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Oxygen Capture by Sulfur in Nickel Thiolates

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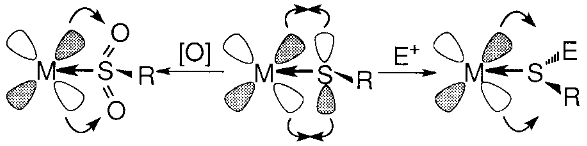
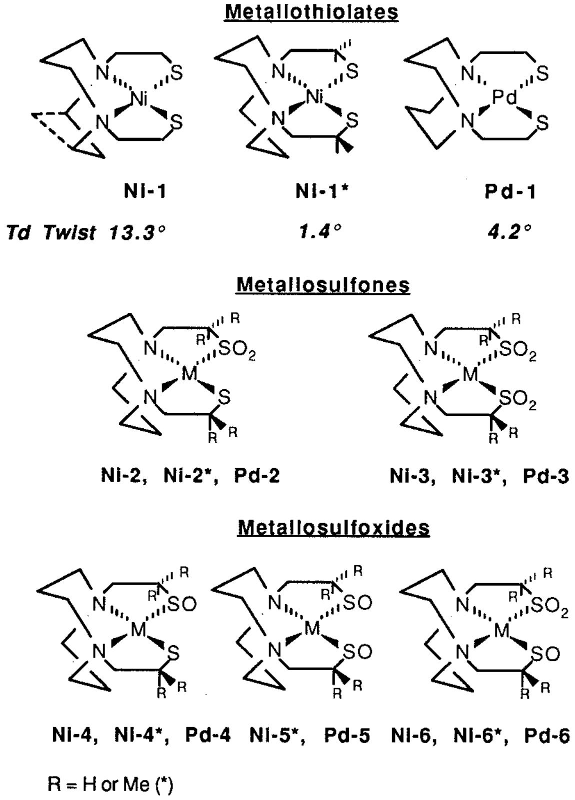
The study of transition metal thiolates (especially late transition metals and anionic complexes) is frequently complicated by air sensitivity and a tendency to form polymetallic complexes with bridging μ-SR groups. Both problems may be ascribed to the character of the HOMO which is S-based and substantially antibonding.[1] The four-electron destabilizing interaction of lone pairs of electrons on thiolate sulfur with filled metal d-orbitals is relieved by electron transfer, generating thiyl radicals, or by reaction with electrophiles such as carbonium sources, metal ions, or oxygen, Scheme 1. Strategies to avoid unwanted reactivity involve sterically encumbered thiolates or a ligand rigidity which prohibits the offending reaction path. On the other hand, sulfur-site nucleophilicity may be used to advantage, as demonstrated in particular by the alkylation of *cis*-dithiolates in the templated synthesis of dithioether polydentate or macrocycle ligands.[2,3] The air sensitivity of transition metal thiolates typically results in degradation of enzymatic and catalytic sites due to disulfide, expulsion of metal ion, and metal oxide formation. There exists, however, the potential for O-uptake by sulfur with retention of M−S bonding, resulting in subtle modification of metal properties, particularly redox potentials. Hence an examination of innocuous if not profitable roles for S-oxygenation or S-metalation of metal thiolates is timely in view of current research activity in sulfur-rich metalloenzymes such as [NiFe]hydrogenase and CO dehydrogenase.[4,5]

Scheme 1[21]



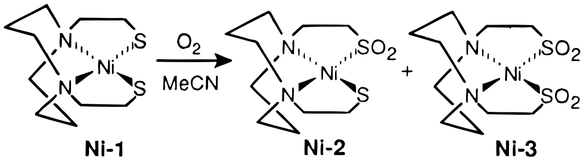
dπ-sulfur lone pair π^* interaction

Scheme 2[14]



Synthesis and Characterization of the S-Oxygenates

The *cis*-dithiolate [1,5-bis(2-mercaptoethyl)-1,5-diazacyclooctanato]nickel(II), **Ni-1**,[6] was among the first complexes[7−9] for which discrete metal-bound S-oxygenates were demonstrated to result from reaction of O_2, eq 1.



(1)

Scheme 2 shows the array of nickel S-oxygenates that have been prepared in our laboratories on the basis of reactions of ground state, or $^3\Sigma$, O_2, excited state, or $^1\Delta$, O_2, or H_2O_2 with **Ni-1, Pd-1**, and an analogue, **Ni-1***, which has steric encumbrance by methyl groups on the carbons α to sulfur.[6,9−15] Optimal reaction conditions differ for each, and the oxygenates can be isolated in yields ranging from 18% for the bis(sulfoxide) **Ni-5*** to 85% for the bis(sulfone) **Ni-3**. Product mixtures are separable by silica gel or

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Marcetta York Darensbourg, a Kentuckian by birth and Inorganic Chemist by profession, received her Ph.D. from the University of Illinois, Champaign/Urbana, in 1967, with Professor T. L. Brown. Following initial lecturing appointments at Vassar College and SUNY Buffalo, her academic research career began at Tulane University (1971−1982) and continued at Texas A&M (1982−present). Organometallic reaction mechanisms and the coordination chemistry involved in the active site of [NiFe]Hydrogenase have inspired a synthesis program that has produced among other works approximately 12 publications over the past 6 years devoted to the production and mechanistic understanding of nickel-bound S-oxygenates. Her e-mail address is marcetta@chemvx.tamu.edu.

