Study of Sulfinate and Sulfenate Complexes Derived from the Oxygenation of Thiolate Sulfur in [1,5-Bis(2-mercapto-2-methylpropyl)-1,5-diazacyclooctanato(2−)]nickel(II)

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Abstract: A series of nickel(II) complexes containing sulfinate and sulfenate S-donor sites has been prepared from systematic oxygenations of the dithiolate complex [1,5-bis(2-mercapto-2-methylpropyl)-1,5-diazacyclooctanato-(2−)]nickel(II) ((bme*-daco)Ni, **1***) and the whole series characterized by mass spectrometry and X-ray crystallography. The dithiolate complex reacts in organic solvents with molecular oxygen to produce sulfinate ($NiS(O)_2R$) complexes, while reactions with hydrogen peroxide have, in addition, permitted the isolation of sulfenate (NiS(O)R) products. The X-ray crystal structures of the complexes [1-(2-mercapto-2-methylpropyl)-5-(2-sulfino-2-methylpropyl)-1,5-diazacyclooctanato(2−)]nickel(II) (**2***), [1,5-bis(2-sulfino-2-methylpropyl)-1,5-diazacyclooctanato-(2−)]nickel(II) (**3***), [1,5-bis(2-sulfeno-2-methylpropyl)-1,5-diazacyclooctanato(2−)]nickel(II) (**5***), and [1-(2-sulfeno-2-methylpropyl)-5-(2-sulfino-2-methylpropyl)-1,5-diazacyclooctanato(2−)]nickel(II) (**6***) were determined and metric data compared with previously characterized **1*** and **4***, [1-(2-mercapto-2-methylpropyl)-5-(2-sulfeno-2-methylpropyl)-1,5-diazacyclooctanato(2−)]nickel(II). Analysis of the $Ni-S_{(av)}$ bond distances for homoleptic complexes reveals that the bond distances are in the order Ni−S(O)R (2.167(5)) > Ni−SR (2.159(3)) > $Ni-S(O)_2R$ (2.127(3)). The average nickel sulfinate S−O distance at 1.459 Å is ca. 0.1 Å shorter than the average nickel sulfenate S−O distance at 1.545 Å. These bond dimensions correlated well with spectroscopic and reactivity data. Electrochemical studies find the $Ni^{II/I}$ reversible couple to be stabilized by ca. 100 mV with conversion of thiolate-S to sulfenate-S donor, while conversion of a sulfenate to a sulfinate stabilized the Ni^{I} state by an additional 200 mV. Mass spectrometry delineated O-atom loss pathways to dominate initial fragmentation patterns from the parent ions in the protic matrix thioglycerol; however, SO_2 extrusion also occurs and is prominent in a nitrobenzyl alcohol (NBA) matrix. The sulfenate complexes are unexpectedly stable and do not undergo either inter- or intramolecular disproportionation reactions to thiolate and sulfinate, nor do they transfer oxygen to triphenyl- or tributylphosphine. Sulfur dioxide removed oxygen from the sulfenates, yielding thiolates and SO_3, whereas no reaction occurred with the sulfinate complexes. Complexes that represent partial oxidation of the sulfurs further reacted with hydrogen peroxide to produce higher oxygenates and also reacted with electrophiles such as alkyl halides to produce S-bound sulfoxide ligands.

Introduction

It has long been known that thiols (including cysteine) undergo aerial oxidation to form disulfides (cystine) and that this reaction is catalyzed by the presence of transition metals such as nickel.[1] Nickel-containing enzymes such as CO-dehydrogenase[2] and [NiFe] hydrogenase[3] possess a sulfur-rich (cysteinate) environment around nickel and display interesting and complicated air sensitivity, which includes reversible inhibition of activity and irreversible deactivation of the enzyme by dioxygen. Electrochemical and spectroscopic evidence from enzyme studies supports the hypothesis that the deactivated species might involve oxidized Ni and also products of oxygen addition at sites other than the metal.[3] The possible sulfur oxygenates are sulfinate ligands, or metallosulfones, $M-SO_2R$, and sulfenates, or metallosulfoxides, M−S(=O)R. To date, there are two nickel thiolate complexes that have provided examples of the latter,[4] whereas three potential thiolate model complexes have demonstrated production of sulfinates from reactions with H_2O_2 or gaseous O_2. Such $NiSO_2R$ complexes are all S-bound and the oxygen atoms have not been removable by chemical agents. Hence an S-bound sulfinate could represent an irreversibly oxygen-damaged enzyme. No examples of O-bound sulfinate ligands, of the type characterized by Zubieta et al. from the reaction of a ruthenium *cis*-dithiolate with dioxygen, have been found.[5]

Other research groups have reported results on the direct oxygenation of nickel thiolate complexes as models for oxygen-degraded enzymes. Maroney[6] et al. have shown that a nickel(II) complex with *trans* thiolates reacts with dioxygen to form a thiolate/sulfinate complex, which is no further reactive with dioxygen. Schrauzer[7] has reacted dioxygen with an anionic

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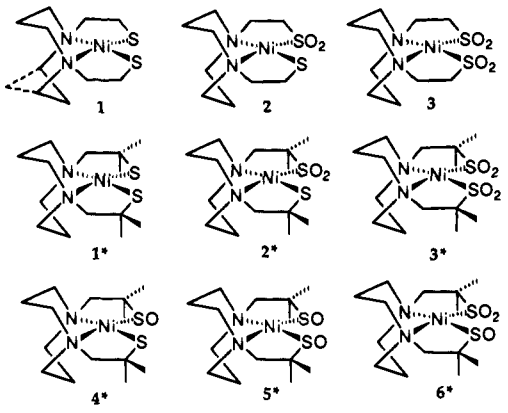
Scheme 1



nickel complex containing two sets of *cis* thiolate sites to produce a *cis* disulfinate complex. The remaining *cis* thiolate sites showed no further reaction with dioxygen nor with hydrogen peroxide. The nickel(II) dithiolate complexes based on the bis(mercaptoethyl)diazacyclooctanato ligand (**1**)[8] undergo aerial oxidation at sulfur, in organic solvents, to produce sulfinate complexes **2** and **3** (Scheme 1) rather than the conventional product of thiolate oxidation, the disulfide.

A similar, but more sterically hindered, complex [1,5-bis(2-mercapto-2-methylpropyl)-1,5-diazacyclooctanato(2−)]nickel-(II) (**1***, (bme*-daco)Ni)[4,9,10] undergoes much slower reactions with molecular oxygen to produce mono- and disulfinate complexes **2*** and **3***, respectively, and also will, as we report below, react with stoichiometric amounts of hydrogen peroxide to produce stable sulfenates **4*−6*** shown in Scheme 1. One such sulfenate complex, **4***, was characterized structurally and reported in communication form.[4] This series permits electrochemical studies to augment those of the (bme-daco)Ni complexes **1−3**, which showed that the accessibility of the $Ni^{II/I}$ couple depends on the substituents on the sulfur donors: SR_2 > $^-S(O)_2R$ > ^-SR . Results herein on complexes **1*−6***, will extend this knowledge to include sulfenates, $^-S(O)R$, expected to be intermediate between thiolates and sulfinates in character.

Earlier papers reported that the thiolate sulfurs of (bme-daco)-Ni react with dioxygen in organic solvents via two separate paths to produce mono- or disulfinate complexes; in each case, dioxygen always adds as a molecule.[11] Isotopic labeling studies[12] indicated that a likely pathway to the disulfinate would involve the formation of a disulfenate (or metallosulfoxide) intermediate by dioxygen addition across *cis* sulfur sites; however, such a disulfenate $Ni(S(=O)R)_2$ could not be isolated. The introduction of steric constraints α to the thiolate sulfurs in the (bme*-daco)Ni complexes has allowed the further stabilization and isolation of stable sulfenate complexes.[4]

Sulfenate complexes are uncommon and have been the target of rather limited research. Reports of stable cobalt(III) complexes[13] show that thiolate ligands may be converted to sulfinates by the action of hydrogen peroxide, and in some cases, sulfenate complexes were also isolated.[14] Dioxygen was not used as an oxygen source in these reactions. Deutsch[14] has characterized a cobalt sulfenate complex by crystallography and ascribes the scarcity of such complexes to the ability of the sulfenate ligand to react as both an electrophile and a nucleophile.[15] In addition to the cobalt derivatives, sulfenate complexes were reported for platinum,[16] iridium,[17] and possibly ruthenium,[18] but not for nickel, outside of this research.

Experimental Section

General Techniques. Complex **1*** was prepared and further reacted with hydrogen peroxide, under anaerobic conditions, while subsequent handling of the sulfur oxygenates was performed in air. Isobutylene sulfide[19] and 1,5-diazacyclooctane[20] (daco) were synthesized by published procedures. Hydrogen peroxide was used as a 30% w/v aqueous solution (Mallinkrodt). ^{18}O-labeled dioxygen (99.8%) was purchased from Isotec. All other reagents were purchased from Aldrich Chemical Co. and used as obtained.

Chromatography. All of the neutral nickel complexes were purified and separated from mixtures by chromatography through a 10 × 1 in. (or 0.5 in.) column of silica gel (60−200 mesh, Aldrich grade 922 or EM Science grade 22, pretreated with aqueous pH 10 buffer and washed with ethanol).[21] Methanol (optimal), ethanol, and ethanol/water were used as eluants.

