Notes

Theoretical Study of the Oxidation of Nickel Thiolate Complexes by O_2

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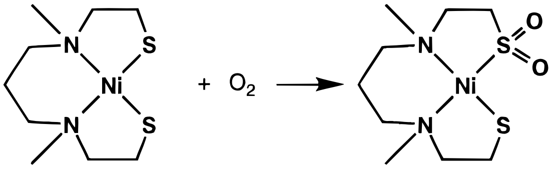
Introduction

The discovery of nickel-containing enzymes that catalyze redox reactions[1−5] and the association of these biological Ni centers with cysteinate ligands or with S-oxidation products have spurred recent interest in the redox chemistry of nickel thiolate complexes. Studies of the products of oxidations of nickel(II) thiolate complexes reveal that in many cases the thiolate ligands are oxidized in preference to the metal center.[6−10] One such reaction is the oxidation of nickel(II) thiolate complexes with O_2 to yield Ni(II) complexes containing sulfinate ligands.[6,8−10] The stoichiometric oxidations of nickel(II) thiolate complexes by O_2 (*e.g.* Scheme 1) have been studied in detail for several dithiolato complexes and are characterized by sluggish second-order kinetics (first order in [Ni] and in [O_2]), the incorporation of both atoms of O_2 (dioxygenase-like chemistry), the oxidation of only one of the two thiolates, and the absence of evidence for intermediates such as O_2 complexes or for the involvement of radicals or singlet oxygen.[8] These features of the reaction led to a proposed mechanism based on nucleophilic attack by thiolate on O_2 leading to a thiadioxirane-like intermediate, in analogy with the oxidation of thioethers by $^1O_2$.[8] Here we report the results of *ab initio* molecular orbital calculations aimed at examining the electronic structure of both *cis*- and *trans*-nickel dithiolates and at gaining insights into the electronic factors involved in the O_2 oxidations.

Experimental Section

RHF/LANL2DZ *ab initio* calculations were performed with the Gaussian 92 for Windows suite of programs[11] running on a 90 MHz Pentium computer. RHF methods were considered adequate because our previous characterization of the complexes (EPR, magnetic susceptibility, etc.) gave no indication of unpaired electrons in the ground state.[8] Including electron correlation for systems of this size would also have been prohibitively expensive. The LANL2DZ basis set[12] was selected for our qualitative orbital analysis because it offered the best balance between computational speed and useful accuracy: The LANL2DZ basis set was developed to make use of effective core potentials (ECP) to model the core electrons of transition metals like nickel, while the double-ζ basis set for the valence electrons was expected to be more accurate at describing the orbital structure of the hypervalent sulfur in the oxidized products than the alternative STO-3G basis set. Details of the calculations are included in the supplemental material.

Scheme 1



Cartesian coordinates for heavy atoms were taken from crystallographic coordinates.[6,8,13,14] The crystal structures of the Ni complexes have C_1 symmetry, and therefore no symmetry was imposed on the theoretical models. The coordinates of the hydrogen atoms in each complex were fully optimized at the RHF/LANL2DZ level, while restricting the coordinates of the heavy atoms to their X-ray positions. This method led to C−H bond lengths of 1.08−1.09 Å, in good agreement with typical aliphatic C−H bond lengths. Given our geometric approximations and the limitations of the basis set, these calculations are not expected to be quantitatively accurate. However, comparing computational results across several related systems, supported by consistent experimental data (*vide infra*), should allow qualitatively correct features and trends to be identified.

The resulting structures, their molecular orbitals, the electron density and the electrostatic potentials were visualized with a Tektronics CAChe workstation. Configuration interaction-singles (CIS) calculations, which model excited states as single substitutions out of the ground state, were employed to examine the electronic absorption spectra. The range of MOs used for complexes **1**−**4** were as follows: 12−113, 14−123, 11−111, and 13−121, respectively. The results of the calculations are expected to be only qualitatively accurate.

Experimental electronic absorption spectra were taken at 25 ± 1 °C by using a OLIS 4300 Cary-14 system on solutions prepared in acetonitrile. For wavelengths between 405 and 900 nm, approximately 2−4 mM solutions and 1 cm pathlengths were used. This would allow the detection of weak transitions ($A \geq 0.01$) in the visible and near-IR regions with $\epsilon \geq 2.5{-}5.0$ M^{-1} cm^{-1}. For the UV region (405−205 nm) of the spectra, 20−40 μM solutions in 1 cm pathlength cells were used.