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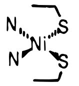
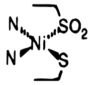
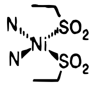
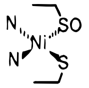
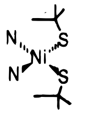
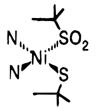
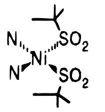
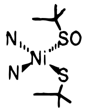
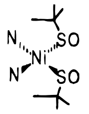
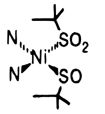
alumina column chromatography. The compounds are fully characterized, including, for most, molecular structures from X-ray crystallography. All oxygenates of this series are S-bound and maintain the square planar geometry of the parent dithiolates; the largest distortion from square planarity exists for the asymmetric monosulfones **Ni-2** and **Ni-2*** where tetrahedral twists of 18 and 15°, respectively, result in paramagnetism for the former complex, while the latter is diamagnetic at room temperature.

Structures. On the whole, the NiN_2S_2 coordination sphere is constant throughout the series shown in Scheme 2. As seen in Table 1, the Ni−N distances are practically invariant at 2.00(±0.01) Å. The Ni−S distances of the NiN_2S_2 coordination are in a narrow range of 2.17−2.11 Å, and the S−O distances are characteristically longer for the metallosulfoxide (average 1.55 Å) than the metallosulfone (average 1.46 Å). The S−O distances correlate with infrared data in the ν(SO) region; the shorter bonds of the sulfones result in characteristic IR bands at ca. 1050 and ca. 1200 cm^{-1}, while the sulfoxides are in the 910−925 cm^{-1} range. [That these stretches are in fact due to sulfur oxygenates has been confirmed by comparisons with ^{18}O-labeled oxygenates. For example, a 35 cm^{-1} shift is observed for both the symmetric and asymmetric ν(SO)-bands of **Ni-2*** when $^{18}O_2$ was used in the synthesis.][9a,11] The invariance of the Ni−S bond distance with level of S-oxygenation suggests the loss of σ-donating ability of S is compensated by the relief of the antibonding character from the Ni-d_π/S-p_π overlap. Two further examples of nickel thiolate derived S-oxygenates (metallosulfones) also show this consistency in Ni−S distances.[7,8]

Table 1. Selected Bond Dimensions and IR Spectroscopy for Ni-1, Ni-1*, and Oxygenates

Compd	Ni-N (Å)	Ni-S (Å)		S-O (Å)	Td Twist[a]	ν(SO) (cm^{-1})[b]
Ni-1[6]	1.985(6) 1.985(6)	2.159(2) 2.159(2)			13.3°	
Ni-2[9a]	2.000(2) 1.982(2)	2.140(1) 2.163(1)		1.456(3) 1.463(2)	18.3°	1053 1182
Ni-3[21]	1.981(9) 1.981(9)	2.133(3) 2.133(3)		1.45(1) 1.472(8)	16.8°	1032 1071 1180 1192
Ni-4[12]	1.991(4) 1.990(4)	2.153(1) 2.153(2)		1.549[c]	4.3°	925
Ni-1*[10]	1.995(3) 1.995(3)	2.152(1) 2.152(1)			0.0°	
Ni-2*[11]	1.99(1) 2.00(1)	2.109(4) 2.132(4)		1.47(1) 1.46(1)	14.9°	1044 1181
Ni-3*[11]	2.006(6) 2.011(7)	2.130(3) 2.125(2)		1.462(6) 1.458(9) 1.463(6) 1.460(9)	3.5°	1032 1071 1180 1192
Ni-4*[9b]	2.016(9) 1.998(7)	2.162(3) 2.148(3)		1.550(8)	7.8°	909
Ni-5*[11]	2.002(6) 1.996(5)	2.170(2) 2.165(2)		1.546(4) 1.533(5)	0.5°	921
Ni-6*[11]	1.989(6) 1.987(5)	2.127(2) 2.144(2)		1.468(6) 1.431(7) 1.551(6)	2.9°	918 1036 1182

[a] Tetrahedral twist is defined as the angle of intersection between the plane defined by N1, N2, X and the plane defined by S1, S2, X, where X is the centroid of N1, N2, S1, and S2. [b] KBr pellet. [c] Bond length determined on the basis of the riding motion model of Busing and Levy.[12]

In most structures the two fused metallodiazacyclohexane rings formed from the diazacyclooctane portion of the ligand are in a boat/chair conformation while the chair/chair conformer occurs in a few cases, notably **Pd-1**.[15] The disorder in the **Ni-1** and **Ni-3** structures is attributed to mixtures of chair/boat and chair/chair conformers.[6,9a] Since the chair/chair is the common conformer for 6-coordinate complexes containing daco, even with the tetramethyl bme*-daco derivatives, the good ability of the daco ligand to impart crystallinity to derivatives is not entirely due to a lack of flexibility of the mesocycle.[2] For the 4-coordinate derivatives of **Ni-1***, the daco ring always adopts the chair/boat conformation with the four methyl groups on the carbon α to the sulfur directed toward the boat creating a sterically hindered "underside" in the complex.[11] In the case of sulfoxides, the oxygen atom(s) is (are) always found on the "topside" of the complex, directed away from the methyl groups, Figure 1.

