

^1H , $\text{CH}_3\text{CHCHCH}=\text{CH}_2$); ^1H NMR spectrum in CDCl_3 Table I; ^{13}C NMR (CDCl_3 , 75.4 MHz) δ 18.44 (q, $J = 123.6$ Hz, $\text{CH}_3\text{CHCHCH}=\text{CH}_2$), 28.55 (t, $J = 164.6$ Hz, $\text{CH}_3\text{CHCHCH}=\text{CH}_2$), 33.77 (q, $J = 128.8$ Hz, $\text{C}(\text{CH}_3)_3$), 46.29 (s, $\text{C}(\text{CH}_3)_3$), 53.07 (d, $J = 163.6$ Hz, $\text{CH}_3\text{CHCHCH}=\text{CH}_2$), 55.23 (d, $J = 160.2$ Hz, $\text{CH}_3\text{CHCHCH}=\text{CH}_2$), 58.75 (d, $J = 169.0$ Hz, $\text{CH}_3\text{CHCHCH}=\text{CH}_2$), 92.52 (d, $J = 16.7$ Hz, $\text{CH}_3\text{CHCHCH}=\text{CH}_2$), 211.39 (br, terminal COs), 217.64 and 219.64 (s, terminal COs); mass spectrum (EI) m/z (rel density) 422 (M^+ , 5), 394 ($\text{M}^+ - \text{CO}$, 7), 366 ($\text{M}^+ - 2\text{CO}$, 19), 388 ($\text{M}^+ - 3\text{CO}$, 18), 310 ($\text{M}^+ - 4\text{CO}$, 22), 282 ($\text{M}^+ - 5\text{CO}$, 51), 226 ($\text{Fe}_2\text{SH}(\text{CH}_3\text{CHCHCH}=\text{CH}_2)^+$, 100), 224 ($\text{Fe}_2\text{SH}(\text{CH}_3\text{CHCHCH}=\text{CH}_2)^+ - 2\text{H}$, 55), 222 ($\text{Fe}_2\text{SH}(\text{CH}_3\text{CHCHCH}=\text{CH}_2)^+ - 4\text{H}$, 14), 171 ($\text{Fe}_2\text{S}(\text{CH}=\text{CH}_2)^+$, 11), 145 (Fe_2SH^+ , 35), 144 (Fe_2S^+ , 57), 81 ($\text{CH}_3\text{CHCHCH}=\text{CH}_2^+$, 22), 79 ($\text{CH}_3\text{CHCHCH}=\text{CH}_2^+ - 2\text{H}$, 24), 77 ($\text{CH}_3\text{CHCHCH}=\text{CH}_2^+ - 4\text{H}$, 8), 66 ($\text{CHCHCH}=\text{CH}_2^+$, 12), 57 (Fe^+ , 28), 52 (CHCHCH^+ , 16). Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{Fe}_2\text{O}_5\text{S}$: C, 42.69; H, 4.30. Found: C, 42.75; H, 4.35.

Reaction of $[\text{Et}_3\text{NH}][(\mu\text{-CO})(\mu\text{-SPh})\text{Fe}_2(\text{CO})_6]$ with 1-Bromohexa-2,4-diene. A reaction of 2.98 mmol of $[\text{Et}_3\text{NH}][(\mu\text{-CO})(\mu\text{-PhS})\text{Fe}_2(\text{CO})_6]$ with 3.08 mmol of 1-bromohexa-2,4-diene was carried out as described above. The solvent was removed in vacuo to leave a red oily solid which was dissolved in pentane/ CH_2Cl_2 (3:1, v/v) and filtered through a thin pad of silica gel, eluting with the same mixture. Concentration of the solution in vacuo and cooling overnight to -20 °C led to 0.45 g (1.02 mmol, 34%) of $(\mu\text{-}\eta^2\text{-}\eta^3\text{-CH}_2=\text{CHCHCHCHCH}_3)(\mu\text{-PhS})\text{Fe}_2(\text{CO})_5$, **24b**, as an air stable, deep red, crystalline solid, mp 145–148 °C: ^1H NMR (CDCl_3 , 300 MHz) δ -0.10 (dd, $J = 13$ and 2 Hz, $\text{CH}_3\text{CHCHCH}=\text{CH}_2$, syn, minor isomer), 0.58 (dd, $J = 13.3$ and 2.2 Hz, $\text{CH}_3\text{CHCHCH}=\text{CH}_2$, syn, major isomer), 0.85 (m, $\text{CH}_3\text{CHCHCH}=\text{CH}_2$, minor isomer), 1.12 (dt, $J = 13.4$ and 7.8 Hz, $\text{CH}_3\text{CHCHCH}=\text{CH}_2$, major isomer), 1.44 (d, $J = 5.2$ Hz, $\text{CH}_3\text{C-}$

