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Singlet Oxygen and the Production of Sulfur Oxygenates of Nickel(II) and Palladium(II) Thiolates

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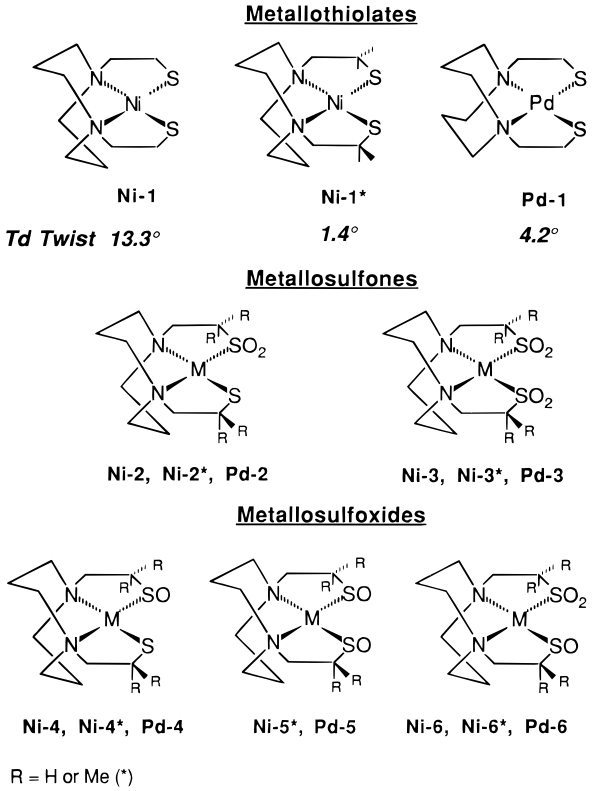
The metal dithiolate [1,5-bis(2-mercaptoethyl)-1,5-diazacyclooctane]nickel(II) (**Ni-1**), a sterically hindered analogue (**Ni-1***), and the palladium analogue **Pd-1** react with $^{1}\Delta\ O_2$ to yield a variety of stable and isolable metallosulfones ($MS(O_2)R$) and metallosulfoxides (MS(O)R). Singlet oxygen was generated both photochemically with the sensitizer Rose Bengal and thermally by decomposition of the 1,4-endoperoxide of 1,4-dimethylnaphthalene. Increased rates and oxygenation yields are observed upon excitation of O_2 from its ground state, $^{3}\Sigma$, to the excited state, $^{1}\Delta$. The reactions are both solvent and concentration dependent, with sulfones generally favored in acetonitrile and sulfoxides favored in methanol. There is also a ligand and metal effect. The proposed mechanistic pathways involving a persulfoxide precursor to single sulfur site O_2 addition (producing metallosulfones) and adjacent sulfur site O_2 addition (producing metallosulfoxides) are consistent with product distribution, comparison to the much studied oxygenation of organic sulfides, and previous isotopic labeling experiments (*J. Am. Chem. Soc.* **1996**, *118*, 1791; **1992**, *114*, 4601; *Inorg. Chem.* **1993**, *32*, 4171).

The reactivity of $^{1}\Delta\ O_2$ has been the subject of intense study over the last 3 decades.[1] Singlet oxygen is known to react with olefins and sulfides and has been implicated in photoinduced disorders such as skin cancer and in the photodegradation of polyolefins. Phenols, such as α-tocopherol (vitamin E), which serve to protect tissue and lipids from oxidative damage, and the much publicized antioxidant *β*-carotene demonstrate nature's resources for $^{1}\Delta\ O_2$ removal.

The quenching of singlet oxygen by metal chelates as polyolefin additives has led to interest in their use as potential photostabilizers.[2] Diamagnetic, square planar nickel(II) complexes, particularly those in sulfur-rich environments, have been shown to quench $^{1}\Delta\ O_2$ at rates comparable to that of *β*-carotene, the most efficient $^{1}\Delta\ O_2$ quencher known.[3] In that study, the quenching ability was measured by $^{1}\Delta\ O_2$ loss, typically assumed to derive from the relatively low d−d triplet excitation energy, 7000−8000 cm^{-1}, in square planar nickel(II) complexes. That the quenching is an energy transfer process, rather than an O_2 capture reaction, is supported by studies which show that the ability of nickel(II) complexes to quench excited state (triplet) pentacene is comparable to their quenching of $^{1}\Delta\ O_2$. Triplet pentacene has an excitation energy of 7000 cm^{-1}, similar to that of $^{1}\Delta\ O_2$, but does not permit reaction with the nickel complex.[3b]

Scheme 1



Whereas the typical air-sensitivity of metal thiolates results in degradation to yield di- or polysulfides and metal oxides, the *cis*-dithiolate [1,5-bis(2-mercaptoethyl)-1,5-diazacyclooctane]nickel(II) (**Ni-1**, Scheme 1) has provided one of the first observations of oxygenation via $^{3}\Sigma\ O_2$ which yields isolable, characterizable sulfur oxygenates.[4−6] Further exploration of the potential for sulfur site oxygen uptake of this ligand and its sterically hindered analogue, 1,5-bis(2-mercapto-2-methylpropyl)-1,5-diazacyclooctane, in nickel and palladium complexes

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(1) Reviews: (a) Ando, W. *Singlet Oxygen*; CRC Press: Boca Raton, FL, 1984; Vol. III, Part 2. (b) Gorman, A. A. *Advances in Photochemistry*; John Wiley and Sons, Inc.: New York, 1992; Vol. 17.

(2) Carlsson, D. J.; Suprunchuk, T.; Wiles, D. M. *J. Polym. Sci., Part B: Polym. Lett.* **1973**, *11*, 61.

(3) (a) Monroe, B. M.; Mrowca, J. J. *J. Phys. Chem.* **1979**, *83*, 591. (b) Furue, H.; Russel, K. E. *Can. J. Chem.* **1978**, *56*, 1595.

(4) (a) Farmer, P. J.; Solouki, T.; Soma, T.; Russell, D. H.; Darensbourg, M. Y. *Inorg. Chem.* **1993**, *32*, 4171. (b) Farmer, P. J.; Solouki, T.; Mills, D. K.; Soma, T.; Russell, D. H.; Reibenspies, J. H.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1992**, *114*, 4601.