Physical Measurements. NMR spectra were recorded using a Varian XL-200 FT NMR spectrometer. UV−vis spectra were recorded by a Hewlett Packard HP8452A diode array spectrophotometer. Infrared spectra were recorded as KBr pellets using an IBM IR/32 Fourier transform single beam spectrophotometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Mass spectra were determined at the Center for Chemical Characterization and Analysis, Texas A & M University. Positive ion fast atom mass spectra were recorded in thioglycerol and nitrobenzyl alcohol (NBA) matrices using a VG-70S spectrometer with a xenon source having particle energy of 10 keV. Data were collected by a VG11-250J data system. Isotopomeric mass analyses were performed using a double laser light desorption (DLLD) technique in conjunction with either a linear time of flight (LTOF) or a Fourier transform ion cyclotron resonance (FTICR) method of ion detection. GC/MS of gas samples were recorded by a Hewlett Packard HP5995C with a quadrupole mass analyzer.

Cyclic voltammographs were obtained using a Bio-Analytical Systems 100A electrochemical analyzer with a glassy carbon stationary electrode and a platinum wire auxiliary electrode. Samples were measured in acetonitrile solution (2.5 mM) with $[n\text{-}Bu_4N][PF_6]$ (0.1 M) as the supporting electrolyte and a $Ag/AgNO_3$ reference electrode. Potentials were standardized with methyl viologen and referenced to NHE.

All X-ray crystal structures were solved at the Crystal & Molecular Structure Laboratory Center for Chemical Characterization and Analysis at Texas A & M University. For complexes **2*−5***, X-ray crystallographic data were obtained on a Nicolet R3m/V single crystal X-ray diffractometer operating at 55 kV and 30 mA, Mo Kα (λ = 0.710 73 Å) radiation, equipped with a Nicolet LT-2 cryostat. Diffractometer control software P3VAX 3.42 was supplied by Nicolet Analytical X-ray Instuments. Structures were solved[22] using SHELXT-PLUS. In all

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(21) The current understanding of $[(bme\text{-}dacoNi)_2Ni]^{2+}$ formation is that it occurs primarily as a result of contact with acidic silica gel during chromatography. Acidification releases a Ni^{2+} ion which rapidly and irreversibly is complexed by two parent (bme-daco)Ni metallothiolate ligands. Base treatment of the silica gel prevents this side reaction.

cases, crystals were mounted on a glass fiber with epoxy cement at room temperature. In the structure determination of complexes **1*** and **6***, a Rigaku AFC5 diffractometer was used, operating at 55 kV and 180 mA, Cu Kα (λ = 1.541 78 Å) radiation. X-ray experimental conditions for all the complexes are shown in Table 3.

Syntheses. The syntheses of complexes **1*** and **4*** have been described elsewhere.[9,4]

1,5-Bis(2-mercapto-2-methylpropyl)-1,5-diazacyclooctane. Isobutylene sulfide (3.00 g, 34 mmol) was added in one portion to a solution of 1,5-diazacyclooctane (1.96 g, 17 mmol) in dry benzene (50 mL) stirred under nitrogen. After 48 h at room temperature, the solution was filtered through Celite to remove any precipitated disulfide and the solvent removed in vacuo, yielding a yellow oil (2.02 g, 40.8% yield).

[1,5-Bis(2-mercapto-2-methylpropyl)-1,5-diazacyclooctanato-(2−)]nickel(II) (1*). The following is a revised version of the previously published method.[9] 1,5-bis(2-mercapto-2-methylpropyl)-1,5-diazacyclooctane (1.80 g, 6.2 mmol) was dissolved in dry toluene (100 mL). To this was cannulated slowly a green solution of $Ni(acac)_2$ (1.52 g, 5.9 mmol) in toluene (200 mL), producing a purple solution with a dark precipitate. The solution was filtered and the purple solid washed with toluene (2 × 100 mL), followed by diethyl ether (2 × 100 mL). The solid was dissolved in a minimum of methanol (5 mL) and purified by chromatography on a silica gel column (10 × 1 in.), eluting with ethanol (95%). A purple solid, **1*** (0.20 g, 10% yield based on Ni(II)), resulted on evaporation of the solvent. Single crystals suitable for X-ray crystal structure analysis were obtained by ether diffusion of an acetonitrile solution. Mp: 298 °C dec. Anal. Calcd (found) for $C_{14}H_{28}N_2NiS_2$: C, 48.45 (47.72); H, 8.00 (7.86); N, 8.00 (7.83).

[1-(2-Mercapto-2-methylpropyl)-5-(2-sulfino-2-methylpropyl)-1,5-diazacyclooctanato(2−)]nickel(II) (2*) and [1-(2-Sulfeno-2-methylpropyl)-5-(2-sulfino-2-methylpropyl)-1,5-diazacyclooctanato-(2−)]nickel(II) (6*). A purple solution of **1*** (1.00 g, 2.88 mmol) in methanol (250 mL) was cooled to −78 °C under nitrogen. A solution of hydrogen peroxide (30% w/v aqueous solution) (0.64 mL, 5.6 mmol) in methanol (20 mL) was then added in 0.1 mL aliquots over a 2 h period. The resulting yellow solution was concentrated and purified by chromatography on a silica gel column with methanol elution. The monosulfinate complex **2*** eluted first as an orange band (0.56 g, 51%). The yield of **2*** is higher when the reaction was performed in methanol at −78 °C than when the reaction was performed in water at room temperature. Single crystals of **2*** suitable for X-ray analysis were grown by the slow evaporation of a concentrated MeCN solution. A summary of the crystallographic parameters for compound **2*** is found in Table 3. Mp: 260 °C dec. Anal. Calcd (found) for $C_{14}H_{28}N_2S_2O_2Ni$: C, 44.36 (44.23); H, 7.39 (7.74); N, 7.39 (6.87).

A second orange band was collected and identified as containing the sulfinate/sulfenate complex **6*** (0.52 g, 48%). Details are presented below.

[1,5-Bis(2-sulfino-2-methylpropyl)-1,5-diazacyclooctanato(2−)]nickel(II) (3*). A solution of **1*** (0.10 g, 0.14 mmol) in water (20 mL) at 22 °C was reacted with excess hydrogen peroxide (30% w/v aqueous solution) (0.32 mL, 2.9 mmol) added in one aliquot, resulting in an immediate color change to bright yellow. The solution was stirred at room temperature for a further 2 h. Chromatography of the product on a silica gel column (10 × 1 in.), eluting with 40% water/ethanol, and subsequent removal of the solvent by vacuum yielded the disulfinate complex **3*** as a bright yellow solid (0.072 g, 60%). Single crystals suitable for X-ray were grown from a H_2O/acetone mixture. A summary of the crystallographic parameters for compound **3*** is found in Table 3. Mp: 250 °C. Anal. Calcd (found) for $C_{14}H_{28}N_2S_2O_4Ni$: C, 33.80 (32.53); H, 5.63 (5.84); N, 7.88 (7.51).

[1-(2-Mercapto-2-methylpropyl)-5-(2-sulfeno-2-methylpropyl)-1,5-diazacyclooctanato(2−)]nickel(II) (4*) and [1,5-Bis(2-sulfeno-2-methylpropyl)-1,5-diazacyclooctanato(2−)]nickel(II) (5*). A solution of **1*** (0.10 g, 0.29 mmol) in methanol (250 mL) was cooled to −78 °C under nitrogen, and a dilute solution of hydrogen peroxide (30% w/v aqueous solution) (16 μL, 0.14 mmol) in methanol (20 mL) was added in 1 mL portions over a period of 2 h. The resulting brown solution was warmed to room temperature and purified by silica gel chromatography. The following products were separated, in order of elution, with ethanol: the starting dithiolate complex **1***, the monosulfenate complex **4*** (50%) as an orange band, and the disulfenate complex **5*** (18%) as a yellow-orange band. X-ray quality crystals of **4*** and **5*** were grown by ether diffusion into saturated dichloromethane solutions of **4*** and **5***, respectively.

For compound **4***, anal calcd (found) for $C_{14}H_{28}N_2S_2ONi\cdot H_2O$: C, 44.09 (43.75); H, 7.87 (7.75); N, 7.34 (7.05). For compound **5***, three attempts to obtain elemental analyses consistent with the X-ray crystal structure determination were unsuccessful. This is ascribed to the hygroscopic nature of the oxygenates as well as the presence of Na^+ from the base-treated separations column. The "best" analysis assumed anal calcd (found) for $C_{14}H_{28}N_2S_2O_2Ni\cdot 2NaOH$: C, 36.62 (36.77); H, 6.59 (6.79); N, 6.10 (5.91).

[1-(2-Sulfeno-2-methylpropyl)-5-(2-sulfino-2-methylpropyl)-1,5-diazacyclooctanato(2−)]nickel(II) (6*). The sulfinate/sulfenate complex **6*** was obtained in 48% yield, as a partial product along with **2***, from the reaction of **1*** (1.0 g, 2.9 mmol) with H_2O_2 (0.64 mL, 5.6 mmol) in MeOH (250 mL) at −78 °C. Compound **6*** was recrystallized by ether diffusion into a concentrated dichloromethane solution. The molecular ion for this complex was observed in the FAB MS in an NBA matrix at *m/z* 396 (396 expected).

Due to cocrystallization, elemental analyses were unacceptable. The crystal structure revealed that the crystal cell contained 71% of complex **6*** and 29% of complex **3***.

Reaction of 1* with O_2. Dioxygen was passed through a purple solution of **1*** (0.1 g, 0.29 mmol) dissolved in dry MeCN (20 mL) for a period of 24 h. The reaction mixture was then sealed and left under a positive O_2 pressure for a further 72 h. The resulting brown solution was reduced in volume by evaporation of the solvent, and the products were separated by column chromatography on silica gel (10 × 1 in.). The products eluted (methanol) in the following order: the purple **1*** (89 mg), the orange monosulfinate complex **2*** (2 mg), and the yellow disulfinate complex **3*** (9 mg).