The two-oxy species are selected as representative molecular structures to view in detail, Figures 1 and 2. View a of Figure 1 shows the orientation of oxygens of the bis(sulfoxide), **Ni-5***, to be syn to the N_2S_2Ni plane and on the same side of the plane as the chair-form, opposite the axial methyl groups of the N to S linker. View b bisects the S−Ni−S angle and illustrates the large O to O separation of 3.862 Å. Analogous views of **Ni-2*** are impressive of the twist in the N_2NiS_2 dihedral planes, as well as the skew of the oxygens of the sulfone away from the metal center, on the "top" side of the N_2S_2Ni plane, and, on the "bottom" side, toward the metal center. Since the **Ni-5** analogue of **Ni-5*** has never been observed, it is tempting to conclude that the steric hindrance of the four methyl groups stabilizes **Ni-5*** perhaps preventing an internal isomerization that might convert **Ni-5** to **Ni-2**. In early work **Ni-2** was assumed to be the more stable in analogy

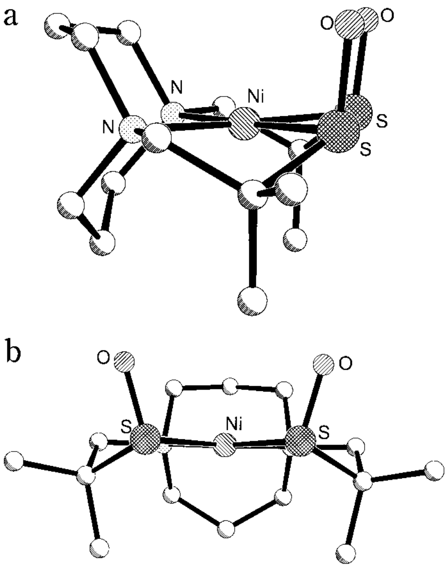


FIGURE 1. (a) Top: Molecular structure of [1,5-bis(2-sulfeno-2-methylpropyl)-1,5-diazacyclooctanato(2−)]nickel(II) trihydrate (**Ni-5***). Hydrogen atoms and water molecules have been omitted. (b) Bottom: Alternate view of **Ni-5***. Adapted from ref 11.

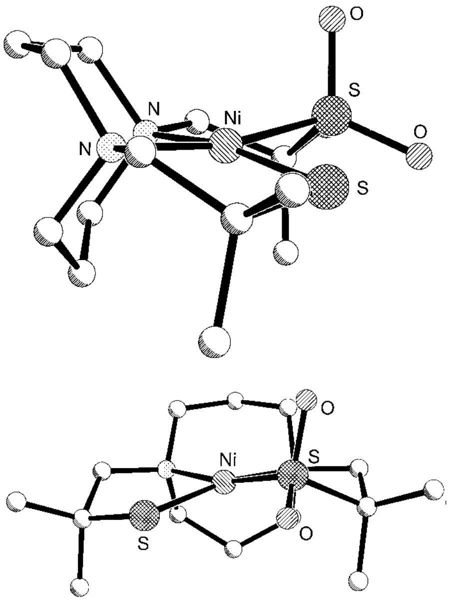


FIGURE 2. (a) Top: Molecular structure of [1-(2-mercapto-2-methylpropyl)-5-(2-sulfino-2-methylpropyl)-1,5-diazacyclooctanato-(2−)]nickel(II) (**Ni-2***). Hydrogen atoms have been omitted. (b) Bottom: Alternate view of **Ni-2***. Adapted from ref 11.

to the stability of $RSSO_2R$ relative to $RS({=}O)S({=}O)R$. Later we found that the palladium bis(sulfoxide), **Pd-5**, is easily formed and is, interestingly, the preferential isomer of the two-oxy species for the Pd series.[13] Such stability has also been observed for platinum sulfoxides in the synthesis program of Weigand where oxidative addition reactions of thiosulfinates ($RSS({=}O)R$) to platinum(0) yields thiolato/sulfenato Pt(II) complexes.[16]

Prior S-oxygenation studies focused on Co(III) thiolates, including cysteine derivatives, which showed stepwise O-atom addition leading to sulfenato (MS(O)R), sulfinato (MSO_2R), and ultimately sulfonato ($MOSO_2R$) complexes.[17] Thus far we have not observed the fully oxygenated, sulfonato derivatives of our nickel complexes, but such a species has been isolated with oxygenation of a more flexible N_2S_2 ligand/nickel complex.[18] Other studies of S-oxygenation in nickel thiolate complexes by molecular oxygen include a dianionic square planar dithiolene complex $Ni(S_2R_2)_2{}^{2-}$ complex yielding the *cis*-disulfone ($Ni(SO_2R)_2$ derivative.[8] Also, an anionic *trans*-dithiolate complex has been shown to add O_2 to one thiolate to yield the monosulfone; however, subsequent O_2 addition to yield the bis(sulfone) complex was not observed.[7] Whereas many of these oxygenates, particularly those resulting from reaction with ground-state oxygen, were discovered serendipitously, the design of S-oxygenation of metal-bound thiolates for useful processes has followed. For example, the development of metal-bound RS=O ligand chemistry for its possible involvement in metal-mediated synthesis of chiral sulfoxides has been a long-term goal of Schenk.[19] Additionally, Gray and Schanze have independently studied ligand-based oxygenation of Pt thiolates via metal-sensitized singlet oxygen production.[20] In each study metallosulfone complexes were observed, while Schanze also reported oxidation of the dithiolate ligand to a dithiolene.

Effects of S-Oxygenation Level on Redox Potentials. The comprehensive series provided by **Ni-1, Pd-1**, and **Ni-1*** offers a unique opportunity to explore the consequences of S-oxygenation on metal and complex properties within the consistent structural basis granted by the bme-daco and bme*-daco ligands. Solution electrochemical data have been obtained by cyclic voltammetry. All complexes display a reversible $Ni^{II/I}$ reduction wave, and those complexes that contain a thiolate show ligand-based, irreversible oxidations, presumably to yield the thiyl radical, releasing Ni^{II} on formation of the disulfide.[11,21] One such product was shown by X-ray crystallography to be an intermolecular coupling of two bme-daco units.[22] As shown in Figure 3, the bis(sulfone) complex also shows a reversible oxidation event approximately 2 V more positive than the $Ni^{II/I}$. The assignment of the oxidation of **Ni-3** to Ni^{III} as well as the reduction of all Ni^{II} derivatives to Ni^{I} was confirmed by EPR spectroscopy.[21] Other examples of Ni^{III} states in derivatives of bme-daco and bme*-daco arise from S-alkylated products such as the dimethylated **Ni-1-Me$_2$**$^{2+}$.[21] That is, the thiolate S must be converted to an S-oxo or an S-alkyl derivative in order for Ni^{III} to be stable relative to S-oxidation.