(5) Mirza, S. A.; Pressler, M. A.; Kumar, M.; Day, R. O.; Maroney, M. J. *Inorg. Chem.* **1993**, *32*, 977.

(6) (a) Schrauzer, G. N.; Zhang, C.; Chadha, R. *Inorg. Chem.* **1990**, *29*, 4104. (b) Nicholson, T.; Zubieta, I. *Inorg. Chem.* **1987**, *26*, 2094.

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has produced the series of complexes shown in Scheme 1.[7,8] Synthetic strategies for optimal yields and selectivity are generally based on stoichiometric addition of H_2O_2, which rapidly adds a single O atom. In some cases, however, molecular oxygen is the reagent of choice. The oxygenates shown in Scheme 1 have been fully characterized by appropriate physical methods (UV−vis, IR, cyclic voltammetry), and in most cases structures have been determined by X-ray crystallography.[4,7−12] The complexes have very similar Ni−N and Ni−S distances but vary in the tetrahedral twist of the MN_2S_2 planes.

The reaction of ground state oxygen, $^3\Sigma$ O_2, with the singlet ground state of d^8 square planar metal complexes is formally spin forbidden. Earlier results indicated that the reactivity of $^3\Sigma$ O_2 with the MN_2S_2 complexes correlates inversely with the planarity of the metal center. As indicated in Scheme 1, **Ni-1** has the greatest tetrahedral twist, 13.3°, resulting in paramagnetism for **Ni-1**, while **Ni-1*** and **Pd-1** are strictly diamagnetic. It is expected that the Td twist provides a thermally accessible triplet state and thus a spin-allowed route for reaction with $^3\Sigma$ O_2. Substantial (25%) oxygenation of the nickel dithiolate **Ni-1** via $^3\Sigma$ O_2 at 1 atm and 22 °C occurs within 24 h, while the **Ni-1*** complex shows little reaction within 1 week.[10] No reaction at all is observed between **Pd-1** and $^3\Sigma$ O_2 within the same time period.[8] The observation of oxygen uptake at sulfur by **Pd-1** under photolysis conditions, however, suggests a low-lying triplet excited state for the complex.[8] Alternatively, excitation of oxygen from its triplet ground state to its singlet excited state provides a way to overcome the fact that the reaction is spin forbidden. Our preliminary report on the reaction of **Ni-1*** with $^1\Delta$ O_2 in methanol is, *to our knowledge, the first designed reactions of sulfur oxygenation in a metal thiolate by* $^1\Delta$ O_2.[13]

Herein we report an extensive investigation of the reaction of **Ni-1**, **Ni-1***, and **Pd-1** with $^1\Delta$ O_2 and its solvent and concentration dependence. As detailed below, the reaction of metal dithiolates with $^1\Delta$ O_2 proceeds more efficiently than that with $^3\Delta$ O_2, i.e., shorter reaction times, greater yields, and better selectivity. Based on the well-established mechanisms for reactions of organic sulfides with $^1\Delta$ O_2, mechanisms for "metallothiaether" S-oxygenation are proposed with the following added considerations: (1) the presence of a redox-active, electrophilic metal center; (2) an increased nucleophilicity of sulfur in NiSR compared to that in RSR; (3) the additional, internal nucleophile provided by the proximal sulfur site. This study also alerts chemists who utilize catalytically active, oxygen sensitive, sulfur-rich metal sites to the possibility of S-oxygenation of S-donor ligands as potentially stable intermediates in S-degradation.

Experimental Section

Materials. Reagent-grade solvents were dried using standard techniques and were freshly distilled before use. **Ni-1**, **Ni-1***, **Pd-1**, and 1,4-dimethylnaphthalene endoperoxide were synthesized according to published procedures.[8,11,12,14] Rose Bengal (RB) and other chemicals were purchased from Aldrich Chemical Co. and used as received.

Instrumentation and Procedures. UV−vis spectra were recorded with a Hewlett Packard HP8452A diode array spectrophotometer. Infrared spectra were recorded as KBr pellets using an IBM IR/32 Fourier transform single-beam spectrophotometer. Ultraviolet photolysis of the reaction solutions was performed in a 100 mL cylindrical Pyrex vessel (Ace Glass, Catalog No. 7878) equipped with a Hanovia medium-pressure mercury vapor lamp hanging inside the reactor. Although the lamp itself became quite hot during photolysis, the water jacket kept the solution near room temperature. The reactor and the hood sash were covered with aluminum foil to contain UV radiation. During irradiation, argon or oxygen was slowly bubbled through the reaction solution.

All of the neutral nickel complexes were purified and separated from mixtures by chromatography through a 10 in. × 1 in. (or 0.5 in.) column of silica gel (60−200 mesh, Aldrich grade 922, or EM Science, grade 22, pretreated with a pH 11 methanolic solution of NaOH and washed with methanol) with methanol as eluant whereas neutral palladium complexes were purified and separated by chromatography through a 12 in. × 1 in. column of untreated silica gel. The complexes eluted in the following order: RB, **Ni-1***, **Ni-4***, **Ni-2***, **Ni-5***, **Ni-6***, **Ni-3***; and RB, **Pd-1**, **Pd-2**, **Pd-4**, **Pd-5**, **Pd-6**, **Pd-3.** In almost all cases of palladium oxygenation, a yellow compound ascribed to a trimetallic complex, $(\textbf{Pd-1})_2Pd^{2+}$, was produced and stayed on top of a silica gel column. Products were identified on the basis of UV−vis and IR data. Yields were determined by weight differences following removal of solvent in preweighed vials or flasks.

Reaction of Ni-1 and Ni-1* with $^1\Delta$ O_2. In a typical experiment, 100 mg (0.334 mmol) of **Ni-1** was dissolved in 20 mL of dry methanol and loaded into the photochemical reactor. Rose Bengal (*ca.* 1 mg) was added as sensitizer. Oxygen was slowly bubbled through the solution as UV radiation was applied for 1 h in 30 min increments to allow cooling of the lamp and inspection of the apparatus. After irradiation, solvent was removed by rotary evaporation. The sample was redissolved in a minimum of methanol, and the components were separated on a silica gel column. Each band was then characterized chemically and quantitatively as described above. When 1,4-dimethylnaphthalene endoperoxide[14] was used as the singlet oxygen source, a 100 mg (0.334 mmol) portion of **Ni-1** was dissolved in 20 mL of dry methanol in a 100 mL round-bottom flask, to which the endoperoxide was added. The solution was stirred overnight. Purification and identification were performed as in the photochemical reactions. Product distributions are reported in Tables 1−4.