$\text{HCHCHCH}=\text{CH}_2$, minor isomer), 1.49 (d, $J = 5.9$ Hz, $\text{CH}_3\text{CHCHCH}=\text{CH}_2$, major isomer), 1.72 (m, $\text{CH}_3\text{CHCHCHCH}=\text{CH}_2$, both isomers), 2.18 (dd, $J = 7$ and 2 Hz, $\text{CH}_3\text{CHCHCHCH}=\text{CH}_2$, anti, minor isomer), 2.30 (dd, $J = 7.3$ and 2.1 Hz, $\text{CH}_3\text{CHCHCHCH}=\text{CH}_2$, anti, major isomer), 3.37 (dd, $J = 8.0$ and 5.5 Hz, $\text{CH}_3\text{CHCHCHCH}=\text{CH}_2$, major isomer), 3.42 (dd, $J = 8$ and 5 Hz, $\text{CH}_3\text{CHCHCHCH}=\text{CH}_2$, minor isomer), 5.82 (dd, $J = 10.1$ and 5.1 Hz, $\text{CH}_3\text{CHCHCH}=\text{CH}_2$, major isomer), 6.11 (dd, $J = 9$ and 4.5 Hz, $\text{CH}_3\text{CHCHCH}=\text{CH}_2$, minor isomer), 6.95 (m, 2 H Ph, minor isomer), 7.05 (m, 3 H Ph, minor isomer), 7.28 (m, 3 Ph, major isomer), 7.53 (m, 2 H Ph, major isomer); ratio major/minor isomer 9/1. ^{13}C NMR (CDCl_3 , 75.4 MHz) δ 18.60 (q, $J = 126.7$ Hz, $\text{CH}_3\text{CHCHCH}=\text{CH}_2$), 28.14 (t, $J = 157.8$ Hz, $\text{CH}_3\text{CHCHCH}=\text{CH}_2$), 53.37 (d, $J = 160.6$ Hz, $\text{CH}_3\text{CHCHCH}=\text{CH}_2$), 54.57 (d, $J = 160.4$ Hz, $\text{CH}_3\text{CHCHCH}=\text{CH}_2$), 59.82 (d, $J = 169.4$ Hz, $\text{CH}_3\text{CHCHCH}=\text{CH}_2$), 92.47 (d, 164.8 Hz, $\text{CH}_3\text{CHCHCH}=\text{CH}_2$), 127.53 (d, $J = 162.1$ Hz, C-4 Ph), 128.62 (d, $J = 158.4$ Hz, Ph), 131.74 (d, $J = 163.6$ Hz, Ph), 137.98 (s, ipso Ph), 210.12 (br, terminal COs), 216.65 and 219.34 (s, terminal COs); major isomer. Anal. Calcd for $\text{C}_{17}\text{H}_{14}\text{Fe}_2\text{O}_5\text{S}$: C, 46.19; H, 3.19. Found: C, 45.97; H, 3.23.

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Supplementary Material Available: IR and mass spectral data, X-ray structure report, tables of positional parameters, bond distances and angles, and torsion or conformation angles (23 pages); table of calculated and observed structure factors (27 pages). Ordering information is given on any current masthead page.

Isotopic Labeling Investigation of the Oxygenation of Nickel-Bound Thiolates by Molecular Oxygen

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Abstract: Discrete compounds resulting from the oxidation and oxygenation of nickel thiolate complexes have been isolated, separated, and characterized. Molecular oxygen or hydrogen peroxide reacted with [*N,N'*-bis(mercaptoethyl)-1,5-diazacyclooctane]nickel(II), (BME-DACO)Ni^{II} (**1**), to produce two oxygenates, [(mercaptoethyl)(sulfinatoethyl)diazacyclooctane]nickel(II), (MESE-DACO)Ni^{II} (**2**), and [bis(sulfinatoethyl)diazacyclooctane]nickel(II), (BSE-DACO)Ni^{II} (**3**), as well as a trimetallic, [(BME-DACO)Ni]₂Ni²⁺ (**4**). Matrix-assisted laser desorption (MALD) ionization was used to obtain Fourier transform ion cyclotron resonance (FT-ICR) mass spectra on isotopomers of **2** and **3**. Isotopic labeling experiments ($^{18}\text{O}_2$ / $^{16}\text{O}_2$ mixtures) demonstrated that both oxygens in the sulfinato ligand of **1** were derived from the same dioxygen molecule. The molecular structures of **2** and **4** were determined by X-ray crystallography. Crystallographic data are given as *a*, *b*, *c*; β ; space group, *Z*, 2θ range, unique observed reflections, $R(R_w)$ (%). (MESE-DACO)Ni^{II}: 8.306 (3), 12.258 (3), 12.773 (4) Å; 101.36 (3)°, $P2_1/n$, 4, 4.0°/50.0°, 2047 ($I > 2.0\sigma(I)$), 2.85 (3.61). [(BME-DACO)Ni]₂NiBr₂: 7.144 (2), 10.931 (2), 17.296 (3) Å; 91.72 (2)°, $P2_1/c$, 4, 4.0°/50.0°, 2053 ($I > 2.0\sigma(I)$), 4.46 (4.84). The pseudo-square-planar NiN₂S₂ complex **2** has cis sulfur donor atoms and a tetrahedral twist of 18.4°. The Ni–S_{sulfinato} distance of 2.140 (1) Å is significantly shorter than the Ni–S_{thiolate} distance, 2.163 (1) Å. The trimetallic **4** contains a staircaselike structure where two molecules of **1** serve as metalothiolate ligands to the central Ni²⁺ creating an NiS₄ square plane (dihedral angle between best square planes = 103.4°).

Introduction

The synthetically vexing air sensitivity of anionic transition-metal thiolate complexes generally reflects ill-understood chemical reactions which, if controlled, might prove useful in the preparation of organic disulfides, sulfoxides, and sulfonic acids. In addition, such reactions are of import to loss of activity of both industrial and enzymatic catalysts which contain sulfidated metal centers. The slow reaction of solutions of the complex [*N,N'*-bis(mercapto-

ethyl)-1,5-diazacyclooctane]nickel(II), (BME-DACO)Ni^{II} (**1**),¹ with O₂ provided opportunity to isolate and characterize products that result from both electron transfer and oxygenation at sulfur, eq 1. This paper reports those results as well as an isotopic labeling

(1) (a) Mills, D. K.; Reibenspies, J. H.; Darensbourg, M. Y. *Inorg. Chem.* **1990**, *29*, 4364. (b) Mills, D. K.; Hsiao, Y. M.; Farmer, P. J.; Atnip, E. V.; Reibenspies, J. H.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1991**, *113*, 1421.