Scheme 3 shows the changes in $Ni^{II/I}$ couples as oxygens are added to the sulfurs for the **Ni-1*** series, spanning an overall gain of ca. 600 mV to more positive potential from the 0- to 4-oxy species, as determined in CH_3CN solutions with $[(Bu)_4N][PF_6]$ as electrolyte.[11] The monosulfoxide stabilizes the Ni^{I} state by 100 mV relative to the nickel dithiolate. Addition of a second oxygen, either to generate the bis(sulfoxide), **Ni-5***, or the mono-(sulfone), **Ni-2***, eases the Ni^{I} formation by another 200 mV. The third oxygen, **Ni-6***, stabilizes the Ni^{I} state by yet another 100 mV and the 4-oxy bis(sulfone) is again stabilized by an additional 200 mV over the 3-oxy species. While the same trend is observed in the (limited) **Ni-1**

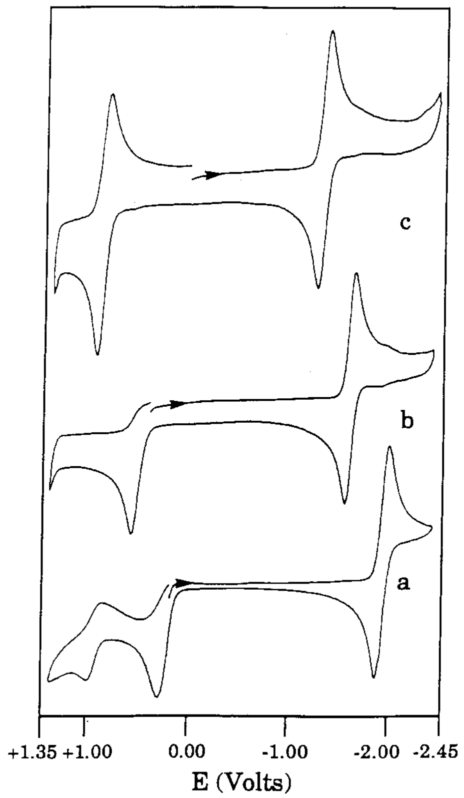
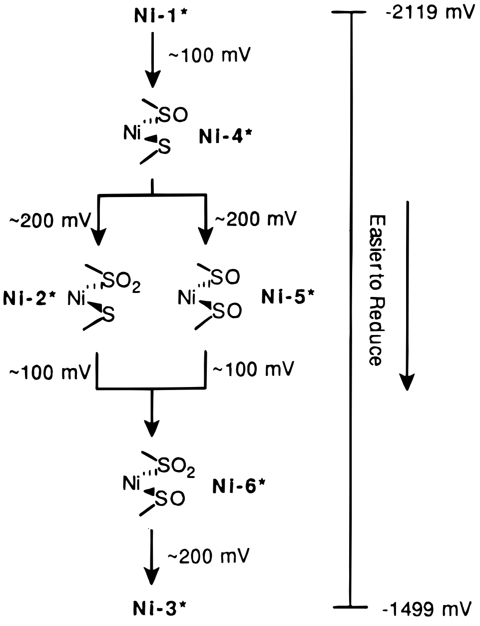


FIGURE 3. Cyclic voltammograms of 2−5 mM solutions of (a) **Ni-1**, (b) **Ni-2**, and (c) **Ni-3** in 0.1 M TBAHFP/MeCN with glassy carbon working electrode at 200 mV/s and scale referenced to NHE using Cp_2Fe/Cp_2Fe^+ standard ($E_{1/2}$ = 400 mV). Reprinted from ref 21. Copyright 1993 American Chemical Society.

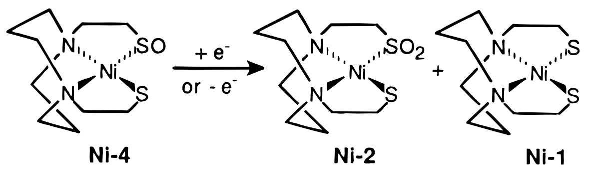
Scheme 3



series,[21] it differs in that in the starting point, the nickel dithiolate, and successive oxygenates, the $Ni^{II/I}$ couples are approximately 175 mV more positive than the corresponding **Ni-1*** analogues; the $Ni^{II/I}$ couple of **Ni-1** itself is at −1944 mV, as contrasted to −2119 mV for **Ni-1***. This is a result of the enhanced electron-donating ability of the thiolate sulfurs adjacent to methyl substituents in **Ni-1***. Similarly the **Pd-1** complex shows a $Pd^{II/I}$ couple at −2105 mV, and an overall smaller, relative to **Ni-1**, positive shift of 530 mV is observed on going through the 0- to 4-oxy series.[13] In addition, the 2-, 3-, and 4-oxy derivatives of **Pd-1** show a second reversible reduction at ca. −2000 mV assigned to $Pd^{I/0}$. It should be mentioned that the relief of the $Ni_{d\pi}$−$S_{p\pi}$ destablizing interaction by alkylation also makes the Ni^{I} oxidation state more accessible, by ca. 700 mV per alkyl group.[21] The generation of cationic charge is a major factor in the positive gain of the reduction potentials in the alkylates.