Reaction of Ni-2 with $^1\Delta$ O_2. In a typical experiment, 15 mg (0.046 mmol) of **Ni-2** was dissolved in 25 mL of dry, degassed acetonitrile (1.8 mM) along with the RB sensitizer (*ca.* 1 mg) in the photochemical reactor described above. Oxygen was slowly bubbled through the solution as UV radiation was applied for 1 h in 30 min increments. After irradiation, solvent was removed by rotary evaporation. The sample was redissolved in a minimum of acetonitrile and chromatographed on an alumina column. A single yellow band, eluted with acetonitrile, was identified as **Ni-3** by UV−vis and IR.

Reaction of Ni-4* with $^1\Delta$ O_2. In a typical experiment, a 23 mg (0.063 mmol) portion of **Ni-4*** was dissolved in 38 mL of dry, degassed acetonitrile (1.7 mM) along with *ca.* 1 mg of RB and placed in the photochemical reactor described above. Oxygen was slowly bubbled through the solution as UV radiation was applied for 1 h in 30 min increments. After irradiation, solvent was removed by rotary evaporation. The sample was redissolved in a minimum of methanol and chromatographed on a silica gel column. The single yellow band which eluted was identified by UV−vis and IR as **Ni-6***.

Reaction of Pd-1 with $^1\Delta$ O_2. Under anaerobic conditions, into a 100 mL Schlenk flask containing 100 mg (0.29 mmol) of **Pd-1** was placed 20 mL of a solution containing 1,4-dimethylnaphthalene endoperoxide[14] (*ca.* 10 mMol). The solution was stirred at 22 °C for at least 12 h. The solvent was removed by rotary evaporation, and the

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(7) Buonomo, R. M.; Font, I.; Maguire, M. J.; Reibenspies, J. H.; Tuntulani, T.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1995**, *117*, 963 and references therein.

(8) Tuntulani, T.; Musie, G.; Reibenspies, J. H.; Darensbourg, M. Y. *Inorg. Chem.* **1995**, *34*, 6279.

(9) Darensbourg, M. Y.; Tuntulani, T.; Reibenspies, J. H. *Inorg. Chem.* **1995**, *34*, 6287.

(10) Buonomo, R. M.; Darensbourg, M. Y.; Font, I.; Maguire, M. J.; Reibenspies, J. H. *Inorg. Biochem.* **1993**, *51*, 343.

(11) Mills, D. K.; Reibenspies, J. H.; Darensbourg, M. Y. *Inorg. Chem.* **1990**, *29*, 4364.

(12) Darensbourg M. Y.; Font, I.; Pala, M.; Reibenspies, J. H. *J. Coord. Chem.* **1994**, *32*, 39.

(13) Grapperhaus, C. A.; Darensbourg, M. Y.; Sumner, L. W.; Russell, D. H. *J. Am. Chem. Soc.* **1996**, *118*, 1791.

(14) Wasserman, H. H.; Larsen, D. L. *J. Chem. Soc., Chem. Commun.* **1972**, *5*, 253.

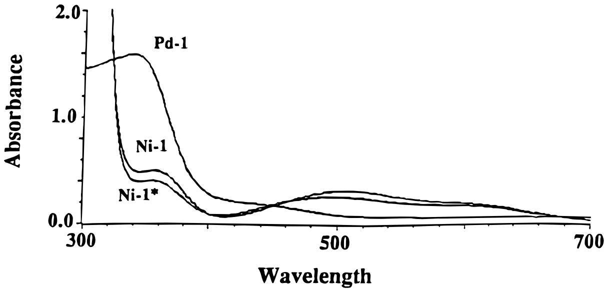


Figure 1. UV−vis spectra of solutions of 2.5 mM **Ni-1**, **Ni-1***, and **Pd-1** in acetonitrile.

residue was redissolved in a 1:1 mixture of CH_3CN/CH_3OH and transferred to a silica gel column. The residual 1,4-dimethylnaphthalene eluted with CH_3CN; other products eluted with methanol. Product distributions are reported in Tables 3 and 4.

Reaction of Ni-1 with $^1\Delta$ O_2 in Acetonitrile/D_2O. In a typical experiment, 100 mg (0.343 mmol) of **Ni-1** was dissolved in 19 mL of dry, degassed acetonitrile along with the RB sensitizer (*ca.* 1 mg) and 1 mL of D_2O in the photochemical reactor described above. Oxygen was slowly bubbled through the solution as UV radiation was applied for 1 h in 30 min increments. After irradiation, solvent was removed by rotary evaporation. The sample was redissolved in a minimum of acetonitrile and chromatographed on an alumina column, yielding **Ni-2** as an orange band and **Ni-3** as a yellow band. Both bands were analyzed by ^{2}H NMR. No deuterium incorporation was observed.

Results And Discussion

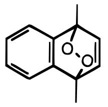
The uptake of O_2 by sulfur in square planar d^8 metal thiolate complexes **Ni-1**, **Ni-1***, and **Pd-1** has been investigated through reactions under a variety of conditions. Singlet oxygen was produced photochemically by bubbling O_2 through solutions containing Rose Bengal (RB) during irradiation via a Hanovia medium pressure mercury vapor lamp. The Pyrex reaction vessel acts as a filter for wavelengths below 280 nm. Figure 1 shows an overlay of the UV−vis spectra for **Ni-1**, **Ni-1***, and **Pd-1** in acetonitrile (2.5 mM). The charge transfer band of **Pd-1** near 350 nm may explain the increased oxygenation of **Pd-1** under photolysis.[8] This band is much less intense in **Ni-1** and **Ni-1***, consistent with the fact that, when nonsensitized photolysis is employed, little increase in oxygenation is observed from ambient conditions. To examine the possibility that photoactivation of the metal complex produced the oxygenation under $^1\Delta$ O_2 conditions (RB-sensitized photolysis), oxygenation was also carried out in the absence of UV irradiation by employing 1,4-dimethylnaphthalene endoperoxide as a thermal source of $^1\Delta$ O_2 ($t_{1/2} = 5$ h at 25 °C).