The disulfenate complex **5*** also showed uptake of molecular oxygen, and this was followed by GC/MS and ^{18}O-labeling studies. The complex **5*** was shown to convert under bubbling oxygen in MeCN solution to the disulfinate complex **3***, the reaction having a half-life of 8 h. For the labeling study, **5*** (2.4 mg, 6.4 μmol) was dissolved in MeCN (1 mL) in a flask containing 45% dioxygen (6:1 $^{18}O_2$:$^{16}O_2$, 0.5 mmol total). The product was isolated after 7 days and shown by FAB MS to be complex **3*** that had incorporated one molecule of $^{18}O_2$ per nickel.

Results and Discussion

Synthesis. The preparation of complex **1*** and the nucleophilic activity of its sulfur sites have been reported previously.[9] In that report, the steric effect of the four methyls α to the sulfurs was demonstrated by analysis of structural differences in macrocyclic complexes derived from **1*** vs **1**.

The sulfur oxygenates presented below were obtained by reaction of the dithiolate complex **1*** with hydrogen peroxide as described in the Experimental Section. The yields of individual complexes were optimized by variation of reaction stoichiometry, temperature, and dilution. Further studies of the reactivities of the sulfurs in the complexes with O_2 and electrophiles are presented later.

Infrared Studies. Table 1 lists the ν(SO) absorptions for the oxygenate complexes **2***−**6***. The assignment of the bands in the 900−1200 cm^{-1} region for the title series to ν(SO) was confirmed by comparisons of the IR spectra of ^{18}O-labeled representative complexes. For example, bands for complex **2*** typically seen at 1181 and 1054 cm^{-1} were shifted to 1146 and 1019 cm^{-1} in ^{18}O-labeled **2*** when the complex was prepared by reaction with $^{18}O_2$. The sulfinate complexes show a two-band set, $\nu(SO)_{asym}$ and $\nu(SO)_{sym}$ in the range 1190−1030 cm^{-1},

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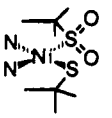
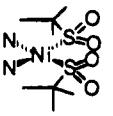
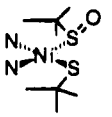
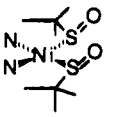
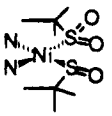
Table 1. Physical and Spectroscopic Properties of Compounds 1*−6*

	 1*	 2*	 3*	 4*	 5*	 6*
color	purple	orange	yellow	orange	orange	yellow
IR[a] ν(SO) (cm^{-1})						
Ni−SO				909	921	918
Ni−SO_2 (asym)		1044	1032, 1071			1036
Ni−SO_2 (sym)		1181	1180, 1192			1182
UV[b] (nm (ϵ))[c]						
LMCT	352 (192)	302 (6727)	320 (10 476)	360 (4697)	374 (5968)	368 (6717)
d−d	486 (70)	422 (51)	380 (938)	474 (534)	472 (689)	450 (1827)
^{1}H NMR[d,e] (ppm)	1.42, s (12H)	1.37, s (6H)	1.27, s (12H)	1.66, s (3H)	1.51, s (6H)	1.60, s (3H)
		1.25, s (6H)		1.56, s (3H)	1.47, s (6H)	1.37, s (3H)
				1.32, s (3H)		1.17, s (3H)
				1.22, s (3H)		1.16, s (3H)
FAB (*m/z*) $[M + H]^+$[f]	347	379	411	363	379	395

[a] KBr pellets. [b] Measured in methanol solution. [c] ϵ in M^{-1} cm^{-1}. [d] Methyl region. [e] CD_3OD, TMS reference. [f] Thioglycerol matrix.

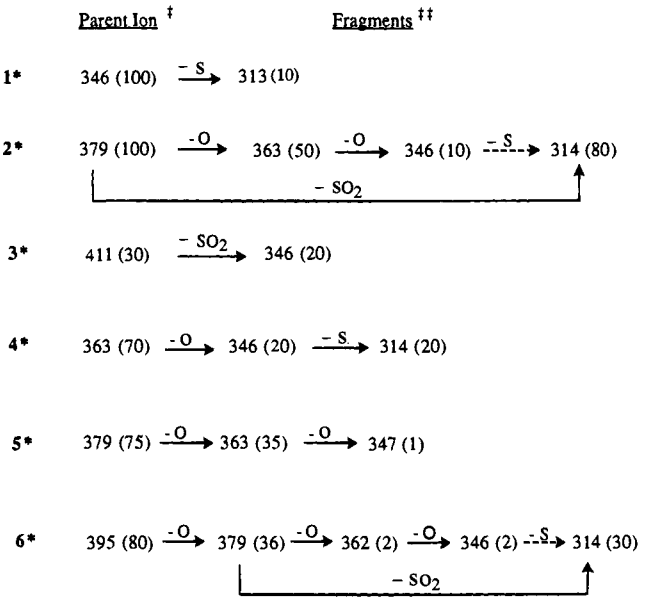
whereas the sulfenates show ν(SO) as single absorbances at lower wavenumber, ca. 900−920 cm^{-1}. The lower frequency of the ν(SO) stretches of the sulfenates as compared to that of their sulfinate rivals indicates a weaker S−O bond in the sulfenate complexes[5] and is consistent with X-ray crystal structure data, *vide infra*. A comparison of the ν(SO) absorption frequencies for the sulfinate complexes **2*** and **3*** vs analogous **2** and **3** revealed only minor differences.

^{1}H NMR Studies. The previous series of oxygenates based on the bme-daco ligand displayed appreciable tetrahedral twists[23] from the N_2S_2Ni square plane, resulting in paramagnetism (for d^8 nickel(II)) which precluded NMR studies. The series of oxygenates based on the bme*-daco ligand are all diamagnetic, presumably due to a more rigorously square planar structure imposed by the substituent methyl groups on the carbon α to the sulfurs. Characterization of the complexes by NMR spectroscopy finds the methyl region of the ^{1}H NMR spectra particularly diagnostic; chemical shift data for the methyl region of complexes **1*−6*** are given in Table 1. The symmetry about the central nickel dictates the number of methyl resonances observed. At room temperature, all four methyl groups in the starting material, **1***, are equivalent and appear as a single resonance at 1.42 ppm (12H); whereas the disulfenate complex, **5***, displays two pairs of nonequivalent methyl groups and hence two singlets (6H) and the monosulfinate, **4***, has four nonequivalent singlet (3H) resonances, similarly to **6***. These simple symmetry guidelines can be used to identify the products.

The low-temperature spectrum of **1*** was expected to resolve the singlet (12H) into two singlets (6H), as the ligand's thermal motion slowed with respect to the NMR time scale and the axial and equatorial methyl groups became nonequivalent. However, the signal remained a singlet, with some broadening, at −78 °C in methanol solution.

Mass Spectrometry. The complexes in the series of oxygenates **2*−6*** were examined by FAB MS in both thioglycerol and nitrobenzyl alcohol matrices. All spectra show parent ions, and these are listed in Table 1. Additionally, all complexes show the presence of a stable fragment ion assignable to the dithiolate complex **1***, indicating that both sulfinate- and sulfenate-containing complexes undergo loss of oxygen. The path of oxygen loss from the ligands, however, is dependent on both complex and matrix. For example, analysis of the sulfinate complex **3*** in the thioglycerol matrix shows a stepwise loss of atomic oxygen from the molecular ion, yielding sulfenate intermediates, whereas in NBA loss of a fragment of mass 64 suggests SO_2 is extruded (Scheme 2). Complex **2*** readily loses SO_2, showing a signal at *m/z* 314 whose great intensity suggests direct production from the parent ion rather than stepwise loss of two O and one S atom. These SO_2 fragments were observed directly with use of the DLLD technique and were useful diagnostics in $^{16}O_2/^{18}O_2$ isotopic labeling studies.[11]

Scheme 2



[a] ‡For **1***, the molecular ion $[M^+]$; for oxygenates, $[M + H^+]$. ‡‡NBA matrix. Relative % in parentheses.

The parent ions of the sulfenate complexes, **4*−6***, degrade initially by loss of atomic oxygen (Scheme 2). The magnitude of the signal at *m/z* 314 for complex **6*** indicates SO_2 loss from the remaining sulfinate moiety. The spectra of sulfenate complexes **4*** and **5*** do not show loss of SO_2. Therefore the mechanism of oxygen loss from **5*** is unlikely to involve disproportionation (or intramolecular O-atom transfer) to the monosulfinate complex **2***.[24] Spectra of complexes **5*** and **6***,

(23) The tetrahedral twist angles are determined as the angle of the intersection of the normals of the S(1)−X−S(2) and N(1)−X−N(2) planes, where X is the centroid of the N_2S_2 plane. As the nickel is not always equidistant from the nitrogens and the sulfurs, the centroid rather than the nickel is used to define the planes.

(24) An alternate possibility for the production of ions of *m/z* 32 units lower could involve loss of dioxygen.