The solvent dependence of the $Ni^{II/I}$ reduction potential was investigated for the mono(sulfone) **Ni-2** and the bis(sulfone) **Ni-3**.[21] As compared to acetonitrile solutions, the $Ni^{II/I}$ couples of the oxygenates are about 550 mV more positive in water. Titrations of water to acetonitrile solutions of the oxygenates show a specific solvent interaction; i.e., the major change in potential occurs within a solvent mixture of 10% H_2O/90% CH_3CN. The ease of $Ni^{II/I}$ reduction in water is attributed to H-bonding to the sulfinato oxygens which stabilizes the reduced member of the couple. The propensity for H-bonding is also observed by the greater solubility of the sulfones in water as compared to acetonitrile as well as the ubiquitous inclusion of H_2O in the X-ray crystal structures of the oxygenates.[9a]

The cyclic voltammogram for the mono(sulfoxide), **Ni-4**, is complicated by redox promoted disproportionation, eq 2.[12] Multiple scans through both the oxidation or reduction region of **Ni-4** result in peaks assignable to the dithiolate **Ni-1** and the mono(sulfone) **Ni-2**. Since reduction should create a weaker S═O bond, or a better O-donor, a working hypothesis is that the $\mathbf{Ni\text{-}4}^{\bullet -}$ mono(sulfoxide) radical anion donates an oxygen to an unreduced **Ni-4**. Support for this hypothesis was obtained by interception of the O-atom transfer upon reduction in the presence of Ph_3P which yielded $Ph_3P{=}O$ and **Ni-1**. [Key to this interpretation was the fact that none of the Ni^{II} S-oxygenates are O-atom donors to pure Ph_3P.] In contrast one-electron oxidation of the oxygenate, $\mathbf{Ni\text{-}4}^{\bullet +}$ should create a better O-atom acceptor from a neutral **Ni-4**, again yielding **Ni-1**, from **Ni-4**, and **Ni-2**, from $\mathbf{Ni\text{-}4}^{\bullet +}$. In this case, addition of Ph_3P has no effect on the oxidation-promoted disproportionation. The key point demonstrated here is that O-modification of nickel thiolate with formation of S═O bonds is potentially reversible in the presence of reductants and O-atom acceptors; oxygen-damaged, S-rich catalytic sites are thus capable of repair. Nevertheless, we have not observed any reversibility at the sulfone level of oxygenation.



(2)

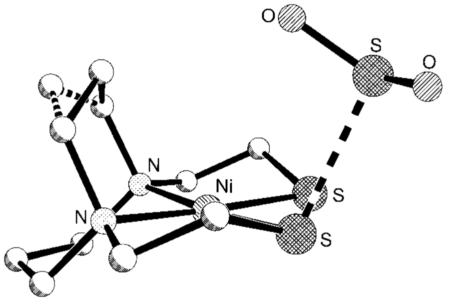
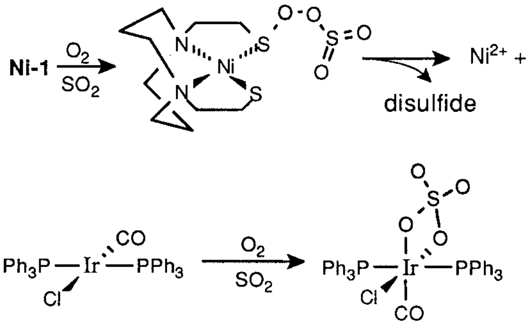


FIGURE 4. Molecular structure of [1,5-bis(mercaptoethyl)-1,5-diazacyclooctanato(2−)]nickel(II)−sulfur dioxide (**Ni-2·SO₂**). Hydrogen atoms have been omitted. Adapted from ref 31.

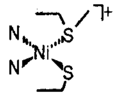
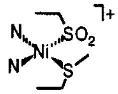
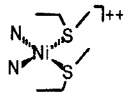
Scheme 4



Mechanism of Oxygenation of Nickel Dithiolates

Nucleophilicity of Nickel Thiolates. Nickel(II) has been suggested to bind O_2 as a 2 electron donor ligand in a hard pentaaza (N_5) donor environment, resulting in oxidation of hydrocarbon linkers within the ligand.[23,24] The possibilities of S-oxygen (ligand-based) O_2 uptake versus metal-based oxidation or electron transfer is a mechanistic issue. The nucleophilic character of d^8 transition metals in oxidative addition reactions is well-known for phosphine complexes of Rh(I) and Ir(I), which activate small molecules, including O_2 to yield M(III) peroxo species.[25−29] While first-row d^8 metals are much less reactive, presumably because the electron density is less accessible, these metals facilitate π-donor ligand-based nucleophilicity.[1] For example, while Ir(I) forms a metal-based SO_2 adduct,[30] the nickel dithiolate **Ni-1** yields a ligand-based SO_2 adduct ($S\cdots SO_2 = 2.597$ Å), Figure 4.[31] Both the SO_2 adducts of Ir(I) and of the nickel dithiolate demonstrate insertion of O_2 into the Ir−SO_2 or Ni−S···SO_2 interaction.[15,26,30,31] The mechanism of the Ir(I) to Ir(III) sulfate-forming reaction is understood to involve displacement of SO_2 from Ir(I) by O_2, followed by formation of a peroxy-SO_2 adduct; a similar process is expressed in Scheme 4 for the **Ni-1** sulfur-based reaction.[26,30] Whereas the reductant in the former is the metal (Ir(I) → Ir(III) + $2e^-$), the latter utilizes oxidation of thiolate sulfurs to derive the two electrons required for the "sulfate" reaction. The S-based reactivity is consistent with ab initio calculations by Maroney et al., which show the HOMO for a square-planar nickel dithiolate complex analogous to **Ni-1** to lie on the thiolate sulfur.[32] Calculated electrostatic potentials confirm that the thiolates are the most nucleophilic sites in the complex.[32] Hence, the observed wealth of S-based reactivity of these complexes is well expected, and kinetic studies have demonstrated a correlation of rates of S-alkylation with electron-richness of the complexes as measured by redox potentials, Table 2.[33] That is, there is an indirect correlation of the accessibility of Ni^I with rate constants for the second-order (S_N2) reaction of MeI with **Ni-1** and its derivatives.