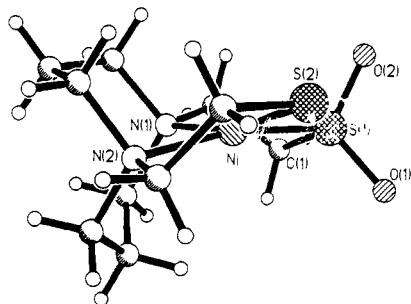


Figure 1. Molecular structure of (MESE-DACO)Ni^{II}. Selected bond lengths (Å): Ni–S1 2.140 (1); Ni–S2 2.163 (1); Ni–N1 2.000 (2); Ni–N2 1.982 (2); S1–O1 1.463 (2); S1–O2 1.456 (3). Selected bond angles (deg): S1–Ni–S2 91.8 (1); S1–Ni–N1 90.5 (1); S2–Ni–N2 91.3 (1); N1–Ni–N2 89.3 (1); Ni–S1–O1 114.4 (1); Ni–S1–O2 117.4 (1); O1–S1–O2 114.3 (2); Ni–S1–C1 97.1 (1); O1–S1–C1 106.1 (1); O2–S1–C1 104.8 (2); Ni–S2–C10 98.2 (1).

mechanistic study of the oxygenate production from molecular oxygen.

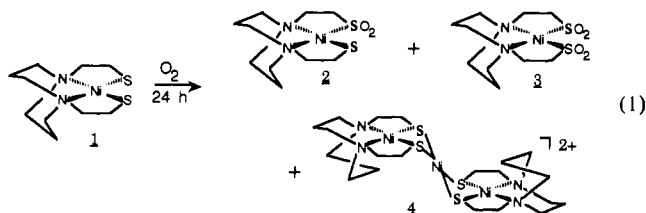


Figure 2. Molecular structure of [(BME-DACO)Ni]₂NiBr₂. The atoms labeled a are related by a crystallographic center of symmetry. Selected distances (Å): Ni1–Ni2 2.685 (1); Ni1–S2 2.195 (1); Ni1–S1 2.204 (1); Ni2–S1 2.155 (1); Ni2–S2 2.148 (1); Ni2–N1 1.961 (4); Ni2–N2 1.953 (4). Selected bond angles (deg): S1–Ni1–S2 80.6 (1); S2–Ni1–S1a 99.4 (1); S2–Ni2–S1 82.8 (1); S1–Ni2–N2 91.7 (1); N2–Ni2–N1 92.4 (2); C10–S1–Ni1 111.5 (2); C10–S1–Ni2 97.3 (2); Ni2–S1–Ni1 76.0 (1).

zation was supported by the shift to lower frequencies of the four strong $\nu(\text{SO})$ IR bands in the 1000–1200-cm⁻¹ region upon substitution with ¹⁸O. The identifying UV–vis absorptions of samples obtained directly from the column, 365 and 440 nm, changed upon crystallization to 380 and 420 nm. The nature of this transformation is thought to be linkage isomerism, but neither solid state FTIR or mass spectrometric analysis distinguished the two.

The red-brown trimetallic (BME-DACO)₂Ni₃²⁺, **4**,^{1b} remained on the top of the column but was desorbed on stirring that portion of the column material in a MeOH solution of Et₄N⁺Br⁻. Such methanol solutions contained intense absorptions in the UV–vis region, λ_{max} (ϵ , cm⁻¹ M⁻¹) 408 (3033), 486 (1316), and 564 (851) nm, as is typical of complexes containing an NiS₄ donor environment.⁶ The absorptions are identical with those of an authentic (characterized by elemental analysis and X-ray structural analysis) sample which was prepared by reacting **1** with NiBr₂ in a 2:1 ratio. Complex **4** is also formed in quantitative yields by reaction of **1** with single-electron oxidants such as cerium ammonium nitrate or NOBF₄ in a 3:2 ratio or upon exposing **1** to acids. The latter ligand-protonation route releases a nickel ion, rapidly scavenged by unprotonated **1** complexes. The former route, and the most reasonable route for the formation of **4** in the dioxygen reaction, generates disulfides, either by an intra-⁷ or intermolecular⁸ route, and also releases Ni²⁺ ions to initiate the aggregation. In fact, the ease with which the trimetallic, **4**, is formed and its stability have typically thwarted studies of monomeric N₂S₂ complexes of nickel.

The molecular structure of **4** shown in Figure 2 has the familiar⁶ stepped structure with average Ni–S distances in the central NiS₄ environment (2.200 Å) significantly longer than that in the NiN₂S₂ portion of the complex (2.152 Å). The severe folding angle between the NiS₄ square plane and the best plane calculated for a NiN₂S₂ unit (Ni is 0.17 Å above the N₂S₂ best plane) is 103.4° resulting in Ni–Ni distances of 2.685 (1) Å.

The Oxygenation Reaction. A typical material distribution ($\pm 5\%$) obtained from the molecular oxygen reaction with **1**, eq 1, was 50% **1**, 20% **2**, 5% **3**, and 10% **4**. This distribution was not changed on carrying out the reaction in the dark. Hydrogen peroxide could also be used as the oxygen source and reacted on time of mixing with (BME-DACO)Ni^{II} in MeOH to yield the same mixture of products as the O₂ reaction, eq 1. The yields of the three products depended on the amount of H₂O₂ used as oxidant, with stoichiometry suggesting that one O atom was transferred per H₂O₂ molecule used. The yield of **2** was optimized (45%) at 2 equiv of H₂O₂, and **3** was the predominant (85%) product for 4 equiv of H₂O₂ in MeOH or CH₃CN, with the remainder being **4**.

A major difference in O₂ and H₂O₂ reactivity was indicated by the following experiments. *Isolated and purified 2 is unreactive with dioxygen under the same conditions as the original reaction*

Results and Discussion

Product Characterization. The products shown in eq 1 were obtained from a 0.3 mM solution of **1** in triply dried acetonitrile stirred under 1 atm O₂ for 24 h at 22 °C. The mixture was efficiently separated by dry column flash chromatography on silica gel.² The unreacted purple **1** starting material eluted first, followed by an orange and then a yellow fraction. Elemental, spectral, and X-ray crystal structure analyses³ characterized the orange product as [(mercaptoethyl)(sulfinatoethyl)diazacyclooctane]nickel(II), (MESE-DACO)Ni (**2**), adding to the rare examples of a sulfinate ligand produced by direct oxygenation of metal-bound sulfur.^{4,5} Assignment of the two strong IR bands at 1182 and 1053 cm⁻¹ to $\nu(\text{SO})$ was confirmed by ¹⁸O labeling; samples prepared from 98% ¹⁸O₂ showed shifts to 1146 and 1018 cm⁻¹.