Although the nickel complexes were stable in the presence of RB in the absence of O_2, the palladium dithiolate degraded. The oxygenation of **Pd-1** with $^1\Delta$ O_2 was performed exclusively via the endoperoxide. Each metal complex was exposed to $^1\Delta$ O_2 in both protic (MeOH) and aprotic (MeCN) solvents; these results are summarized in Tables 3 and 4, respectively. The solubility of O_2 is 8.1 mM and 10.1 mM in MeCN and MeOH, respectively. As detailed in the Experimental Section, oxygenation ($^1\Delta$ O_2) reactions of **Ni-1** and **Ni-1*** were performed on a 100 mg scale in approximately 25 mL of solvent for the higher concentration (17 mM) and 40 mg in 80 mL of solvent for the lower concentration (1.7 mM). A lower metal complex concentration may also be considered as a higher $[O_2]$:[**M-1**] ratio since the $[O_2]$ is maintained constant by O_2 purge during reaction. Due to the limited solubility of **Pd-1** in acetonitrile, the highest concentration achieved was 3.0 mM. The reactions were carried out at room temperature (22 ± 1 °C) for a total of 1 h in the case of photolysis and for 24 h in the thermal (endoperoxide decomposition) reactions.

Table 1. Product Distribution (%) for Reactions of [1,5-Bis(2-mercaptoethyl)-1,5-diazacyclooctane]nickel(II) (**Ni-1**) with O_2 in Acetonitrile at 22 °C

entry	conditions	Ni-2	Ni-3	Ni-6	total oxygenation
	17 mM **Ni-1**				
1	$^3\Sigma$ O_2 (1 day)	20	5		25
2	$^3\Sigma$ O_2 ($h\nu$)[a]	16	trace[b]		16
3	$^1\Delta$ O_2 ($h\nu$, RB)[a]	19	4	6	29
4	$^1\Delta$ O_2 (endoperoxide)[c]	32		50	82
	1.7 mM **Ni-1**				
5	$^3\Sigma$ O_2 ($h\nu$)[a]	35	24		59
6	$^1\Delta$ O_2 ($h\nu$, RB)[a]		100		100

[a] $h\nu = 2 \times 30$ min irradiation via medium-pressure Hg vapor lamp; RB = Rose Bengal. [b] Trace amounts were detected by UV−vis spectroscopy, but accurate weights could not be determined. [c] Endoperoxide = 1,4-dimethylnaphthalene endoperoxide:



After cessation of the reactions, solvent was removed by rotary evaporation, and the products were separated on a silica gel column. Isolated yields were determined for each band eluted following evaporation of the solvent in a preweighed vial. Due to the relatively small quantities of product (typically 10−60 mg), the reproducibility associated with this technique may be assumed to be on the order of ±5%. Most experiments were double runs with product distributions within this error; average values are reported. Attempts to utilize typical spectroscopic techniques to identify products in the reaction mixture were unsuccessful; the paramagnetism of **Ni-1** prevented quantitative analysis by NMR, while overlap of absorption peaks complicated the use of UV−vis spectroscopy.

Reactivity of $^1\Delta$ O_2 with Ni-1: Establishing a Role for $^1\Delta$ O_2. Product distributions for the reaction of **Ni-1** with O_2 under various conditions in acetonitrile are given in Table 1. Although only 25% oxygenation, entry 1, is observed after 24 h under ambient conditions, i.e., with $^3\Sigma$ O_2 as oxygen source under laboratory lighting, exposure to UV radiation in the presence of $^3\Sigma$ O_2 yields 16% oxygenated products, entry 2, within 1 h. Addition of the singlet oxygen sensitizer Rose Bengal (RB) during irradiation almost doubles the yield in the same period, 29% oxygenation, entry 3. Finally, addition of excess 1,4-dimethylnaphthalene endoperoxide in 30-fold excess, a chemical source of $^1\Delta$ O_2, to **Ni-1** in the absence of light produced high levels of oxygenated products, entry 4. The role of singlet oxygen becomes even more evident at low **Ni-1** concentrations (or higher O_2:**Ni-1** ratios), entries 5 and 6. Nonsensitized photooxygenation of **Ni-1** yields 59% oxygenated products; in the presence of sensitizer, yields increase to 100% of the fully oxygenated **Ni-3**.

Analogous studies in methanol are listed in Table 2. Exposure of **Ni-1** to $^3\Sigma$ O_2 for 1 day, entry 7, yields 3% oxygenation, leading primarily to the monosulfone, **Ni-2**. In 1 h, photolysis of **Ni-1** and $^3\Sigma$ O_2 also produces 3% oxygenated products at 17 mM and even less (trace amounts) at lower **Ni-1** concentration, entries 8 and 10. Addition of RB during irradiation increases oxygenation from 3% to 10%, entries 8 and 9. At low **Ni-1** concentrations (or higher O_2:**Ni-1** ratio), the effect is dramatic, increasing oxygenation from trace amounts to 62%, entries 10 and 11.

A summary of the above results follows: (1) Although some increased oxygenation is observed upon photolysis of the metal solutions, addition of sensitizer for $^1\Delta$ O_2 production significantly increases product yield. (2) Oxygenation occurs with

Table 2. Product Distribution (%) for Reactions of [1,5-Bis(2-mercaptoethyl)-1,5-diazacyclooctane]nickel(II) (**Ni-1**) with O2 in Methanol at 22 °C

entry	conditions	**Ni-2**	**Ni-3**	**Ni-4**	total oxygenation
	17 mM **Ni-1**				
7	$^3\Sigma$ O_2 (1 day)	3	trace^b		3
8	$^3\Sigma$ O_2 ($h\nu$)^a	3	trace^b	trace^b	3
9	$^1\Delta$ O_2 ($h\nu$, RB)^a	8		2	10
	1.7 mM **Ni-1**				
10	$^3\Sigma$ O_2 ($h\nu$)^a	trace^b			0
11	$^1\Delta$ O_2 ($h\nu$, RB)^a	10	52		62

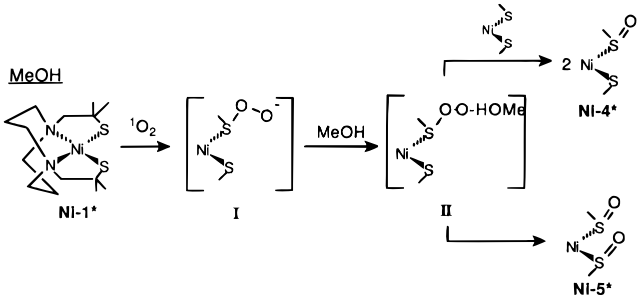
[a] $h\nu = 2 \times 30$ min irradiation via medium-pressure Hg vapor lamp (see Experimental Section); see Table 1 for RB and endoperoxide description. [b] Trace amounts were detected by UV spectroscopy, but accurate weights could not be determined.