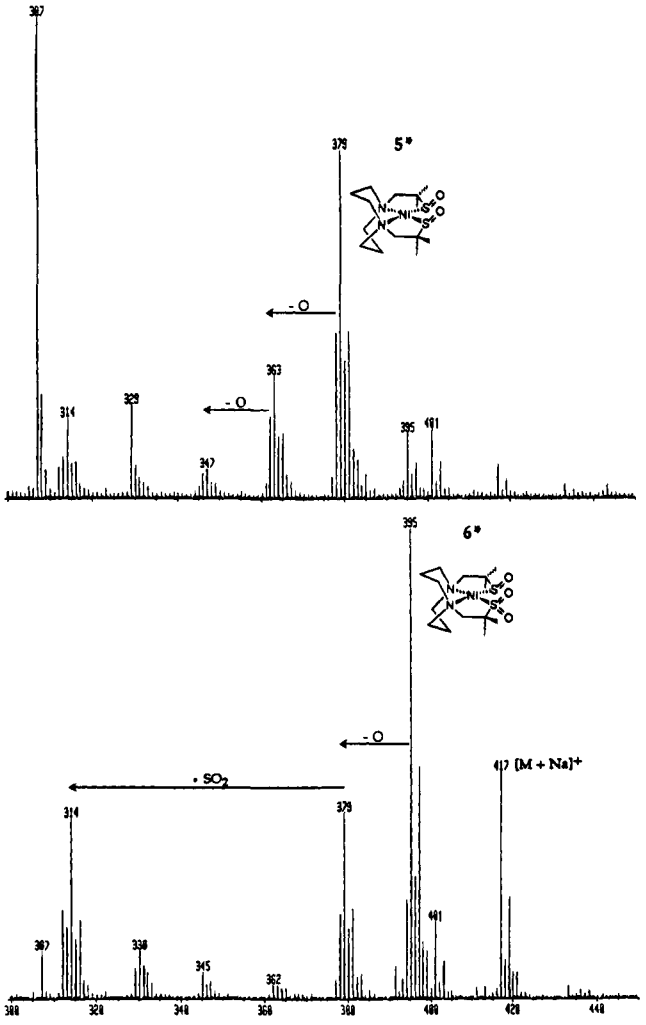


Figure 1. +FAB MS spectra of complexes **5*** and **6***. Spectra recorded in NBA matrix.

representative of the fragmentation patterns for sulfenates and sulfinates, respectively, are shown in Figure 1. Under these conditions, there has been no indication of SO loss from any of the sulfenates. Furthermore, a DLLD MS study on the sulfinate/sulfenate complex **6*** showed loss of SO_2 at 64 Da but no signal at 48 Da that would relate to an SO fragment.

Uptake of molecular oxygen ($^{16}O_2$ and $^{18}O_2$) by the disulfenate complex **5***, to yield **3***, *vide infra*, was followed by FAB MS. The starting material **5*** shows a molecular ion at *m/z* 379, and the disulfinate complex prepared from **5*** and $^{16}O_2$ has a molecular ion at *m/z* 411. The product derived from addition of $^{18}O_2$ to **5*** showed a molecular ion at *m/z* 415, indicating addition to yield doubly ^{18}O-labeled **3***. The presumption that $^{18}O_2$ added across the two sulfur sites of **5*** was further supported by the fragmentation patterns produced by double laser light desorption mass spectrometry.

Previous FTICR MS results of the isotopically labeled disulfinate complex of (bse-daco)Ni, **3**, prepared from a mixture of $^{16}O_2$ and $^{18}O_2$, found $S^{16}O^{18}O$ fragments, observed at 66 Da, indicating scission of the O−O bond across *cis* sulfur sites.[11] In the latest study, complexes were examined using LTOF MS techniques after laser excitation. The disulfinate complex, **3***, formed by reaction of $^{18}O_2$ (contaminated with $^{16}O_2$) with the ^{16}O-disulfenate complex, **5***, showed SO_2 photofragment signals at mass 64 and 66 Da, corresponding to natural abundance SO_2 and the expected mixed label $S^{16}O^{18}O$ fragment, respectively.

Cyclic Voltammetry. Cyclic voltammographs for complexes **1***, **3***, and **5*** are shown in Figure 2, and a compilation of the

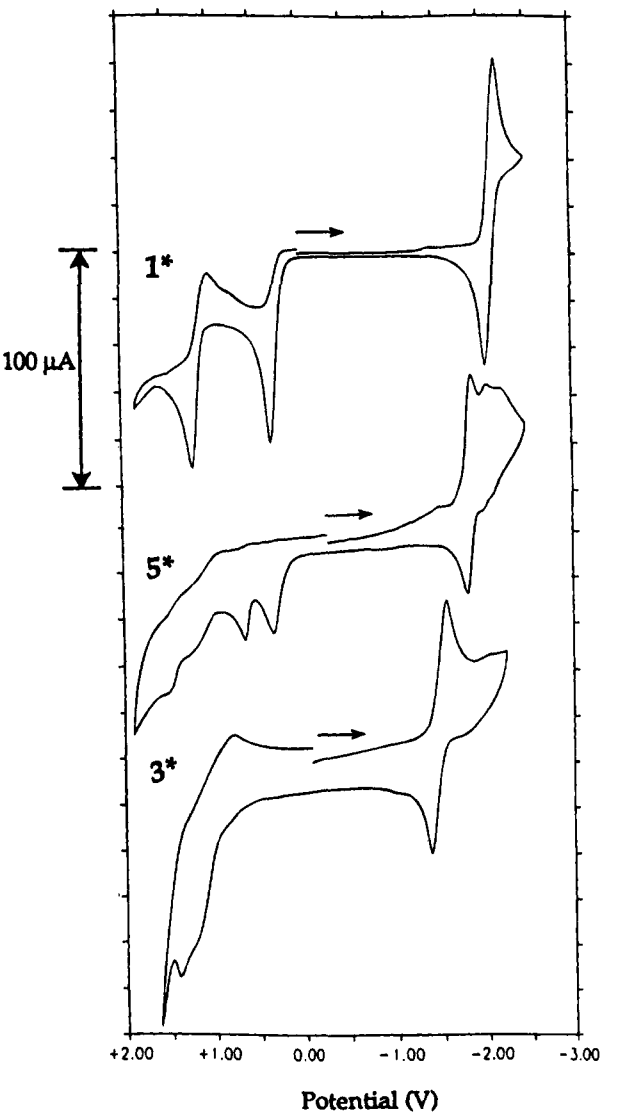


Figure 2. Cyclic Voltammographs for complexes **1***, **3***, and **5***. Samples recorded as 2.5 mM solutions in 0.1 M TBAHFP/MeCN using a glassy carbon electrode at 200 mV s^{-1}. Potentials referenced to NHE with MeV^{2+}/MeV^{+}.

Table 2. Potential[a] and Reversibility Data from Cyclic Voltammetry in CH_3CN[b] for Compounds 1*−6*

	rev Ni^{II}/Ni^{I}			irrev$_{ox}$	
compd	$E_{1/2}$ (mV)	DE (mV)	i_{pa}/i_{pc}	E_{pa} (mV)	E_{pa} (mV)
1*	−2119	85	0.95	+264	
2*	−1829	74	0.88	+574	+318.5
3*	−1488	76	0.89	+1290	
4*	−2030	68	0.75	+310.8	−62.2
5*	−1833	71	0.71	+845.9	+294
6*	−1720	69	0.80	+800.7	+324

[a] All potentials scaled to NHE referenced to a MeV^{2+}/MeV^{+} standard ($E_{1/2}^{NHE}$ = −440 mV). [b] 0.1 M TBAHFP electrolyte measured vs a $Ag/AgNO_3$ reference electrode.

electrochemical data for the series of complexes **1*−6*** is displayed in Table 2.

The electrochemical data for (bme*-daco)Ni (**1***) and its derivatives are very similar to that for the analogous (bme-daco)-Ni series.[25] The cyclic voltammographs show reversible $Ni^{II/I}$ reduction waves for all the complexes, and complexes that contain a nickel thiolate moiety show S-based irreversible

Table 3. Crystallographic Data for Compounds 1*–6*

complex	1*	2*	3*	4*	5*	6*
chem. form.	$C_{14}H_{28}N_2S_2Ni$	$C_{14}H_{28}N_2O_2S_2Ni$	$C_{14}H_{38}N_2O_9S_2Ni$	$C_{14}H_{29}N_2O_1Ni$	$C_{14}H_{33}N_2O_4S_2Ni$	$C_{14}H_{30}N_2O_9S_2Ni$
FW (amu)	347.2	379.3	501.3	375.7	424.3	501.3
space group	*Pnma*	*Pbca* (no. 61)	$P\bar{1}$	*P*2(1)/*c*	$P\bar{1}$	*C*2/*c* (no. 15)
a (Å)	11.307(2)	13.655(5)	8.066(2)	10.643(4)	7.9210(2)	19.967(8)
b (Å)	19.579(3)	13.004(4)	10.159(3)	22.047(12)	11.802(2)	7.970(2)
c (Å)	7.4790(10)	19.128(4)	14.231(5)	7.912(3)	12.0580(10)	24.287(5)
V (Å^3)	1655.7(4)	3396(2)	1110(6)	1749.2(13)	1008.5(2)	
α (deg)			96.67(3)		105.760(10)	107.44
β (deg)			105.70(3)	109.58(3)	96.400(10)	
γ (deg)			93.02(2)		107.920(10)	
Z	4	8	2	4	2	8
temp (K)	296	296	296	193	296	296
R (*R*$_w$)[a] (%)	4.1 (4.1)	6.8 (7.1)	5.4 (3.9)	6.14 (6.08)	5.0 (5.2)	6.0 (6.1)

[a] Residuals: $R = \Sigma|F_o - F_c|/\Sigma F_o$; $R_w = \{[\Sigma w(F_o - F_c)^2]/[\Sigma w(F_o)^2]\}^{1/2}$.

