2}O\textsubscript{2}−) in five-coordinate [Ni(NO)]\textsuperscript{10} species\textsuperscript{85} (highly reduced NO, with a severely bent Ni–N–O angle = 130°).

\section*{Conflicts of interest}

There are no conflicts to declare.

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