Table 3. Product Distribution (%) for Reactions of **Ni-1**, **Ni-1***, and **Pd-1** with $^1\Delta$ O_2 in Methanol

entry	conditions	**M-2**	**M-3**	**M-4**	**M-5**	**M-6**	total oxygenation
12	**Ni-1** (17 mM)^a	8		2			10
13	**Ni-1** (1.7 mM)^a	10	52				62
14	**Ni-1*** (17 mM)^a			13	12		25
15	**Ni-1*** (1.7 mM)^a			25	37		62
16	**Pd-1** (3.0 mM)^b			15		4	19

[a] $^1\Delta$ O_2 derived from $h\nu$/RB (1 h total photolysis) as described in the Experimental Section. [b] $^1\Delta$ O_2 derived from endoperoxide, see Table 1, 24 h at 22 °C.

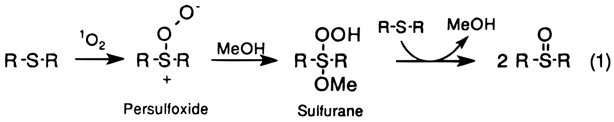
Scheme 2



endoperoxide, a chemical source of $^1\Delta$ O_2 which is released in a dark thermal reaction. The latter observation further limits the possibility that photoexcitation of the metal complexes is a requisite for reaction. *It is concluded that singlet oxygen is primarily responsible for the dramatic increase in oxygenated product when the solution is irradiated in the presence of the singlet oxygen sensitizer Rose Bengal.*

Comparisons of Reactivity of M-1 (Ni-1, Ni-1*, Pd-1) with $^1\Delta$ O_2 in Methanol. The results of these reactions are summarized in Table 3. Reaction of **Ni-1** (17 mM solution) with $^1\Delta$ O_2 in methanol produces the monosulfone **Ni-2** (8%) and the monosulfoxide **Ni-4** (2%) in low yields, entry 12. Entry 13 shows that, at lower **Ni-1** concentrations, **Ni-4** is no longer observed, and metallosulfones **Ni-2** (10%) and **Ni-3** (52%) are produced. Unlike **Ni-1**, photooxygenation of the sterically hindered analogue **Ni-1*** in methanol yields only metallosulfoxides **Ni-4*** (13%) and **Ni-5*** (12%), entry 14. On increasing the O_2:**Ni-1*** ratio, product yields are increased, and the product distribution shifts slightly toward the bissulfoxide, entry 15. As shown in entry 16, the palladium analogue yields modest amounts of monosulfoxide **Pd-4** (15%) and sulfoxide/sulfone **Pd-6** (4%) in methanol; the sulfones **Pd-2** and **Pd-3** are not observed.

The mechanism proposed in Scheme 2 accounts for the observed product distributions of **Ni-1*** oxygenates in methanol and is analogous to the mechanism proposed for the well-studied oxygenation of organic sulfides with singlet oxygen (eq 1).[15,16]



The reaction of $^1\Delta$ O_2 with organic sulfides has been investigated by trapping with electrophilic (diphenyl sulfoxide) and nucleophilic (diphenyl sulfide) agents, isotopic labeling, and theoretical studies.[15−19] As indicated in eq 1, the proposed initial persulfoxide intermediate is expected to deprotonate the solvent, yielding a sulfurane (the sulfurane is also capable of being trapped by diphenyl sulfoxide), which then is subject to nucleophilic attack by a second equivalent of thioether (eq 1).[17] That initial reaction of dioxygen with the metal dithiolates is sulfur and not metal based is supported both by *ab initio* calculations, which show that the HOMO in nickel dithiolates is sulfur based,[20] and the isolation and full characterization of S-based SO_2 adducts of **Ni-1** and **Pd-1**.[9]

Attempts to trap the intermediate(s) of metal dithiolate oxygenation with diphenyl sulfoxide did not produce diphenyl sulfone as in organic thioethers.[15,16e] This suggests that, if a persulfoxide intermediate is formed, either it does not subsequently form a metallasulfurane analogous to the organic counterpart in eq 1 or the metallasulfurane, if formed, is not reactive. It is expected, however, that a H-bonded intermediate, **II** in Scheme 2, decreases the electron density of the oxygen, making the oxygen electrophilic. The lack of diphenyl sulfoxide production upon addition of diphenyl sulfide is not unexpected, given the presence of a second nucleophilic S site in **Ni-1** and **Ni-1***; i.e., internal trapping leads to formation of the bissulfoxide. As reported previously, isotopic labeling studies show that the bissulfoxide, **Ni-5***, is the result of O_2 addition across the *cis* S sites.[13]

An interesting issue is the reversal of sulfoxide/sulfone stabilities in **Ni-1*** vs **Ni-1** oxygenates. Whereas the bissulfoxide **Ni-5*** is the prominent reaction product of **Ni-1***/$^1\Delta$ O_2 in methanol, **Ni-5** has never been observed, despite its implication as an intermediate in the formation of **Ni-3**.[4] Scheme 3 suggests the possibility of an internal isomerization of **Ni-5** to **Ni-2** in competition with further oxygen reactivity of **Ni-5** to yield **Ni-3**. It is expected such an isomerization would be more difficult with the sterically hindered analogue. Molecular mechanics calculations to address this supposition are underway.

The reaction of **Pd-1** and $^1\Delta$ O_2 yielded only the monosulfoxide **Pd-4** and the mixed sulfoxide/sulfone **Pd-6**. The thermodynamically stable bissulfoxide **Pd-5** has only been produced in reactions of **Pd-1** with the stoichiometric O atom source H_2O_2. The increased S−S distance in **Pd-1** (3.353 Å) compared to that in **Ni-1*** (3.012 Å) may arguably account for the lack of molecular O_2 addition across the *cis* S sites. Curiously, the sulfoxide/sulfone **Pd-6** is generated from further

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(15) Foote, C. S.; Peters, J. W. *J. Am. Chem. Soc.* **1971**, *93*, 3795.