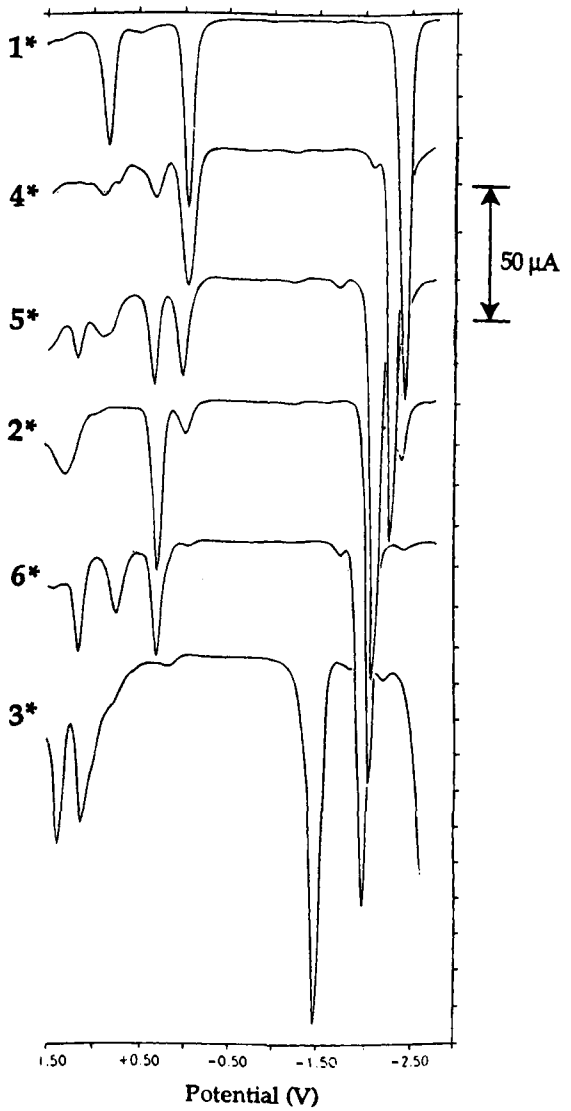


Figure 3. Square-wave voltammograph spectra for complexes 1*–6*. Samples recorded as 2.5 mM solutions in 0.1 M TBAHFP/MeCN using a glassy carbon electrode at 200 mV s^{-1}. Potentials referenced to NHE with MeV^{2+}/MeV^{+}.

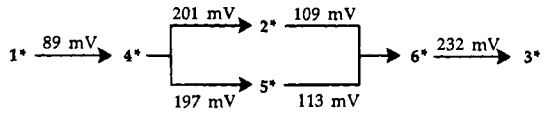
oxidations. On the basis of previous EPR identification of the Ni^{I} species in reduced **3**,[25] the reversible reduction waves in all complexes are assigned to Ni$^{II/I}$. The Ni$^{II/I}$ couple for **1***, at an $E_{1/2}$ of −2119 mV (vs NHE), is 175 mV more difficult to attain than that for (bme-daco)Ni (at −1944 mV), accountable to the fact that the methyl substituents of **1*** increase the electron density on the sulfurs, which subsequently destabilizes the electron-rich Ni^{I} oxidation state.

Since the bme*-daco free ligand has an irreversible oxidation at ~+285 mV, the first of two irreversible oxidations (+264 and +1074 mV) of complex **1*** is assigned to ligand oxidation. This oxidation is 75 mV more accessible than for (bme-daco)-Ni, again accountable to increased electron density at sulfur. The second oxidation wave of **1*** is possibly metal-based, but attempts to isolate the Ni^{III} state of **1*** by chemical oxidation were unsuccessful.

Complexes **2*** and **3*** have reversible Ni$^{II/I}$ couples at $E_{1/2}$ of −1829 and −1488 mV (vs NHE), respectively. The Ni$^{II/I}$ couples for **2*** and **3*** are less accessible by 198 and 149 mV than their respective bme-daco complexes **2** and **3**. The most notable difference between the (bme-daco)Ni and (bme*-daco)-Ni systems is that complex **3*** has an irreversible oxidation at +1290 mV rather than the reversible couple seen for **3** at +847 mV. Complex **2*** has an irreversible oxidation wave at +574 mV.

The effect of sulfenato ligands on nickel redox potentials was established by cyclic voltammetry of **4***–**6***. Table 2 summarizes the electrochemical data for the series, and the stacked square-wave plots for complexes **1***–**6*** in Figure 3 show the progression of accessibility of the Ni$^{II/I}$ couple with each O added to S, which is summarized in Scheme 3. The addition of one oxygen to complex **1*** causes a stabilization of the Ni^{I} oxidation state by 89 mV. Further addition of oxygen to complex **4*** yields two distinct products, **2*** and **5***. In both cases, the addition of a second oxygen either to the sulfenate (Ni−S(O)R) or to the second thiolate (Ni−SR) stabilizes the Ni^{I} by approximately 200 mV. Addition of another oxygen atom to either **2*** or **5*** yields the same product, **6***. The Ni$^{II/I}$ stabilization obtained from either process amounts to ~110 mV. The final oxygenation yields complex **3*** with a stabilization of 232 mV for this step. In essence, even to odd changes in number of oxygens increase the accessibility of the Ni$^{II/I}$ couple by ~100 mV, while odd to even changes are ~200 mV, with an overall stabilization of Ni^{I} in going from **1*** to **3*** of >600 mV.

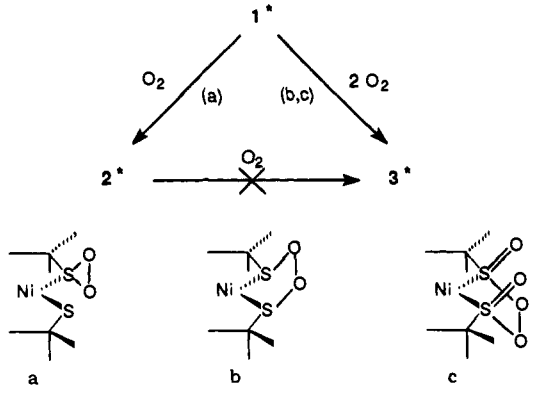
Scheme 3



These data validate the 300 mV (~6.9 kcal mol^{-1}) stabilization on the oxidation of a nickel-bound thiolate (Ni−SR) to a sulfinate (Ni−SO$_2$R) first found for (bme-daco)Ni and its sulfinate derivatives.[25] These shifts in potential should be

(25) Darensbourg, M. Y.; Farmer, P. J.; Lindahl, P. A.; Reibenspies, J. H. *J. Am. Chem. Soc.* **1993**, *115*, 4665.

Scheme 4



accurate reflections of the difference in donor ability between the thiolate and the sulfinate ligands since the charge of the complex remains the same. Interestingly, the d−d transitions for complexes **1***−**6*** (Table 1) also agree that the SO_2R ligands are stronger field ligands, with a similar progression of d−d splitting as seen in the stabilization of the electron-rich Ni^I.

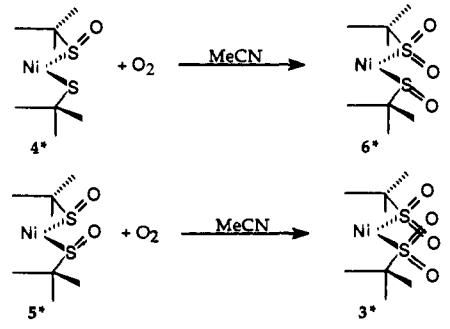
Although the nickel(II) sulfenate complexes are thermally stable, repeated cyclic scans of complex **4*** produced waves attributed to **1*** and **2***. That is, the sulfenate complex is observed to disproportionate under electrochemical reducing conditions. This phenomenon has been studied in detail for complex **4** and is the subject of a separate paper.[4b]

Reactivity. Reactions with Molecular Oxygen. Thiolates: Complex **1*** reacts slowly with dioxygen in acetonitrile solution under ambient conditions (pyrex glassware, laboratory light, 22 °C) to produce the mono- and disulfinate complexes **2*** and **3***. Over the course of 1 week, there is <10% conversion. In contrast, the less sterically hindered dithiolate **1** shows ca. 25% conversion to **2** and **3** (20% **2** and 5% **3**) in 24 h. The reactions of both **1** and **1*** complexes with O_2 are greatly accelerated under UV photolysis, to give a range of sulfinate and sulfenate products, the full report of which is under preparation.[26]

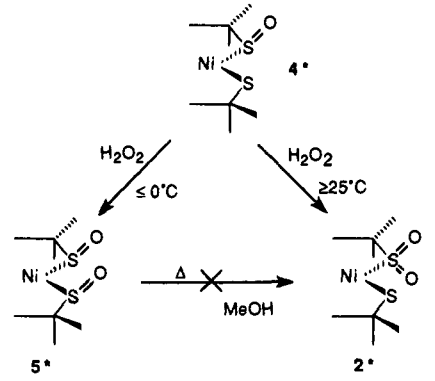
Sulfinates: Both the monosulfinate **2*** and the sulfenate/sulfinate complex **6*** were recovered unchanged from acetonitrile solutions stirred under dioxygen under ambient conditions over the course of 1 week. The presence of a sulfinate moiety in the complex **2** was previously shown to reduce the nucleophilicity of the remaining thiolate sulfur as compared to precursor complex **1**,[12] and this effect is operative with the bme*-daco derivative as well. Mechanistic studies[11] of the production of the sulfinates from reaction with molecular oxygen are interpreted as involving two independent operative pathways. By analogy, the monosulfinate complex **2*** is expected to be formed by addition of a molecule of oxygen at one thiolate site, presuming a thiadioxirane intermediate a, whereas the disulfinate complex **3*** is formed by addition of two molecules of oxygen across the *cis* thiolate sites (Scheme 4). This second path is blocked in **2** or **2***, consistent with the lack of reaction of isolated **2** or **2*** with O_2. The second path may involve a concerted addition of two dioxygen molecules or may involve the formation of a disulfenate intermediate; intermediates such as b and c in Scheme 4 are proposed.