Table 2. Comparison of Redox Potentials and Rate of Methylation with MeI for Ni-1, Ni-2, and Ni-1Me⁺ in Acetonitrile[a]

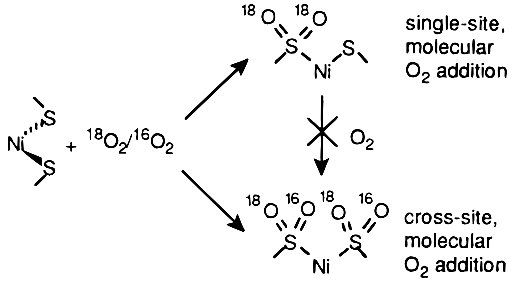
Reactant	Product	$E_{1/2}$ (red) (mV)	E_{pc} (ox,) irrev	k_2 (s^{-1} M^{-1})
Ni-1		-1940	+360	3.7 ± 0.3
Ni-2		-1630	+620	0.15 ± 0.01
Ni-1Me⁺		-1200	+960[b]	(1.7 ± 0.2) x 10^{-3}

[a] All potentials scaled to NHE referenced to MeV^{2+}/MeV^+. Kinetic data was recorded by UV−vis spectroscopy under pseudo-first-order conditions of excess MeI and expressed as the second-order rate constant, k_{obs}/[MeI]. [b] Oxidation peak for BF_4^- salt; the oxidation peak of the iodide salt is obscured by oxidation of the counterion.

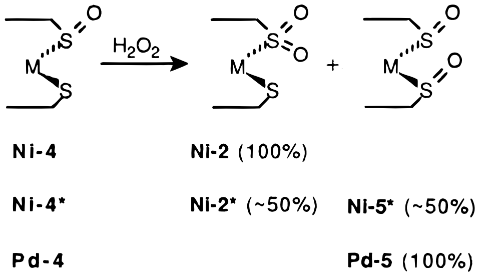
The **Ni-1** complex reacted with ground-state oxygen, $^3\Sigma$ O_2, in MeCN to generate 20% mono(sulfone), **Ni-2**, and 5% bis(sulfone), **Ni-3**, within 24 h.[9a] Since the isolated monosulfone, **Ni-2**, was unreactive toward ground-state O_2 under the original reaction conditions, a deactivation of the remaining thiolate sulfur was indicated. Stronger oxygen donor sources such as H_2O_2 or $^1\Delta$ O_2 were required for attack on the deactivated remaining thiolate sulfur.[9a,14]

Mass spectrometry has been invaluable in elucidation of the oxygenation mechanism. In collaboration with D. H. Russell's laboratories, the isotopic distribution of products synthesized under an $^{18}O_2/^{16}O_2$ atmosphere were determined. For the metallosulfones, matrix-assisted laser desorption ionization (MALDI) mass spectrometry was employed to show that both oxygens of the monosulfone, **Ni-2**, were from the same O_2 molecule and that the bis(sulfone), **Ni-3**, resulted from the addition of two O_2 molecules.[9a] That the bis(sulfone) appeared in the original product mixture but could not be synthesized from **Ni-2** and $^3O_2$ implicated competing reactions. This possibility was confirmed by utilizing double laser pulse Fourier transform ion cyclotron resonance mass spectrometry to induce fragmentation of SO_2 which was analyzed to determine the isotopic distribution.[9b] The results, as summarized in Scheme 5, indicate cross-site, molecular addition of O_2 (to within 90%) in the production of the bis(sulfinate) **Ni-3** complex. This result suggested the intermediacy of a bis(sulfoxide), rather than mono(sulfone), in the production of **Ni-3**, consistent with the lack of reactivity of isolated **Ni-2**. As noted in Scheme 2, the bis(sulfoxide) **Ni-5** analogue has not yet been isolated,

Scheme 5



Scheme 6[13]



whereas the **Ni-5*** and **Pd-5** analogues are known. We were able to follow the course of O_2 uptake in the production of **Ni-5*** and demonstrate by isotopic labeling that the two oxygen atoms were derived (to within 85%) from the molecular addition of O_2.[34] For the metallosulfoxide, electrospray ionization (ESI) mass spectrometry provided more reproducible results than MALDI. The presence of ca. 15% of mixed-label bis(sulfoxide) **Ni-5*** is not surprising, given that **Ni-4*** was also produced in the reaction. Curiously, **Pd-5** can be obtained only via successive addition of H_2O_2 while molecular O_2 addition produces only mono(sulfone), **Pd-2**.[13]

Singlet O_2, $^1\Delta$ O_2, is the reagent of choice for oxygenating the sterically hindered, strictly square planar **Ni-1*** as $^3\Sigma$ O_2 is of low (almost no) reactivity.[14] Both nickel dithiolates, **Ni-1** and **Ni-1***, show a great increase in O_2 reactivity when O_2 is excited to the $^1\Delta$ state, particularly in MeOH solutions where $^3\Sigma$ O_2 is practically unreactive. In our studies, $^1\Delta$ O_2 was produced photochemically, by use of Rose Bengal as sensitizer, and thermally, with 1,4-dimethylnaphthalene endoperoxide as a dark source for proof of the presence of singlet oxygen, rather than a Ni-based photolytic process. Within 1 h in MeOH, **Ni-1*** reacts with $^1\Delta$ O_2 to generate **Ni-4*** and **Ni-5*** with yields as high as 25% and 37%, respectively. For **Ni-1** in dilute concentrations (1.7 mM) the dithiolate is quantitatively converted to the 4-oxy species **Ni-3** within 1 h in the presence of $^1\Delta$ O_2.