The molecular structure of **2** is shown in Figure 1, and selected bond lengths and bond angles are listed in the caption. The distortion from strict square-planar geometry is toward a tetrahedral twist of 18.4° and is sufficient to make the complex paramagnetic. As was observed by Maroney and co-workers for a square planar complex containing both nickel thiolate and nickel sulfinate groups,⁴ the Ni–S_{sulfinate} distance of 2.140 (1) Å is shorter than is the Ni–S_{thiolate} distance, 2.163 (1) Å. The latter is essentially the same as in the parent complex **1**, 2.159 (2) Å.¹

Elemental, mass spectral (vide infra), and spectroscopic analyses of the yellow product obtained from the third fraction were consistent with its formulation as the [bis(sulfinatoethyl)diazacyclooctane]nickel(II), (BSE-DACO)Ni (**3**). This characteri-

(2) Harwood, L. M. *Alarichim. Acta* **1985**, *18*, 25.

(3) X-ray diffraction data were collected at –80 °C for [(BME-DACO)Ni]₂NiBr₂ and at 23 °C for the (MESE-DACO)Ni^{II} complexes and the structures solved by standard procedures with semiempirical absorption corrections applied. Crystallographic data are given as *a*, *b*, *c*; β ; space group, *Z*, 2θ range, unique observed reflections, $R(R_w)$ (%). [(BME-DACO)Ni]₂NiBr₂: 7.144 (2), 10.931 (2), 17.296 (3) Å; 91.72 (2)°, $P2_1/c$, 4, 4.0°/50.0°, 2053 ($I > 2.0\sigma(I)$), 4.46 (4.84). (MESE-DACO)Ni^{II}: 8.306 (3), 12.258 (3), 12.773 (4) Å; 101.36 (3)°, $P2_1/n$, 4, 4.0°/50.0°, 2047 ($I > 2.0\sigma(I)$), 2.85 (3.61).

(4) Kumar, M.; Colpas, G. J.; Day, R. O.; Colpas, G. J.; Maroney, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 8323.

(5) Schrauzer, G. N.; Zhang, C.; Chadha, R. *Inorg. Chem.* **1990**, *29*, 4104. Nicholson, T.; Zubieta, J. M. *Inorg. Chem.* **1987**, *26*, 2094.

(6) Wei, C. H.; Dahl, L. F. *Inorg. Chem.* **1970**, *9*, 1878. Turner, M. A.; Driessen, W. L.; Reedijk, J. *Inorg. Chem.* **1990**, *29*, 3331. Drew, M. G. B.; Rice, D. A.; Richards, K. M. *J. Chem. Soc., Dalton. Trans.* **1980**, *9*, 2075.

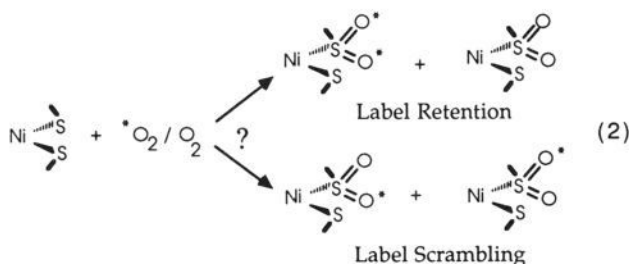
(7) Kumar, M.; Day, R. O.; Colpas, G. J.; Maroney, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 5974.

(8) Kruger, H. J.; Holm, R. H. *Inorg. Chem.* **1989**, *28*, 1148.

(CH₃CN solvent, bubbling O₂, 24 h). In contrast, reaction of **2** with hydrogen peroxide yielded **3** quantitatively.

Direct oxygenation (O₂) of thioether sulfur sites occurs readily under photochemical conditions, generating singlet oxygen (¹O₂), and produces both sulfoxides, RS(O)R, and sulfones, RS(O)₂R, with the former predominating.⁹ Recent isotopic labeling experiments demonstrated that the major pathway of the sulfone formation is by direct addition of both oxygen atoms in ¹O₂ to the same sulfur.^{9b} In contrast to the organosulfur compounds, our work and that of others^{4,5} find the MSR functionality in coordination complexes reacts directly with ³O₂ (no photolysis) to yield metallosulfonates, MSO₂R. The propensity to form MSO₂R from MSR extends to single O-atom-transfer reagents, such as H₂O₂ or dioxiranes.¹⁰ To our knowledge, only one family of complexes, bis(ethylenediammine)cobalt(III) thiolates, has been shown to yield isolable sulfenato (CoS(O)R) derivatives upon stoichiometric addition of H₂O₂, and those readily react further or disproportionate in solution to yield the sulfinato, CoS(O)₂R.¹¹

Isotopic Labeling Studies. Since both the single O-atom-transfer agent H₂O₂ and dioxygen produce the same products on reaction with **1**, we queried whether ³O₂ serves, in the presence of the nickel complex, as an oxygen atom source, or whether direct addition of one O₂ molecule occurs at one sulfur site. The former would imply the existence of a metallosulfenato (MS(O)R) intermediate, highly reactive toward another O₂ molecule or oxygen atom source. Maroney and co-workers earlier established by isotopic labeling that ¹⁸O₂ addition to a thiolate sulfur of MeSCH₂CH₂N-(CH₂CH₂S)₂Ni(CN)⁻ in DMF did not incorporate unlabeled oxygen from the solvent and concluded that sulfur-based, oxygen-scavenging radicals were not involved as intermediates.⁴ In order to differentiate between the possibilities expressed by eq 2, we examined the reaction of **1** with a mixture of ¹⁸O₂ and ¹⁶O₂ and subjected the isolated products to analysis by FT-ICR laser desorption mass spectroscopy.¹²