Sulfenates: Consistent with Scheme 4, the sulfenate-containing complexes were observed to react faster with O_2 than comparable thiolates, with the reactions proceeding to completion under a static 1 atm of O_2 within 4 days (Scheme 5). For example, the monosulfenate **4*** reacts with dioxygen in acetonitrile solution to produce the sulfenate/sulfinate complex **6*** as the only product in 20 h, and reaction of the disulfenate complex **5*** with O_2 produces only the disulfinate complex **3***. As presented above, reaction of **5*** with $^{18}O_2$ yielded **3***, which when photoionized produced the SO_2 isotopomer of mass 66 Da, i.e., $S^{16}O^{18}O$, consistent with the proposal that **3*** is derived according to intermediate c in Scheme 4.

Scheme 5



Scheme 6



Reactions with H_2O_2 as an O-Atom Source. Reaction of **1*** with excess hydrogen peroxide produced a mixture of products. As with (bme-daco)Ni, sulfinate complexes **2*** and **3*** are formed. These sulfinate complexes result when the reactions are carried out at room temperature with excess of peroxide. However, formation of the monosulfenate complex **4***, as well as the disulfenate complex **5***, is favored at low temperatures and high dilution. Complex **6*** is specifically produced on reaction of a deficiency of H_2O_2 with **5***.

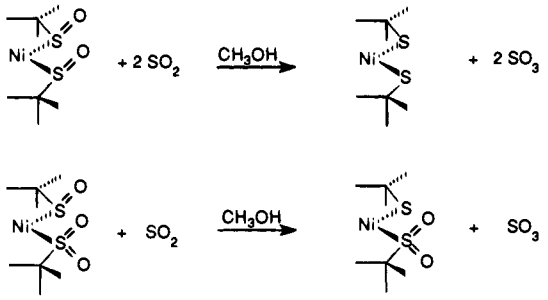
Reactions of the monosulfenate complex **4*** with hydrogen peroxide were monitored by ^1H NMR spectroscopy at ca. 25 and ca. 0 °C. At room temperature, the formation of the sulfinate product **2*** is favored 5:1 over disulfenate formation, while the opposite result is observed at lower temperature (Scheme 6). A typical interpretation of these results is that complex **5*** is the kinetic product while **2*** is the thermodynamically stable product. *Contrary to this attractive explanation, isolated* **5*** *did not convert into* **2*** *even in refluxing acetonitrile or toluene.* That is, the expected[27] internal disproportionation of two sulfenates to a thiolate and sulfinate was not observed. This is further discussed below.

Oxygen Transfer Reactions. Attempts to remove oxygen from sulfenate complexes with known oxygen-atom acceptors have been generally unsuccessful. The monosulfenate complex **4*** did not undergo reaction with dimethyl sulfide or triphenyl- or tricyclohexylphosphine. Alkyl phosphines such as tributylphosphine that have a smaller cone angle were also used.

(26) Darensbourg, M. Y.; Grapperhaus, C.; Maguire, M. J.; Soma, T. Unpublished results.

(27) (a) Schenk, W. A.; Frisch, J.; Adam, W.; Prechtl, F. *Inorg. Chem.* **1992**, *31*, 3329. (b) Wienman, D. J.; Abrahamson, H. B. *Inorg. Chem.* **1987**, *26*, 3034.

Scheme 7



Complex **6*** showed no reaction in acetonitrile solution with 2 equiv of PBu_3 over the course of 10 days; as monitored by ^{31}P NMR spectroscopy, no phosphine oxide was observed. These results can be compared to those for a sulfenate complex of (bme-daco)Ni, **4**, which also did not undergo oxygen transfer reaction with PPh_3 but did show rapid reaction with PBu_3.[4b] Hence, the sulfenate complexes derived from the sterically hindered bme*-daco ligand system are apparently more resistant to oxygen transfer reactions than those from bme-daco. These reactions can be promoted electrochemically, as described elsewhere.[4b]

Removal of oxygen from sulfinate complexes was not possible with O-atom acceptors as strong as SO_2. Sulfenate complexes, however, readily underwent reaction with bubbling SO_2 to produce thiolate complexes and SO_3 that was detected by GC/MS.[28] The reactions were monitored by ^1H NMR spectroscopy and showed that both complexes **4*** and **5*** reacted with SO_2 in methanol solution to produce the dithiolate **1***. An intermediate ascribed to an adduct of SO_2-bound through its sulfur to the sulfenate oxygen was detected in the NMR spectrum, and further characterization is underway. The reaction of **6*** with SO_2 produced **2*** and SO_3, as shown in Scheme 7, again highlighting the inertness of the sulfinate group. The complex (bme-daco)Ni has previously been shown to promote dioxygen uptake in the presence of SO_2 using the formation of disulfide as the reducing equivalents for sulfate ion production.[29]

Reaction with Electrophiles. As seen in the (bme-daco)Ni system, complexes containing thiolate sulfur can react with electrophiles such as alkyl halides to produce thioethers. The sterically hindered **1*** was also effective at template electrophilic addition reactions with dibromopropane, linking the two sulfurs and forming a macrocyclic ligand.[30,31] Although the thiolate sulfur in **2*** is electronically compromised by the presence of the sulfinate group and is not sufficiently nucleophilic to react with dioxygen, it is able to undergo an electrophilic addition reaction with methyl iodide to form a sulfinate/thioether complex. Complex **6***, which does not possess thiolate sulfur, also undergoes rapid reaction with methyl iodide at the sulfenate sulfur, as does the disulfenate complex **5***, yielding [Me_2**5***]-$(I)_2$.[32] Such reactivity of the sulfenate groups allows the use of template-effect ring closure reactions, demonstrated in Scheme 8 for the reaction of complex **5*** with dibromopropane, which results in alkylation of both sulfurs and the formation of a new

(28) The head gas over the reaction of **4*** or **5*** with SO_2 in CH_3CN was found by GC to have an SO_3:SO_2 ratio of 1:2 whereas a control (equivalent amount of SO_2 dissolved in CH_3CN) found the ratio to be 1:58.

(29) Darensbourg, M. Y.; Reibenspies, J. H.; Tuntulani, T. *Inorg. Chem.* **1994**, *33*, 611.

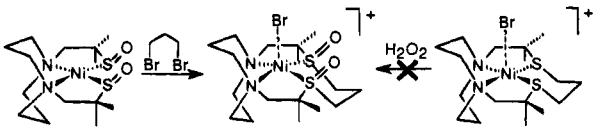
(30) Schenk, W. A.; Frisch, J.; Adam, W.; Prechtl, F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1609. Darensbourg, M. Y.; Musie, G.; Reibenspies, J. H. Manuscript in preparation.

(31) Darensbourg, M. Y.; Font, I.; Mills, D. K.; Pala, M.; Reibenspies, J. H. *Inorg. Chem.* **1992**, *31*, 4965.

Table 4. Selected Bond Dimensions of Compounds 1*−6*

Compound	Ni-N (Å)	Ni-S (Å)		S-O (Å)	S–S (Å)
1*	1.995(3) 1.995(3)	2.159(3) 2.159(3)			
2*	1.99(1) 2.00(1)	2.109(4) 3.132(4)		1.47(1) 1.46(1)	3.029(4)
3*	2.006(6) 2.011(7)	2.130(3) 2.125(2)		1.462(6) 1.458(9) 1.463(6) 1.460(9)	3.098(3)
4*	1.996(6) 2.018(8)	2.149(3) 2.156(3)		1.550(8)	3.003(3)
5*	2.002(6) 1.996(5)	2.170(2) 2.165(2)		1.546(4) 1.533(5)	3.028(3)
6*	1.989(6) 1.987(5)	2.127(2) 2.144(2)		1.468(6) 1.431(7) 1.551(6)	

Scheme 8



14[ane]$N_2(SO)_2$ macrocyclic complex.[32] The ν(SO) stretches of 1061 and 1204 cm^{-1} are consistent with S-bonded sulfoxide.[33] Mass spectral data for this complex suggest that one of the bromides tightly binds or ion pairs into the complex, presumably to the metal. Interestingly, this complex could not be prepared by the action of hydrogen peroxide on the thioether sulfurs of the macrocyclic complex [Ni(bme*-bicycle)]Br_2, although more potent O-atom delivery agents have not been explored.[30]

X-ray Crystal Structure Analyses. Selected bond dimensions for the complexes **1*−6*** are given in Table 4. The molecular structures of complexes **1*** and **4*** have already been the subject of communications,[9,4] but their character will be discussed in comparison with those of the complexes **2***, **3***, **5*** and **6*** shown in Figures 4, 5, 6, and 7, respectively. Additional bond dimensions within the coordination sphere of each structure are presented in the figure captions. Full data for these complexes are available in the supplementary material.

All the complexes in the series **1*−6*** show fundamentally similar structures, comprised of square planar nickel(II) sites with *cis* nitrogens and *cis* sulfurs. The diazacyclooctane portion of the ligand is incorporated into two fused metallodiazacyclohexane rings that occupy a chair/boat conformation. In complexes **1*−6***, there is none of the disorder which resulted in examples of chair/chair conformation seen for the analogous (bme-daco)Ni complexes. The pendant thiolate arms are

(32) [Me_2**5***]I_2. UV MeOH (nm): 258, 390, 470. IR (cm^{-1}): 1204, 1061. Anal. Calcd (found) for $C_{16}H_{34}I_2N_2S_2O_2Ni$: C, 28.24 (28.76); H, 5.34 (5.55); N, 4.12 (4.03). [Ni(bicycle)O_2]Br_2. UV/MeOH (nm): 242, 332, 418. FABMS (thioglycerol matrix): {[Ni(bicycle)O_2]Br}$^+$ *m/z* 469, [Ni(bicycle)-O_2]$^{2+}$ *m/z* 388.