(16) For example: (a) Jensen, F. *J. Org. Chem.* **1992**, *57*, 6478. (b) Watanabe, Y.; Kuriki, N.; Ishiguro, K.; Sawaki, Y. *J. Am. Chem. Soc.* **1991**, *113*, 2677. (c) Ando, W.; Akasaka, T. *Stud. Org. Chem.* **1988**, *33*, 99. (d) Clennan, E. L.; Zhang, H. *J. Org. Chem.* **1994**, *59*, 7952. (e) Liang, J. J.; Gu, C. L.; Kacher, M. L.; Foote, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 4717. (f) Akasaka, T.; Sakurai, A.; Ando, W. *J. Am. Chem. Soc.* **1991**, *113*, 2696.

(17) Clennan, E. L.; Greer, A. *J. Org. Chem.* **1996**, *61*, 4793.

(18) Ishiguro, K.; Hayashi, M.; Sawaki, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7265.

(19) Jensen, F. *J. Org. Chem.* **1992**, *57*, 6487.

(20) Maroney, M. J.; Choudhury, S. B.; Bryngelson, P. A.; Mirza, S. A.; Sherrod, M. J. *Inorg. Chem.* **1996**, *35*, 1075.

Scheme 3

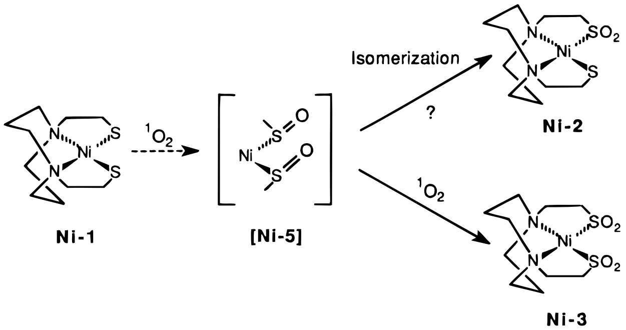

Table 4. Product Distribution (%) for Reactions of **Ni-1**, **Ni-1***, and **Pd-1** with $^1\Delta$ O_2 in Acetonitrile

entry	conditions	M-2	M-3	M-4	M-6	total oxygenation
17	**Ni-1** (17 mM)[a]	19	4		6	29
18	**Ni-1** (1.7 mM)[a]		100			100
19	**Ni-1*** (17 mM)[a]			14	15	29
20	**Ni-1*** (1.7 mM)[a]	11			10	21[c]
21	**Pd-1** (3.0 mM)[b]	21	11		7	39

[a] $^1\Delta$ O_2 derived from $h\nu$/RB (1 h total photolysis) as described in the Experimental Section. [b] $^1\Delta$ O_2 derived from endoperoxide, see Table 1, 24 h at 22 °C. [c] No starting material was recovered, and an unidentified white solid was present.

Scheme 4

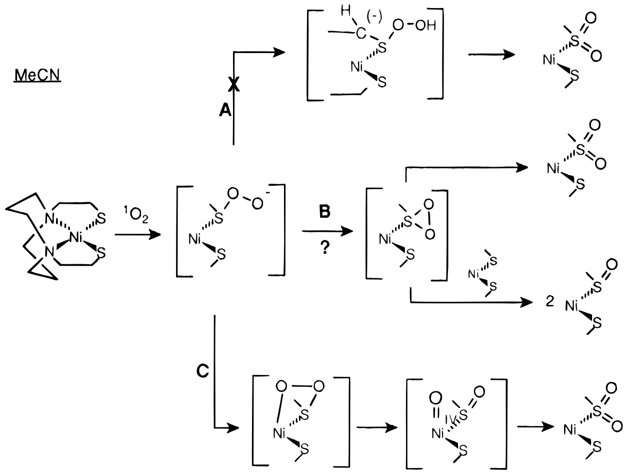

Table 5. Comparison of Redox Potentials and Oxygen Reactivity for **Ni-1**, **Ni-2**, and **Ni-Me$^+$** in Acetonitrile[a]

compound	$E_{1/2}$ (red) (mV)	E_{pc} (ox), irrev	reactivity	
			$^3\Sigma$ O_2	$^1\Delta$ O_2
Ni-1	−1944	+360	20% **Ni-2** 5% **Ni-3**	100% **Ni-3**
Ni-2	−1631	+620	NR[c]	100% **Ni-3**
Ni-Me$^+$	−1204	+956[b]	NR[c]	NR[c]

[a] All potentials scaled to NHE referenced to MeV^{2+}/MeV^+. $^3\Sigma$ O_2 reactivity based on 24 h reaction. $^1\Delta$ O_2 reaction based on 1 h photolysis in the presence of Rose Bengal. [b] Oxidation peak for BF_4^- salt; the oxidation peak of the iodide salt is obscured by oxidation of the counterion. [c] No reaction.

reaction of **Pd-4** with $^1\Delta$ O_2. Since the S−S distance basically is unchanged in **Pd-4**, addition of O_2 across the S sites is unlikely, suggesting that either O_2 adds as a molecule to the remaining thiolate or an intermolecular mechanism is operative. Isotope labeling experiments to examine these possibilities are underway.

Comparisons of Reactivity of M-1 with $^1\Delta$ O_2 in Acetonitrile. Listed in Table 4 are the results of the following reactions. The photooxygenation of **Ni-1** in acetonitrile at high (17 mM) concentration yields the monosulfone **Ni-2** (19%), the bissulfone **Ni-3** (4%), and the sulfoxide/sulfone **Ni-6** (6%), entry 17. At the lower **Ni-1** concentrations (and higher O_2:**Ni-1** ratio), entry 18, the bissulfone **Ni-3** is generated exclusively. At high **Ni-1*** concentration, **Ni-4*** (14%) and **Ni-6*** (15%) are produced in modest yields, entry 19. As shown in entry 20, when the metal complex concentration is lowered, **Ni-2*** (11%) and **Ni-6*** (10%), as well as an unidentified white solid, are observed. No **Ni-1*** is recovered. Reaction of the isolated **Ni-3*** with $^1\Delta$ O_2 again resulted in formation of the white solid. Similar to **Ni-1**, **Pd-1** reacts with $^1\Delta$ O_2 in acetonitrile to yield **Pd-2** (21%), **Pd-3** (11%), and **Pd-6** (7%), entry 21.