The mass spectra of isolated **2** or **3** showed small parent ion signals and other signals associated with fragmentation or combination. More intense signals were obtained for intact **2** and **3** by attachment of Na⁺ or K⁺ ions to form [M + Na]⁺ or [M + K]⁺, respectively. The K⁺ ions showed greater ability to ionize the complexes under these desorption conditions. Excellent quality spectra for isotopic analysis were obtained on samples in which the 4-nitroaniline matrix was doped with Cs⁺ (chosen for its isotopic purity). Assignment of these signals was checked with fully ¹⁸O-labeled and natural abundance ¹⁶O-labeled **2** and **3** (Figures 3a,c and 4a,c) and further by comparing the results from samples deliberately doped with Na⁺, K⁺, and Cs⁺ ions.

For the formation of **2** in the mixed-labeling experiment, the mass spectral pattern associated with each limiting extreme of O₂ "label scrambling" vs O₂ "label retention", eq 2, can be pre-

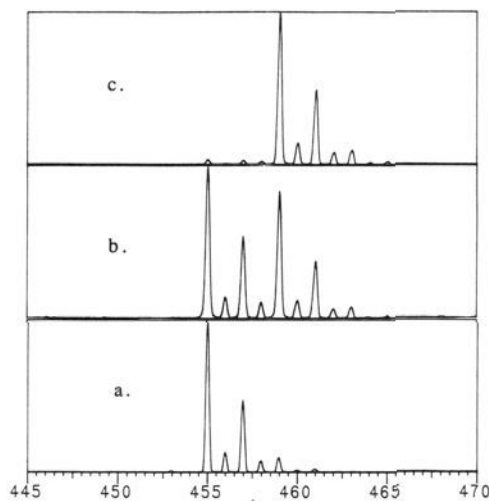


Figure 3. FT-ICR mass spectra in the [M + Cs]⁺ region of (MESE-DACO)Ni (**2**) isolated from the reaction of **1** with (a) natural abundance ¹⁶O₂, (b) a 56:44 mixture of ¹⁶O₂:¹⁸O₂, and (c) 98% ¹⁸O₂. All spectra were obtained in the broad-band mode averaging 200 laser shots at 128K data points.

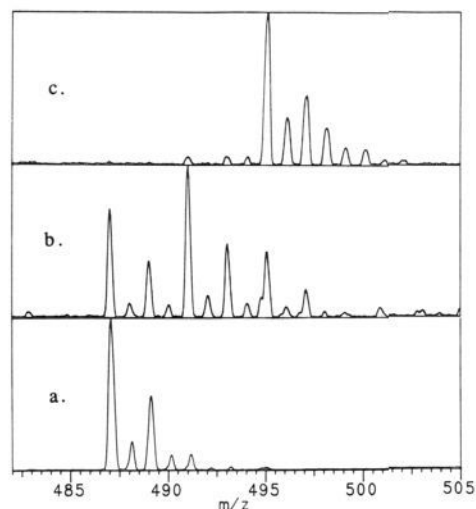


Figure 4. FT-ICR mass spectra in the [M + Cs]⁺ region of (BSE-DACO)Ni (**3**) isolated from the reaction of **1** with (a) natural abundance ¹⁶O₂, (b) a 56:44 mixture of ¹⁶O₂:¹⁸O₂, and (c) 98% ¹⁸O₂. All spectra were obtained in the broad-band mode averaging 200 laser shots at 128K data points.

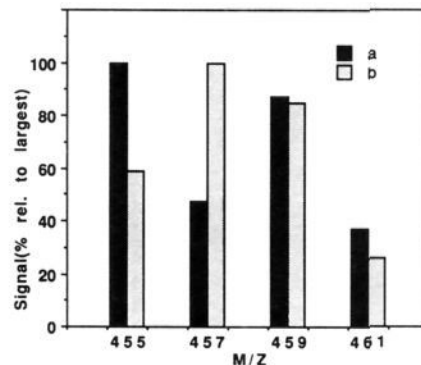


Figure 5. Predicted ion abundances for the mass spectrum in the [M + Cs]⁺ region of (MESE-DACO)Ni (**2**) from the reaction of **1** with a 56:44 mixture of ¹⁶O₂:¹⁸O₂ (a) by molecular O₂ addition only (label retention) and (b) by O-atom addition or exchange (label scrambling).¹³

dicted considering only the main isotopomers, ⁵⁸Ni (68.3%), ⁶⁰Ni (26.1%), ⁶²Ni (3.6%), ³²S (95.0%), ³⁴S (4.2%), and the ratios of

(9) (a) For example: Foote, C. S.; Peters, J. W. *J. Am. Chem. Soc.* **1971**, *93*, 3795. (b) Akasada, T.; Sakurai, A.; Ando, W. *J. Am. Chem. Soc.* **1991**, *113*, 2696.

(10) (a) Schenk, W. A.; Frisch, J.; Adam, W.; Prechtel, F. *Inorg. Chem.*, in press. (b) Weinmann, D. J.; Abrahamson, H. B. *Inorg. Chem.* **1987**, *26*, 3034.

(11) (a) Adzamlı, I. K.; Lisbon, K.; Lydon, J. D.; Elder, R. C.; Deutsch, E. *Inorg. Chem.* **1979**, *18*, 303. (b) Herting, D. L.; Sloan, C. P.; Cabral, A. W.; Krueger, J. H. *Inorg. Chem.* **1978**, *17*, 1649.