(33) Cotton, F. A.; Francis, R.; Horrocks, W. D., Jr. *J. Phys. Chem.* **1960**, *64*, 1534.

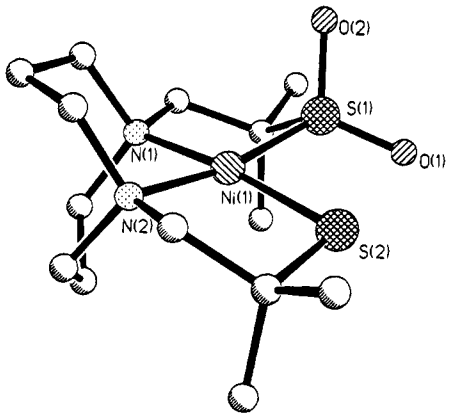


Figure 4. Molecular structure of [1-(2-mercapto-2-methylpropyl)-5-(2-sulfino-2-methylpropyl)-1,5-diazacyclooctanato(2−)]nickel(II) (**2***). Hydrogen atoms and water molecules have been omitted for clarity. Selected bond lengths (Å): Ni(1)−S(1) 2.109(4); Ni(1)−S(2) 2.132-(4); Ni(1)−N(1) 1.99(1); Ni(1)−N(2) 2.00(1); S(1)−O(1) 1.46(1); S(1)−O(2) 1.47(1); S(1)−C(1) 1.84(1); S(2)−C(10) 1.85(1). Selected bond angles (deg): S(1)−Ni(1)−S(2) 91.2(1); S(1)−Ni(1)−N(1) 88.2-(3); S(2)−Ni(1)−N(1) 170.1(4); S(1)−Ni(1)−N(2) 168.4(3); S(2)−Ni(1)−N(2) 91.5(3); N(1)−Ni(1)−N(2) 91.1(4); Ni(1)−S(1)−O(1) 122.2(4); Ni(1)−S(1)−O(2) 107.1(4); O(1)−S(1)−O(2) 114.4(6); Ni-(1)−S(1)−C(1) 100.2(5); Ni(1)−S(2)−C(10) 100.0(5).

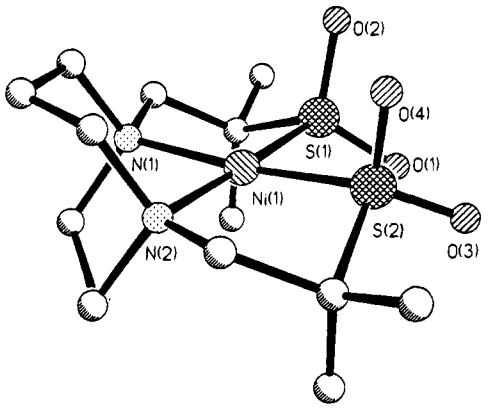
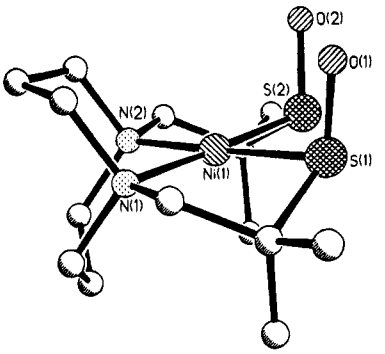


Figure 5. Molecular structure of [1,5-bis(2-sulfino-2-methylpropyl)-1,5-diazacyclooctanato(2−)]nickel(II) pentahydrate (**3***). Hydrogen atoms and water molecules have been omitted for clarity. Selected bond lengths (Å): Ni(1)−S(1) 2.130(3); Ni(1)−S(2) 2.125(2); Ni(1)−N(1) 2.006(6); Ni(1)−N(2) 2.011(7); S(1)−O(1) 1.462(6); S(1)−O(2) 1.458-(9); S(1)−C(1) 1.855(8); S(2)−O(3) 1.463(6); S(2)−O(4) 1.460(9). Selected bond angles (deg): S(1)−Ni(1)−S(2) 93.5(1); S(1)−Ni(1)−N(1) 88.2(2); S(2)−Ni(1)−N(1) 173.1(3); S(1)−Ni(1)−N(2) 178.3-(3); S(2)−Ni(1)−N(2) 87.1(2); N(1)−Ni(1)−N(2) 91.1(3); Ni(1)−S(1)−O(1) 118.4(3); Ni(1)−S(1)−O(2) 108.7(3); O(1)−S(1)−O(2) 114.4(4); Ni(1)−S(1)−C(1) 101.1(3); Ni(1)−S(2)−O(3) 121.4(3); Ni-(1)−S(2)−O(4) 105.0(3); O(3)−S(2)−O(4) 114.5(4); Ni(1)−S(2)−C(10) 101.0(2).

eclipsed across the N_2S_2Ni square plane and the α-methyl substituents adopt an eclipsed equatorial/axial conformation, with the axial groups on the same face of the nickel as the bridgehead methylene of the boat conformer. This results in the formation of a sterically crowded pocket on the "underside" of the metal complex and a more open environment on the upper face. It also accounts for the rigidity of the ligand framework, as the methyl groups of the opposite orientation conformer should encounter greater steric hindrance from the CH_2 units α to nitrogen in the chair form of the metallodiazacyclohexane ring. Structures of the sulfinate complexes **2*** and **3*** parallel those of the less bulky bme-daco system,[12] while the sulfenate



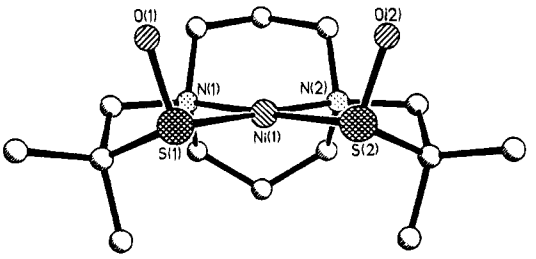


Figure 6. Two views of the molecular structure of [1,5-bis(2-sulfeno-2-methylpropyl)-1,5-diazacyclooctanato(2−)]nickel(II) trihydrate (**5***). Hydrogen atoms and water molecules have been omitted for clarity. Selected bond lengths (Å): Ni(1)−S(1) 2.170(2); Ni(1)−S(2) 2.165-(2); Ni(1)−N(1) 2.002(6); Ni(1)−N(2) 1.996(5); S(1)−O(1) 1.546(4); S(1)−C(1) 1.825(8); S(2)−O(2) 1.533(5); S(2)−C(10) 1.834(6). Selected bond angles (deg): S(1)−Ni(1)−S(2) 88.6(1); S(1)−Ni(1)−N(1) 90.5(2); S(2)−Ni(1)−N(1) 177.5(1); S(1)−Ni(1)−N(2) 177.7(2); S(2)−Ni(1)−N(2) 89.7(2); N(1)−Ni(1)−N(2) 91.2(2); Ni(1)−S(1)−O(1) 107.0(2); Ni(1)−S(1)−C(1) 95.7(2); Ni(1)−S(2)−O(2) 107.2(2); Ni-(1)−S(2)−C(10) 95.9(2).

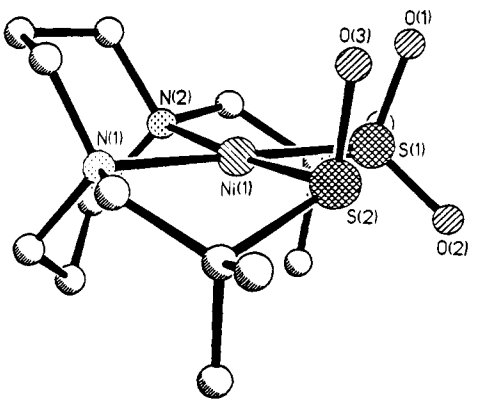


Figure 7. Molecular structure of [1-(2-sulfenato-2-methylpropyl)-5-(2-sulfino-2-methylpropyl)-1,5-diazacyclooctanato(2−)]nickel(II) monohydrate (**6***). Hydrogen atoms and water molecule have been omitted for clarity. Selected bond lengths (Å): Ni(1)−S(1) 2.127(2); Ni(1)−S(2) 2.144(2); Ni(1)−N(1) 1.987(5); Ni(1)−N(2) 1.989(6); S(1)−O(1) 1.468(6); S(1)−O(2) 1.431(7); S(2)−O(3) 1.551(6). Selected bond angles (deg): S(1)−Ni(1)−S(2) 89.7(1); S(1)−Ni(1)−N(1) 179.7(2); S(2)−Ni(1)−N(1) 90.3(2); S(1)−Ni(1)−N(2) 89.2(2); S(2)−Ni(1)−N(2) 175.4(2); N(1)−Ni(1)−N(2) 90.7(2); Ni(1)−S(1)−O(1) 108.4(2); Ni(1)−S(1)−O(2) 118.1(3); O(1)−S(1)−O(2) 116.14(4); Ni(1)−S(1)−C(1) 96.7(2); Ni(1)−S(2)−O(3) 105.9(3); Ni(1)−S(2)−C(10) 100.4(2).

complexes **5*** and **6*** have no previously characterized analogues. We have recently reported the synthesis and structure of complex **4**, which is analogous to **4***.[4b]

The uniformity in the ligands across the series is such that the average Ni−N distance for complexes **1***−**6*** varies little

from 1.99 Å, as shown in Table 4, and is the same as the Ni−N distances in derivatives of **1**. In addition, the Ni−S distances of the bme*-daco derivatives are within the range of the bme-daco complexes, suggesting the steric effect of the substituent methyl groups is primarily at sulfur; they do not alter the N_2S_2 ligand cavity size.