Three possible routes to sulfone synthesis in acetonitrile are depicted in Scheme 4. The cross S site addition shown in Scheme 2 is not consistent with the absence of the bissulfoxide **Ni-5*** in the product mixture. It has been noted that, for organic sulfides, deuterium from D_2O is incorporated at the α carbon during the $^1\Delta$ O_2 oxygenation in aprotic solvents (spiked with D_2O). This result was interpreted in terms of proton abstraction generating a hydropersulfoxy ylide intermediate on the path to sulfone synthesis.[18] Path A invokes a similar mechanism for the production of **Ni-2**. However, neither the mono- nor the bissulfone synthesized in the presence of 5% D_2O incorporated deuterium (determined by ^2H NMR), as expected for this pathway. Path B involves formation of a thiadioxirane directly from singlet oxygen. While the production of sulfoxides from thiadioxiranes in organic thioethers has been postulated, organic sulfones appear to derive via a different mechanism. In addition, the presence of the positive metal center would seem to provide a better site for persulfoxide rearrangement. A metal-assisted path would appear to be reasonable for the oxygenated products observed in acetonitrile, path C. This path, however, would require a Ni^{IV}=O intermediate.

Electron Richness of Sulfur. The effect of electron richness and S-nucleophilicity on the reaction of nickel thiolates with $^1\Delta$ O_2, i.e., the redox potentials of **Ni-1**, **Ni-2**, and the monomethylated analogue of Ni(bme-daco), **Ni-Me$^+$**, are considered in the data of Table 5. As the thiolate is changed to a sulfone or thioether, the electron richness of the metal complex is decreased, as evidenced by increased accessibility of the $Ni^{II/I}$ reduction potential and decreased accessibility of the oxidation potential. That the redox potentials provide a measure of the nucleophilicity of the thiolate has been evidenced by kinetic measurements of the rate of alkylation of these thiolates via iodomethane, **Ni-1** > **Ni-2** > **Ni-Me$^+$**.[21] As stated previously, **Ni-1** reacts slowly with $^3\Sigma$ O_2 in acetonitrile (entry 1, Table 1) but quantitatively with $^1\Delta$ O_2 (entry 7, Table 1). The monosulfone **Ni-2** is unreactive with $^3\Sigma$ O_2 even after 1 week but is quantitatively converted to the bissulfone in 1 h via singlet oxygen. Quite interestingly, **Ni-Me$^+$** is completely unreactive with both $^3\Sigma$ O_2 and $^1\Delta$ O_2. It should be noted that the lack of reactivity of **Ni-Me$^+$** is a kinetic and not a thermodynamic barrier, as the monosulfone/monomethylated nickel complex can be synthesized by reaction of **Ni-2** with iodomethane or, alternatively, from **Ni-Me$^+$** on reaction with H_2O_2.[22]

The increased oxygen-donating ability of $^1\Delta$ O_2 is most notable in the monosulfone **Ni-2**, which shows no reaction with $^3\Sigma$ O_2 but quantitative production of **Ni-3** with $^1\Delta$ O_2. *This is contradictory to the established pathway for the generation of **Ni-3** from $^3\Sigma$ O_2 in MeCN* and interesting in light of theoretical

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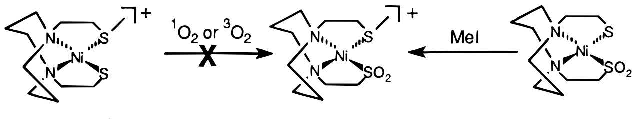
[21] Buonomo, R. M.; Bellefeuille, J. A.; Reibenspies, J. H.; Darensbourg, M. Y. Manuscript in preparation.

[22] Farmer, P. J.; Reibenspies, J. H.; Lindahl, P. A.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1993**, *115*, 4665.



Ni-Me$^+$ **Ni-2**

studies (RHF/LANL2DZ *ab initio* calculations) of *cis*-dithiolates and *cis*-sulfone/thiolate.[18] Consistent with the great nucleophilicity of sulfur established for **Ni-1** and **Ni-1*** [11,21] and with our proposed electrophilic attack of O_2 on thiolate sulfur, the HOMO for the nickel dithiolates lies on the sulfur.[18] Maroney *et al.* calculated that, in the sulfone/thiolate, the HOMO shifts to the sulfone oxygen. This result was used to rationalize the loss of dioxygen reactivity at the second thiolate.[18] Our results make the important distinction that, although the oxygenation of the second thiolate by $^3\Sigma$ O_2 is *kinetically* limited, it is clearly *thermodynamically* possible, and $^1\Delta$ O_2 overcomes the kinetic barrier. Previous studies have shown that H_2O_2 also allows conversion of the monosulfone **Ni-2** to the bissulfone **Ni-3**.[4] Furthermore, other electrophilic substrates such as MeI readily add to the remaining thiolate of **Ni-2**.[22]

Comments

Although the reactions of singlet oxygen with organic compounds have been studied extensively, its reactivity with metal complexes has largely been limited to $^1\Delta\ O_2 \rightarrow {}^3\Sigma\ O_2$ quenching possibilities.[2,3,23−25] Only recently have products been isolated and reported from such reactions.[26−28] The oxidative addition of O_2 to Ir^I, forming the Ir^{III} peroxide derivatives of Vaska's type complexes from dioxygen, provides precedent for metal-based reaction of d^8 square planar metal complexes with $^1\Delta$ O_2.[26−28] In such studies, Foote *et al.* have estimated that the rate of oxygenation of Ir^I is enhanced by at least 9 orders of magnitude when O_2 is excited from the ground to singlet state.[28,29] Such an increase is well within that expected on the basis of activation parameters for the slow, spin-forbidden reaction of ground state oxygen, $^3\Sigma$ O_2, with $IrX(CO)(PPh_3)_2$, ($X = Cl$, Br, or I),[29] where values of $\Delta H^\ddagger$ ranging from 10.9 to 13.1 kcal/mol and of $\Delta S^\ddagger$ ranging from −24 to −21 eu were determined by Chock and Halpern.[29] Since the $^3\Sigma$ O_2 to $^1\Delta$ O_2 excitation energy is 22.4 kcal/mol,[1] the energy of activation of the reaction is easily met; in fact, diffusion-controlled rates might be expected.[28]

Analogously, the reaction rates of ground state oxygen, $^3\Sigma$ O_2, with square planar d^8 metal dithiolates may be accelerated by excitation of oxygen to the $^1\Delta$ state. A simplified cartoon of the orbital control and energetics is given in Figure 2. While only one component of the $^1\Delta$ state of O_2 is represented in Figure 3, this state is more accurately represented as a combination of wave functions with both *xx*, *yy* and *xy*, *xy* components.[30] Note that this drawing limits reactivity strictly to the sulfur of MSR, in analogy to R_2S, and neglects any metal orbital interactions.