(12) Hanson, C. D.; Castro, M. E.; Kerley, E. L.; Russell, D. H. *Anal. Chem.* **1990**, *62*, 520. Solouki, T.; Russell, D. H. *Proc. Natl. Acad. Sci. U.S.A.*, in press.

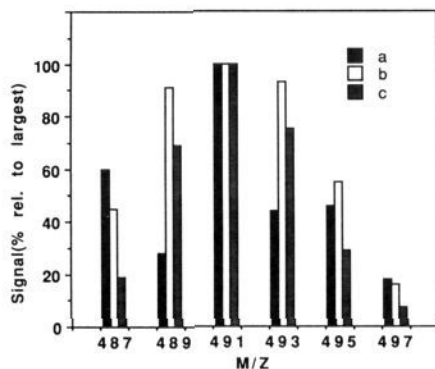


Figure 6. Predicted ion abundances for the mass spectrum in the $[M + Cs]^+$ region of (BSE-DACO)Ni (**3**) from the reaction of **1** with a 56:44 mixture of $^{16}O_2$: $^{18}O_2$ (a) by label retention only, (b) by half retention/half scrambling, and (c) by scrambling only.¹³

^{16}O and ^{18}O used.¹³ Scrambling would imply a sulfenato ($RS(=O)Ni$) intermediate by O-atom addition or subsequent exchange. Label retention implies direct sulfinate formation by molecular O_2 addition. For the latter case, the expected relative abundances for the $[M + Cs]^+$ signals are seen in Figure 5a; those for the scrambling case are seen in Figure 5b. Parts a, b, and c of Figure 3 display the spectra in the $[M + Cs]^+$ mass region for **2** isolated from reaction of **1** with natural abundance $^{16}O_2$, a 56:44 mixture of $^{16}O_2$: $^{18}O_2$, and $^{18}O_2$ (98%), respectively. For the mixed-labeling experiment, the observed spectrum (Figure 3b) qualitatively matches best that predicted for the molecular addition pathway (Figure 5a); a quantitative fit of that match is described below.

Because of the small number of isotopomer combinations which contribute to their ion abundances, m/z 455 and 457 were chosen for analysis of the formation of **2** in the mixed-labeling experiment. For the label retention pathway, the ratio of predicted relative abundances is 68:32, with no contribution from ^{18}O to the signal at m/z 457. For the scrambling pathway, the ratio is 33:67, with a large contribution to the m/z 457 peak coming from ^{18}O . The experimentally observed ratio is 65:35. A fit of the data to a combination of the two pathways finds that greater than 90% of the product is formed by molecular addition (fit values: 92% label retention, 8% scrambling).¹³

A similar consideration of the formation of the bisulfinate, **4**, predicts the relative abundance values given in Figure 6a for the case of O_2 molecular addition to complex **1**. In this case, the term "double label retention" may signify the product in which one $^{16}O_2$ and one $^{18}O_2$ adds to **1** at individual sulfur sites, producing the $S^{16}O_2/S^{18}O_2$ isotopomer, or across sulfur sites,⁵ producing the $(S^{16}O^{18}O)_2$ isotopomer. Mass spectral analysis of the parent ion cannot distinguish the two possibilities. For the scrambling case, two possibilities exist. The first is that oxygenation of the first sulfur is by molecular addition and the subsequent formation of **3** scrambles O_2 ; the second is that both SO_2 units of **3** are formed solely by O-atom addition or a random-exchange process. The relative abundance values predicted for these mechanisms are seen in parts b and c of Figure 6. The ratios of the predicted values for the first two signals, m/z 487 and 489, are 68:32 by retention/retention, 33:67 for retention/scrambling, and 22:78 for complete scrambling. These predicted values were compared with the experimental value (66:34) and fit to a combination of retention/retention and retention/scrambling pathways. Again, the fit finds that > 90% of the product is formed by molecular addition (fit values: 94% retention/retention and 6% retention/scrambling).

Comments. The mass spectral analysis of the isotopically labeled compounds clearly demonstrates that by far the major pathway for oxygen addition to nickel thiolato sulfur sites of **1** proceeds

with no scrambling of molecular oxygen atoms. Questions concerning the stability and reactivity of possible sulfenato ($NiS(=O)R$) intermediates are thus rendered moot in reactions with dioxygen (although their intermediacy in the H_2O_2 oxygenations is plausible—but as yet unsubstantiated). This significant conclusion is obtained in the face of what appears to be an extraordinary problem. The production of the bisulfinate is also via a non-scrambling dioxygen addition pathway. Yet the isolated, purified monosulfinate complex will not react further with molecular oxygen, while it is reactive with the single O-atom source, H_2O_2 . Hence, we conclude that some species in the original reaction (eq 1) catalyzes the bisulfinate production.

Despite the paucity of examples of molecular oxygen adducts of nickel in the literature,¹⁴ the most reasonable dioxygen activation mechanism here is that of an O_2 adduct formation with the original dithiolate, $1 \cdot O_2$, which precedes sulfinate formation and which transfers the intact O_2 molecule to thiolate sulfur in an intramolecular or intermolecular fashion. Experiments to test this hypothesis are underway.

Experimental Section

Materials. Reagent-grade solvents were dried using standard techniques.¹⁵ (BME-DACO)Ni^{II} was synthesized by published procedures.^{1a} $^{18}O_2$ (99.1%) was obtained from Isotech, Inc., in a 250-mL breakseal flask. All other chemicals were purchased from Aldrich Chemical Co. and used as obtained.