In the series of structures, the complexes **1***, **3***, and **5*** can be considered as having homoleptic symmetrical N_2S_2 ligand sets, and therefore, the most reliable trends can be identified by their comparison. Analysis of the $Ni-S_{(av)}$ bond distances for these complexes reveals bond distances in the following order: Ni−S(O)R (2.167(5) Å) > Ni−SR (2.159(3) Å) > $Ni-S(O)_2R$ (2.127(3) Å). This is in agreement with previous studies which concluded that the Ni−S bond distance was governed by competing factors: (1) the σ-donor ability, expected to be best in the thiolate and to decrease with increasing oxygenation, (2) a contraction in the size of the sulfur atom as the formal oxidation state of the sulfur changes from −2 to +2 through the series SR^-, $S(=O)R^-$, and SO_2R^-, and (3) the destabilization due to repulsive interaction between the metal's filled d orbitals and two lone pairs on the thiolate sulfur and one lone pair on the sulfenate sulfur. Factors 2 and 3 evidently overwhelm 1 to position the $Ni-S(O)_2R$ last in the bond length series; however, factors 3 and 1 must cooperatively compromise the distance of Ni−S(=O)R relative to Ni−SR. The asymmetrical S-donor complexes have Ni−S bond lengths consistent with these arguments. That is, this order of Ni−S distances is maintained within a pair of S-donors; however, analogous Ni−S distances are shorter in **2***, **4***, and **6*** than in **1***, **3***, and **5***. Specifically, for example, the $Ni-S_{thiolate}$ distance in **2*** is quite short (2.132(4) Å) (actually within the range of the $Ni-SO_2R$ of complex **3*** (average of 2.128 Å)) and considerably smaller than the $Ni-S_{thiolate}$ distances in **1*** (2.159(3) Å). Nevertheless, the $Ni-S_{sulfinate}$ distance is even shorter, 2.109(4) Å. In other words, the asymmetric N_2SS' donor sets appear to generate a smaller ligand cavity than would be predicted on the basis of the homoleptic N_2S_2 donors.

Consistent with other published nickel(II) sulfinate complexes,[6] the S−O bond lengths average to ca. 1.46 Å, while in the sulfenates, S−O bonds are typically about 0.1 Å longer, ca. 1.55 Å. In all but one structure, waters of hydration are included in the crystals via H-bonding to the oxygenate sites. All oxygenates are hygroscopic.

There are slight tetrahedral twists in the N_2S_2 donor set of all complexes but considerably less in the bme*-daco derivatives as compared to bme-daco analogues. The disulfinate complex **3***, shown in Figure 5, has a tetrahedral twist[23] of only 3.5° from the square plane, whereas the distortion from planarity in disulfinate **3** is 15.9°.

The structure of the disulfenate complex **5*** is shown in Figure 6. The oxygens of the sulfenate groups sit above the square plane on the face opposite of the axial methyl groups, are mutually eclipsed, and have a Ni−S−O angle of 107.0(2)°. Similarly, the monosulfenate complex **4*** [4] has a Ni−S−O angle of 105.9(3)°. The sulfenate oxygens lean away from each other in **5***; the O−O distance is measured at 3.862(5) Å, while the S−S distance is 3.028(5) Å. Such pyramidality at sulfur orients the two sulfur lone pairs on the underside of the molecule toward each other, generating bifunctional nucleophilic sites for further reactivity.

Complex **6*** represents the penultimate oxygenation level in the series of complexes. This complex cocrystallized with complex **2***; the crystal contained the complexes in a **6***:**2*** ratio of 71:29. The crystal structure of **6***, refined to R (R_w) of 6.0% (6.1)%, shown in Figure 7, is totally consistent with the rest of the series. The oxygen atom in the sulfenate group for **6*** is disordered on both sides of the N−Ni−S plane. It appears at the major site with metric parameters Ni−S (2.144(2) Å), S−O (1.551(6) Å), and Ni−S−O (105.9(3)°) but also on the opposite face, labeled as O(4), with site ocupancy of 31% that has less idealized dimensions of Ni−S (2.127(2) Å), S−O (1.35(2) Å), and Ni−S−O (121.5(8)°).

Concluding Remarks

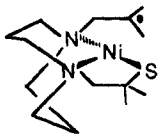
Contrary to the general impression that oxygenations are relatively uncontrollable, this series of nickel complexes demonstrates a remarkable range of oxygenation levels which induces subtle and predictable effects on the (physico)chemical characteristics.

As compared to the (bme-daco)Ni^{II} derivatives, the addition of methyl substituents on the pendant thiolate arms for the (bme*-daco)Ni complexes results in a more rigorously square planar geometry in the N_2S_2 donor set, a fortunate (for the purposes of NMR studies) diamagnetism of the complexes, and a greater rigidity of the ligand framework. The steric effect of the four methyl groups is not, however, important for the immediate N_2S_2 coordination sphere about nickel, as the metric data from X-ray crystallographic studies find Ni−S and Ni−N distances to be substantially the same in analogous bme- and bme*-daco complexes. The steric effect is more prominently operative at sulfur. This is confirmed by the slower reactions of **1*** with molecular oxygen as compared to those of **1**, as well as the observed stabilization of the sulfenato ligand, Ni−S(=O)R, in bme*-daco derivatives. The steric crowding that stabilizes sulfenates or permits isolation also limits reactivity. Oxygen transfer reactions from sulfenato ligands that might lead to intermolecular disproportionation (2 Ni−S(=O)R → Ni−SR + $Ni-SO_2R$) are evidently impeded in the blockage of close contacts by the methyl substituents adjacent to S, as are O-atom transfers to phosphine acceptors. In this connection, the steric bulk of the methyl groups also apparently obstructs RS bridging ability, as a trimetallic so prominent in the (bme-daco)Ni reactions, i.e., $\{[(bme\text{-}daco)Ni_2]Ni\}^{2+}$,[12] is rarely seen, if at all, in the (bme*-daco)Ni chemistry. The expected intramolecular disproportionation of the disulfenate complex ($Ni(S(=O)R)_2$ → $Ni(SR)(SO_2R)$) is also not observed and accounted for by the inability of the rigid bme*-daco framework to position sulfenato oxygens to within required contact distances to sulfur.

The effect of the electron-donating character of the methyl substituents is reflected in the electrochemical results; $Ni^{II/I}$ reductions are more difficult and complex oxidations (either ligand-based RS^- → $RS^\bullet$ or metal-based $Ni^{II/III}$) are easier in the (bme*-daco)Ni derivatives as compared to (bme-daco)Ni counterparts. The stepwise oxygenation of the S-donors in this series has an additive effect on the $Ni^{II/I}$ redox potential. The observed consistency reflects regular changes in the electron density at the metal as a consequence of the changes in oxidation state at the sulfurs. The sulfenato complexes were found to be intermediate between thiolates and sulfinates in their ability to stabilize the $Ni^{II/I}$ couple, the series being $Ni-S^{2+}O_2R$ > $Ni-S^0(O)R$ > $Ni-S^{2-}R$.

Mass spectral data showing the loss of oxygen atoms was largely consistent with solution preparations utilizing hydrogen peroxide as O-atom source, producing all oxygenation levels. In addition, FAB MS also demonstrated SO_2 loss as a particularly prominent decomposition pathway for the sulfinate

complexes, producing metallofragments of the sort



Whereas the insertion/deinsertion of SO_2 in M−C bonds of organometallic complexes is well-known,[34] this feature has not been observed in the solution chemistry of classical coordination complexes and should be explored as a potential path to M−C bonds from metal thiolates.

The conversion of the disulfenate complex to the disulfinate upon addition of dioxygen shows that sulfenates can be considered as viable intermediates in multiple sulfur oxygenation of *cis* thiolates, as proposed earlier.[12] This work also remains consistent with the hypothesis that thermal additions of $^3O_2$ to *cis*-Ni(SR)$_2$ follow two pathways: one as a molecule at a single sulfur site to make a monosulfinate and a second path involving bridging of two adjacent sulfurs and scission of the O−O bond to produce a disulfenate, which can further add molecular O_2 across the sulfenato sulfur sites to yield the disulfinate. We are currently investigating the role of singlet oxygen in these oxidations and find predominantly O-atom donor characteristics to dominate its reactivity, both to **1** and **1***. It does not appear to play any part in conventional $^3O_2$ oxygenations.[6,26]

(34) (a) Wojcicki, A. *Adv. Organomet. Chem.* **1974**, *12*, 31. (b) Hu, Y. R.; Wojcicki, A.; Calligaris, M.; Nardin, G. *Organometallics* **1987**, *6*, 1561.

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Supplementary Material Available: Table summarizing crystallographic data for compounds **1***−**6***, tables of bond lengths and angles, atomic coordinates, anisotropic displacement parameters, and H-atom coordinates of N-(2-mercapto-2-methylpropyl)-N′-(2′-sulfinato-2′-methylpropyl)-1,5-diazacyclooctanenickel(II) (**2***), N,N′-bis (2-sulfinato-2-methylpropyl)-1,5-diazacyclooctanenickel(II) (**3***), N-(2-mercapto-2-methylpropyl)-N′-(2′-sulfenato-2′-methyl propyl)-1,5-diazacyclooctanenickel(II) (**4***), N,N′-bis(2-sulfenato-2-methylpropyl)-1,5-diaza cyclooctanenickel(II) (**5***), and N-(2-sulfenato-2-methylpropyl)-N′-(2′-sulfenato-2′-methylpropyl)-1,5-diazacyclooctanenickel(II) (**6***), packing diagrams for compounds **2***−**5***, (and text describing data and structure refinement of **6*** (28 pages); listings of observed and calculated structure factors (42 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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