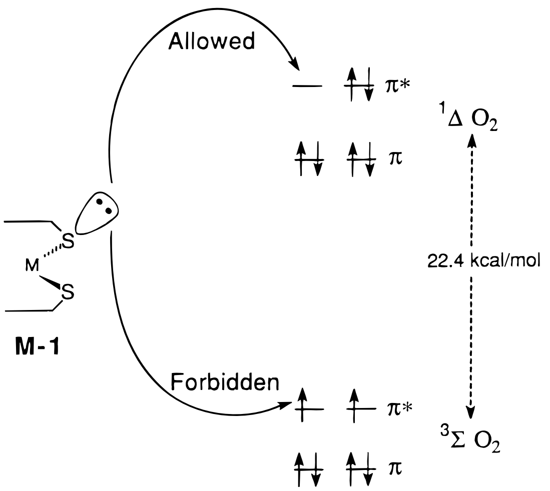


Figure 2. Diagram illustrating the spin-forbidden and spin-allowed reactions of **Ni-1** with $^3\Sigma$ O_2 and $^1\Delta$ O_2, respectively.

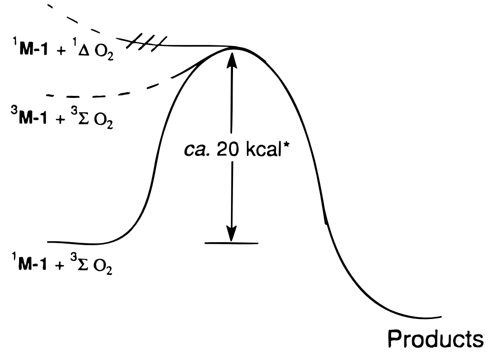
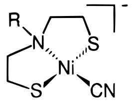


Figure 3. Minimal profiles for the reactions of **M-1** with $^3\Sigma$ O_2 and $^1\Delta$ O_2. $\Delta G^\ddagger$ is based on activation parameters reported by Maroney *et al.* for the reaction of nickel thiolates with $^3\Sigma$ O_2 calculated at 22 °C.[5] The dotted line represents the uncertainty of this reaction surface (see text).

An appropriate kinetic study by Maroney *et al.* established activation parameters for the thiolate S-oxygenation reactions with $^3\Sigma$ O_2 of the three derivatives of **Ni-7** to yield sulfones.[5] The $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values of 13.1−14.7 kcal/mol and −24.2 to −18.7 eu, respectively, result in a $\Delta G^\ddagger$ range of 18.6−21.8 kcal/mol calculated at 22 °C. Making use of the data presented by Maroney, *et al.* a minimal reaction profile for the **M-1** systems is formulated in Figure 3. This profile suggests that, for **M-1**, the oxygenation by $^1\Delta$ O_2 should also be diffusion controlled; i.e., the $^3\Sigma\ O_2 \rightarrow {}^1\Delta\ O_2$ excitation energy overcomes the energy of activation.



Ni-7

$R = CH_2CH_2SCH_3$,
$CH_2CH_2SCH(CH_2C_6H_5)_2$,
$CH_2CH_2CH(C_6H_5)_2$

The metal dithiolate complexes **Ni-1**, **Ni-1***, and **Pd-1** possess an abundance of electrophilic addition chemistry, including S-alkylation,[22] S-metalation,[31] and S-oxygenation. Since these complexes undergo such extensive ligand-based reactivity, it is not unexpected that, as metallothiaethers, they would react with singlet oxygen much like organic sulfides. Like their organic counterparts, these reactions are found to be concentration and solvent dependent, with sulfoxides typically favored in protic solvent and sulfones in aprotic solvent. These reactions apparently differ from their organic counterparts by the observed

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(23) Corey, E. J.; Mehrotra, M. M.; Kahn, A. U. *Science* **1987**, *236*, 68.
(24) Corey, E. J.; Kahn, A. U. *Tetrahedron Lett.* **1990**, *31*, 1389.
(25) Detty, M. R. *Organometallics* **1992**, *11*, 2310.
(26) Selke, M.; Foote, C. S. *J. Am. Chem. Soc.* **1993**, *115*, 1166.
(27) Selke, M.; Foote, C. S.; Karney, W. L. *Inorg. Chem.* **1993**, *32*, 5425.
(28) Selke, M.; Karney, W. L.; Khan, S. I.; Foote, C. S. *Inorg. Chem.* **1995**, *34*, 5715.
(29) Chock, P. B.; Halpern, J. *J. Am. Chem. Soc.* **1966**, *88*, 3511.
(30) Kasha, M. *Singlet Oxygen*; CRC Press: Boca Raton, FL, 1984; Vol. I.
(31) Musie, G.; Farmer, P. J.; Tuntulani, T.; Reibenspies, J. H.; Darensbourg, M. Y. *Inorg. Chem.* **1996**, *35*, 2176.

addition of O_2 across adjacent *cis* sulfur sites (Scheme 2), as well as the possibility for a metal to interact with the persulfoxide intermediate (path C, Scheme 4). While mechanistic considerations, including energy transfer from $^1\Delta$ O_2 to the transition metal thiolates, may be even more complex than those for the organic sulfide counterparts, the products established from these reactions provide profound implications as to the synthesis and stabilities of rare metallo-*S*-oxygenates. We have firmly established a product-directing role for *cis*-dithiolates, as well as an unexpected efficiency for O_2 uptake (up to four oxygen atoms) in sterically nonhindered *cis*-metallothiolates. That the quenching of $^1\Delta$ O_2 by the thiolate-rich metal complexes may be a chemical as well as a physical phenomenon must be a consideration in their role as antioxidants.

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