Instrumentation and Procedures. UV-visible spectra were recorded on an IBM Instruments, Inc., 9420 UV-visible spectrophotometer. Infrared spectra (KBr pellets) were recorded using Mattson Instruments 6021 Galaxy Series FT-IR. X-ray diffraction data were collected on a Nicolet R3m/V diffractometer. A Hewlett-Packard 5995C gas chromatograph/mass spectrometer with a DB-5 column was used to determine the isotopic ratios of $^{16}O_2$: $^{18}O_2$. Typically, six runs were recorded and analyzed with correction for $^{16}O_2$ background by subtracting (32 amu/28 amu background count) \times (28 amu run count) from the 32 amu run count. Gases were transferred with gas-tight syringes and Schlenk line techniques; Ar was used to equalize the pressure. Matrix-assisted laser desorption (MALD) ionization was used to obtain Fourier transform ion cyclotron resonance (FT-ICR) mass spectra. The FT-ICR mass spectrometer consists of a home-built (16-cm-long and 4-cm-diameter) cylindrical ICR cell¹² and vacuum chamber, a 7.0-T superconducting Oxford magnet, and an Extrel FTMS-2001 data acquisition system. A cartridge-type pulsed N_2 laser (Laser Science, Inc., Model VSL-33ND) was used for ionization. MALD mass spectra were obtained by mixing alkali-halide salts with the sample to form cationized molecular ions, e.g., $[M + Na]^+$, $[M + K]^+$, $[M + Cs]^+$. Sample mixtures, 4-nitroaniline, analyte, and alkali-halide salt in a molar ratio of 1:0.01:0.1, were deposited in the probe as solutions in methanol. Mass spectra were obtained in the broad-band mode signal-averaging data from 200 laser shots. The time-domain data consisted of 128K data points to yield a mass resolution for the $[M + Cs]^+$ ion of 2000. The error in ion abundances based on peak height or peak area is less than 5%.

Reaction of (BME-DACO)Ni^{II} (1'**) with O_2 .** A 0.100-g (0.344 mM) sample of **1** was dissolved in 30 mL of triply dried acetonitrile and stirred under 1 atm of O_2 at 22 °C for 24 h during which time the mixture turned from dark purple to brown. The solvent was removed under vacuum and the remaining solid redissolved in a minimum of MeOH and separated by dry column flash chromatography² (50-g silica gel dry column separation with 100-mL aliquots of EtOH/ H_2O eluants in steadily increasing (by 10% v/v) amounts of water). Yields were obtained by weighing the dried solid from filtered fractions in tared flasks, and in some cases, subsequent UV-vis absorbance comparisons with Beer's law calibration plots were made with the authentic compounds.

Reaction of **1 with H_2O_2 .** A 0.100-g (0.344 mM) sample of **1** was dissolved in 50 mL of MeOH and stirred under N_2 . H_2O_2 (30% w/w aqueous solution, 35 μ L/eq) was diluted to 10 mL and added to the reaction solution, resulting in immediate color changes. The resulting product mixtures were separated as above, except that **4**, which was present in all product mixtures, was not quantified. Product yields (based on Ni content): 1 equiv of H_2O_2 , 32% **1**, 34% **2**, 7% **3**; 2 equiv of H_2O_2 , 7% **1**, 45% **2**, 29% **3**; 3 equiv of H_2O_2 , 45% **3**; 4 equiv H_2O_2 , 85% **3**.

(13) Predictions were calculated by statistical analysis of the possible isotopomer combinations. Odd massed isotopes such as ^{61}Ni (1.134%), ^{13}C (1.11%), and ^{33}S (0.76%) were ignored in this analysis. A more complete description, including fitting model, is given in the supplementary material.

(14) Kimura, E.; Sonaka, A.; Machida, R.; Kodama, M. *J. Am. Chem. Soc.* **1982**, *104*, 4255. Chen, D.; Motekaitis, R. J.; Martell, A. E. *Inorg. Chem.* **1991**, *30*, 1396. Berkessel, A.; Bats, J. W.; Schwarz, C. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 106.

(15) Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; J. Wiley and Sons: New York, 1972.

Characterization of [N,N'-(Mercaptoethyl)(sulfinatoethyl)diazacyclooctane]nickel(II), (MESE-DACO)Ni (2). Single crystals suitable for X-ray crystal structure analysis were grown by slow diffusion of Et₂O into concentrated CH₃CN solutions. FTIR peaks were assigned to $\nu(\text{SO})$ absorptions (KBr pellet): ¹⁶O 1182 and 1053 cm⁻¹; ¹⁸O 1146 and 1018 cm⁻¹. UV-vis absorptions were in EtOH solution: λ_{max} (ϵ , cm⁻¹ M⁻¹) 430 (202) and 550 (51) nm. Anal. Calcd (Found) for C₁₀H₂₀N₂S₂O₂Ni: C, 37.17 (37.06); H, 6.24 (6.22); O, 9.90 (8.02).

Characterization of [N,N'-Bis(sulfinatoethyl)diazacyclooctane]nickel(II), (BSE-DACO)Ni (3). The yellow fraction eluted only with > 40% H₂O/EtOH eluant solutions, and the solutions were sensitive to decomposition while heating under vacuum. UV-vis absorptions were in EtOH solution: λ_{max} as obtained off the column, 365 and 440 nm; recrystallized from H₂O/acetone, 380 and 420 nm. Both forms have similar FTIR peaks assigned to $\nu(\text{SO})$ absorptions (KBr pellet): ¹⁶O 1192, 1180, 1071, and 1032 cm⁻¹; ¹⁸O 1163, 1146, 1044, and 991 cm⁻¹. Anal. Calcd (Found) for C₁₀H₂₀N₂S₂O₄Ni: C, 33.80 (32.53); H, 5.63 (5.84); N, 7.88 (7.51).

Synthesis and Characterization of Bis[N,N'-Bis(mercaptoethyl)-1,5-diazacyclooctane]nickel(II) Nickelate Dibromide, [(BME-DACO)₂Ni₂]-Br₂ (4). As NiBr₂·3H₂O (0.0927 g, 0.34 mM) was added to a solution of **1** (0.200 g, 0.687 mM) in 50 mL of MeOH, the color changed immediately from purple to dark brown/red. Concentration under vacuum and subsequent slow evaporation yielded 0.25 g (92%) of microcrystalline **4**. Single crystals suitable for X-ray crystal structure analysis were grown by slow diffusion of Et₂O into concentrated MeOH solutions. UV-vis absorptions were in EtOH solution: λ_{max} (ϵ , cm⁻¹ M⁻¹) 408 (3033), 486 (1316), and 564 (851) nm. Anal. Calcd (Found) for C₂₀H₄₀N₄S₄Ni₂Br₂: C, 29.97 (29.98); H, 4.99 (5.03).