Mechanistic Insight

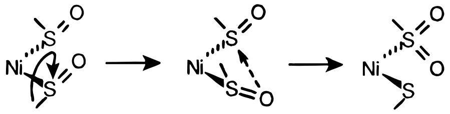
Reaction with O_2. Control experiments to gain mechanistic information for the reaction of **Ni-1** with $^3\Sigma$ O_2 included the lack of effect when the radical trap, 10% molar galvinoxyl, or the O-atom traps, PPh_3 or Me_2S, were added to solutions of **Ni-1**.[9a] The latter reagents suggested that, if produced, single O atoms were trapped by the "built in" oxygen traps in the metal complex, i.e., the *cis*-dithiolates.

The free bme-daco ligand, whether protonated or as the sodium salt, is unreactive with O_2 in acetonitrile even after 2 days exposure.[35] (A white solid, presumably disulfide, is formed upon addition of water.) Possible roles for the metal facilitation of O_2 sulfur-based reactivity are stabilization of the S-oxygenation product and/or activation of O_2.

The greater reactivity of $^3\Sigma$ O_2 with **Ni-1** as compared to **Ni-1*** may be ascribed to the significant (13.3°) tetrahedral twist in the N_2S_2 plane for **Ni-1**, while **Ni-1*** is nearly planar, (1.4°). This result is interpreted in terms of an accessible low lying triplet excited state in the former which overcomes the spin-forbidden character of the reaction which is more significant for the rigorously square planar **Ni-1***. [It is notable that in the ^{1}H NMR spectra only broad signals are observed for **Ni-1** while in **Ni-1*** the resonances are sharp and readily assignable.[9a]]

The oxygenation of RSR with $^1\Delta$ O_2 is known to produce sulfoxides and/or sulfones.[36] In contrast, to the organic sulfide, the thiolate sulfur in MSR′ is formally negative and hence more nucleophilic than in RSR. That the sodium salt of the ligand does not yield S-oxygenates indicates some degree of covalency in the transition metal−sulfur bond, in a sense a "RSR" environment, is required to yield a thermodynamically stable S-oxygenate product.

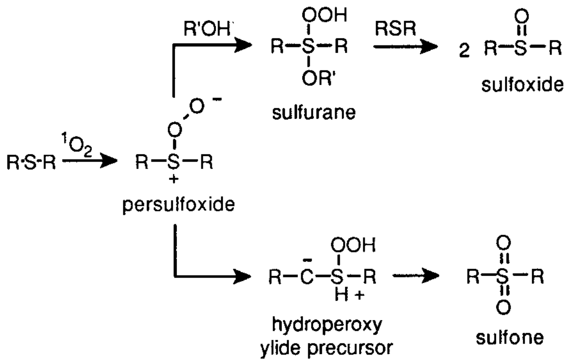
An unresolved issue in the systems studied thus far is the metal and ligand dependent sulfoxide/sulfone stability.[11,13,16] Scheme 6 shows the product distribution for the reaction of H_2O_2 with each of the mono(sulfoxides). The **Ni-1** complex yields exclusively mono(sulfone) product, while **Pd-1** yields only the bis(sulfoxide). The **Ni-1*** yields an equal mixture of the two. That **[Ni-5]** has never been observed under any circumstances could be due to thermodynamic instability leading to isomerization, as with RS(=O)S(=O)R, to the mono(sulfone) **Ni-2**, eq 3.[14]

 (3)

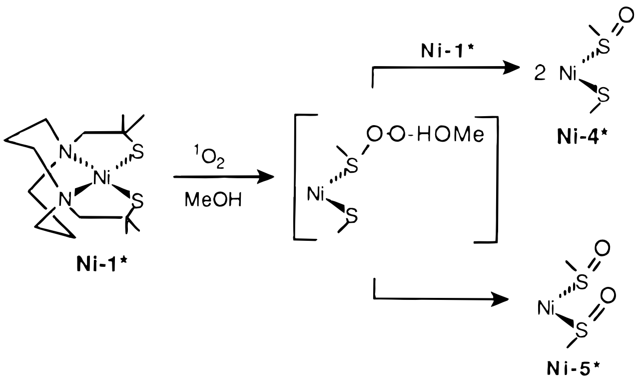
The bis(sulfoxide), **Ni-5***, shows no isomerization in refluxing CH_3CN or toluene; hence, this thermodynamic stability is attributed to the role of the methyl groups on the carbon α to the sulfoxides.