Reaction of **1 with a Deficiency of NOBF₄.** **1** (0.100 g, 0.3435 mM) was dissolved in 30 mL of dry, degassed MeOH and treated with NOBF₄ (0.020 g, 0.171 mM) dissolved in 30 mL of MeOH. The solution color immediately changed from purple to dark red/brown. UV-vis of the resulting solution showed the major product to be **4**. Chromatography of the product mixture lead to recovery of 24% **1** (0.024 g, 0.082 mM); theoretical recovery, 25%.

Mixed-Labeling Reaction of (BME-DACO)Ni^{II} (1**) with ¹⁶O₂, ¹⁸O₂, and ¹⁶O₂/¹⁸O₂ Mixtures.** Three 100-mL flasks were loaded with samples of **1** (0.100 g, 3435 mM) and 30 mL of triply dried, degassed CH₃CN, evacuated, and backfilled 3 times with Ar and then left under a vacuum.

Flask A was charged with natural abundance O₂ and flask B with 99% ¹⁸O₂ in 50-mL (2.23 mM) quantities. The third, flask C, was charged with 25 mL of ¹⁸O₂ and 25 mL of natural abundance O₂. All flasks were then slightly overpressured with Ar. By GC/MS, the isotopic purity for flask B was ~98% ¹⁸O₂ (reflecting minor contamination during transfer). By GC/MS, the isotopic ratio in flask C was 56:44 ¹⁶O₂:¹⁸O₂, with less than 0.1% ¹⁸O:¹⁶O, and was unchanged after the workup. The reaction mixtures were stirred for 3 days, after which the reaction solutions were evaporated and chromatographically separated as above and submitted for FT-ICR/MS.

Reaction of Isolated and Purified **2 with O₂ and H₂O₂.** A solution of chromatographically pure **2** (30 mg, 0.09 mmol) in 25 mL of dry, degassed CH₃CN was purged with O₂ for 30 min and then stirred under an O₂ atmosphere for 48 h without reaction (monitored by UV-vis). The O₂ was evacuated and replaced with N₂, and two 10- μ L portions of 30% H₂O₂ (aqueous) (2 equiv) were injected into the solution. The resulting yellow product was identified as **3** by UV-vis and checked further by chromatography.

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Supplementary Material Available: Statistical analysis of mass spectral data, including predicted and experimental ion abundance ratios and a mathematical fit of predicted-to-experimental data, tables of atomic coordinates, positional and displacement parameters, and bond lengths and angles, and a packing diagram and additional views of C₁₀H₂₀N₂O₂S₂Ni, a packing diagram of C₁₀H₂₀N₂S₂Ni_{1.5}Br, and numbering schemes for (MESE-DACO)Ni^{II} and {[(BME-DACO)Ni]₂Ni}Br₂ (11 pages). Ordering information is given on any current masthead page.

Preparation and Reactivity of a Cationic Dichromium-Semiquinone Complex

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Abstract: The complex described in the literature as the μ -oxo complex (H₂O)₅CrOCr(H₂O)₅⁴⁺ is shown to be a dichromium(III)-semiquinone complex, (H₂O)₅CrOC₆H₄OCr(H₂O)₅⁵⁺. It is prepared by the reaction of 1,4-benzoquinone with Cr²⁺ in acidic, aqueous solution. The reaction also yields Cr(H₂O)₆³⁺ and a dichromium(III)-hydroquinone complex of 4+ charge. The semiquinone complex is reversibly reduced by outer-sphere electron transfer to the dichromium(III)-hydroquinone complex, (H₂O)₅CrOC₆H₄OCr(H₂O)₅⁴⁺. This reduction is accomplished by any of Cr²⁺, Ru(NH₃)₆²⁺, or V²⁺. The hydroquinone complex is reoxidized by Fe³⁺, 1,4-benzoquinone, Br₂, or Ce(IV) to the semiquinone complex. Cyclic voltammograms obtained with either the hydroquinone complex or the semiquinone complex are identical and correspond to a reversible, one-electron process. The standard reduction potential of the semiquinone complex is +0.61 V (NHE). The semiquinone complex decomposes, over a period of hours, by aquation of Cr(III) followed by disproportionation of the organic ligand, yielding hydroquinone, benzoquinone, and Cr(H₂O)₆³⁺. A literature report of the quinone oxidation of ethanol catalyzed by Cr³⁺ is reinterpreted as the reversible formation of a dichromium(III)-semiquinone radical complex.

Introduction

Our interest in the various intermediates in the reaction of Cr²⁺ with O₂ led us to consider the possible involvement of (H₂O)₅CrOCr(H₂O)₅⁴⁺, hereafter CrOCr⁴⁺. In particular, we asked whether this species might be produced in the reaction between the recently-prepared¹ oxochromium(IV) or chromyl ion,

CrO²⁺, and Cr²⁺, or in another² stage of the Cr²⁺-O₂ reaction. Our search was initially guided by reports that CrOCr⁴⁺ is one of several major products of the reaction between Cr²⁺ and 1,4-benzoquinone in aqueous perchloric acid.³ The product identified

(1) Scott, S. L.; Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1991**, *113*, 7787. Scott, S. L.; Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.*, in press.

(2) (a) Brynildson, M. E.; Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1987**, *109*, 4579. (b) Sellers, R. M.; Simic, M. G. *J. Am. Chem. Soc.* **1976**, *98*, 6145.

(3) Holwerda, R. F.; Petersen, J. S. *Inorg. Chem.* **1980**, *19*, 1775.