The reaction of RSR with $^1\Delta$ O_2 is widely accepted to proceed through a persulfoxide intermediate.[37] The fate of the persulfoxide is solvent dependent as shown in Scheme 7.[38,39] A similar intermediate is proposed for the reaction of O_2 with the metal thiolates. As with RSR, solvent stabilization of the persulfoxide would facilitate oxygen transfer either intermolecularly to yield mono(sulfoxide) or intramolecularly to produce bis(sulfoxide) as shown in Scheme 8. Consistent with this proposed mechanism is a shift in the relative distribution of **Ni-4*** to **Ni-5*** from 1:1 to 2:3 upon lowering the **Ni-1*** concentration by a factor of 10.[14]

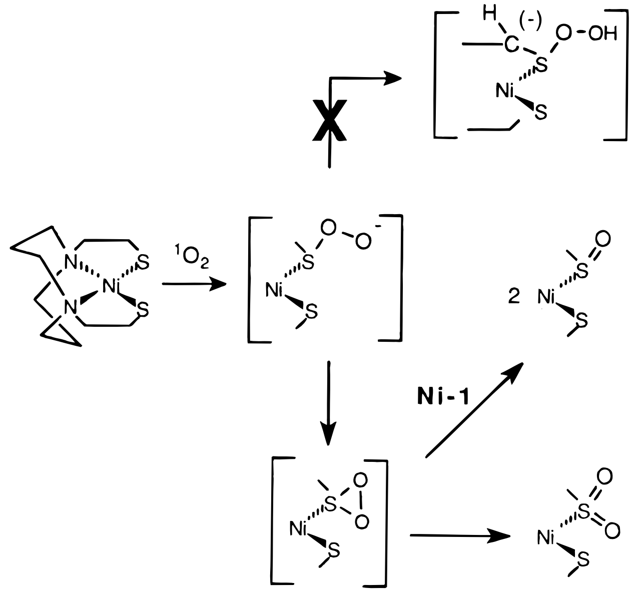
Scheme 7



Scheme 8



Scheme 9

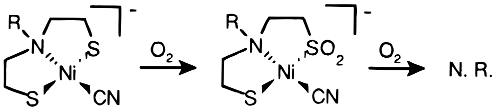


In aprotic solvents the product distribution shifts toward metallosulfones, for which a thiadioxirane intermediate followed by O–O bond cleavage, Scheme 9, is most reasonable.[9a,11] A similar intermediate has been proposed as a precursor to sulfones as well as an O-atom donor leading to 2 equiv of sulfoxide for RSR.[38,39] A recent proposal of sulfone production in RSR/$^1\Delta$ O_2 systems involves deprotonation of the α carbon yielding a hydroperoxy ylide which rearranges to the sulfone. This mechanism is supported by deuterium incorporation at the α carbon when performed in D_2O.[38] As there are no hydrogens on the carbon α to sulfur of **Ni-1***, such a mechanism would conveniently explain the sulfone/sulfoxide distribution differences for **Ni-1** and **Ni-1***. However, the reaction of **Ni-1** with $^1\Delta$ O_2 in acetonitrile spiked with D_2O showed no incorporation of deuterium, as determined by ^2H NMR, in either the mono(sulfone) or the bis(sulfone).[14] Thus, the thiadioxirane would appear to be the most reasonable intermediate in the production of nickel sulfones.

Conclusions/Comments

We have taken advantage of a unique ligand which has yielded structural, electronic, and mechanistic information as to O_2 uptake and storage in *cis*-dithiolates of nickel and palladium. The importance of nickel facilitation of this reactivity in our sterically restricted ligands is underscored by the fact that other metal complexes, including Zn and Fe,[40,41] of bme-daco and bme*-daco have not yielded S-oxygenates. For the Fe analogue of **Ni-1***, O_2 exposure yields a μ-oxo Fe(III) complex.[41] Notably a flexible tripodal dithiolate ligand bound to vanadium(V) was recently shown to form a bis(S-oxygenate) with unusual η^2-S(=O)R bonding at V.[42]

The observation of molecular O_2 addition to adjacent sulfur atoms to yield the bis(sulfone) from the *cis*-dithiolates implicates a special role for this orientation. Noteworthy in this regard, the anionic *trans*-dithiolate investigated by Maroney et al. does not undergo successive addition of $^3O_2$ to yield the bis(sulfone), eq 4.[7] This



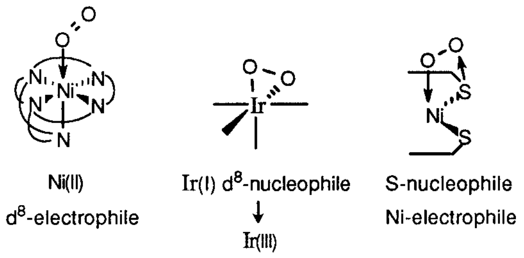
(4)

demonstrates that even the anionic charge on the product is insufficient to overcome the thiolate deactivation by the *trans*-sulfone. Since bis(sulfones) are produced from the neutral dithiolates of **Ni-1** via bis(sulfoxides) the geometrical arrangement of the dithiolates is critical.[9b,34]

The extent to which the activation of O_2 might involve Ni-bound O_2 is still at issue; however, evidence supports Ni–SR as an organometallic version of organic sulfides with reactivity that is largely S-based or at least a Ni–SR combination reactivity site. Certainly, the thermodynamic products are S-oxygenates. The contrast to nickel in hard pentaaza donor environments is the binding of O_2 as an electron donor ligand to the more electropositive Ni(II), Scheme 10. The similarity of the Ni–$(SR)_2$ reactivity site to electron-rich d^8 metals such as Ir(I) and Rh(I) lies in the ease with which all are oxidized by two electrons, resulting in the case of the latter with industrial and catalytic importance. The potential for a two-centered Ni–SR site to function in an oxidative-addition modality is intriguing as nature's answer to achieving such organometallic type reactivity with the widely dispersed and cheap metal, nickel.

We are struck by the extremely small change in geometry and distance data throughout this series of

Scheme 10



oxygenates. While formal donor ability, i.e., anionic charge, of the S remains the same, subtle (or not so subtle) changes in the metal redox potential resulting from different levels of oxygenation can have significant implications for activity of enzymes or industrial catalysts. Thus, controlled S-oxygenation might be examined for ligand modification much as the seemingly minor tweaks in phosphine or amine ligands used in industrial catalysis are used to regulate catalyst function.

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