Results

A. Electronic Structure. The electronic structures of the dithiolates and their monosulfinate oxidation products are summarized by the energy level diagrams in Figure 1. Figure 1 also gives the numbering scheme used in the calculations.

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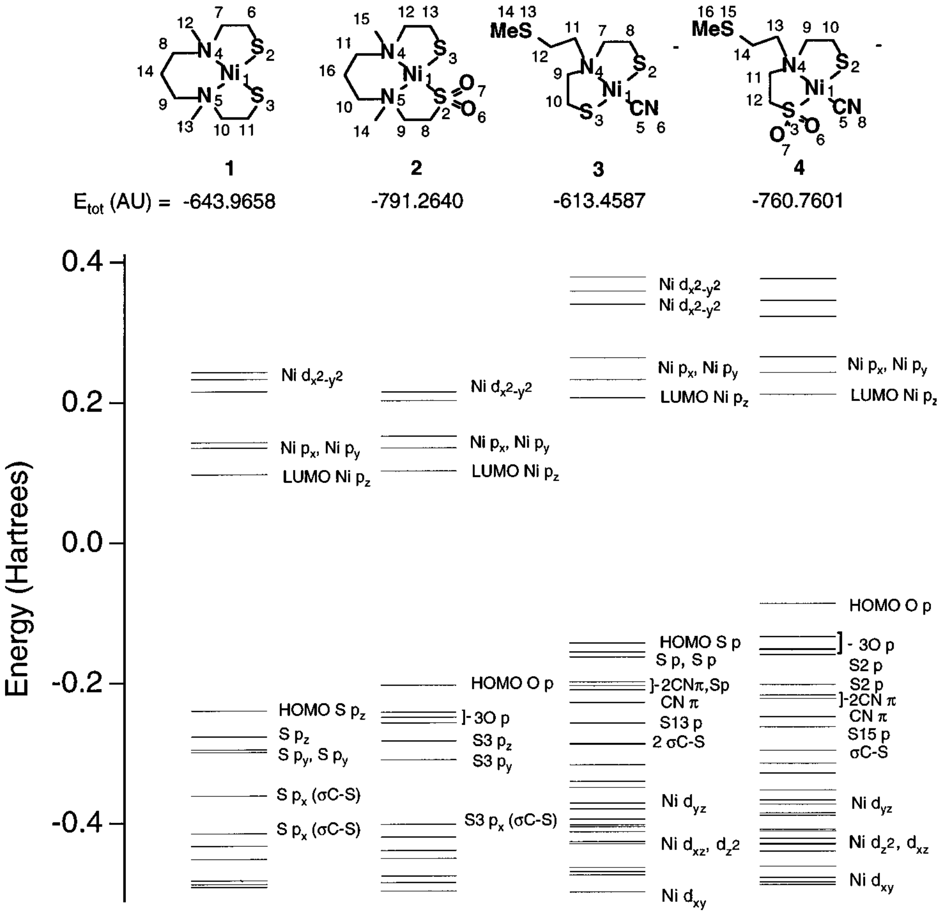

Figure 1. Orbital energy level diagrams. Molecular orbitals with energies between −0.5 and +0.4 hartrees are shown. Labels indicate the principal character of the MO.

The filled FMOs for both dithiolates are predominantly S in character. For the *cis*-dithiolate complex (**1**), the HOMO (MO 59) can be described as predominantly an antisymmetric combination of p_z orbitals on the two S-donors (approximately 88% S and 2% Ni), and is best viewed as S lone pairs. MO 58 (HOMO-1) is the symmetric combination of the S p_z orbitals, which exhibits some S−S π-bonding interaction. MOs 57−54 are best described as antisymmetric and symmetric combinations of in-plane S p orbitals, which also contribute to weak Ni−S σ-bonding and to the C−S σ-bonds. No significant amount of Ni−S π-bonding is observed in any of the FMOs. The filled orbitals with major contributions from Ni-3d orbitals are not found among the FMOs (−0.30 to −0.20 Hartrees), but occur at lower energies (−0.65 to −0.54 hartrees). The LUMO (MO 60) found for the *cis*-dithiolate is a diffuse orbital composed mainly of Ni p_z orbitals. MOs 64 and 65 have major contributions from the $d_{x^2-y^2}$ orbital.

The results obtained for the *trans*-dithiolate (**3**) are completely analogous to those obtained for the *cis*-dithiolate (**1**) except that no S−S interaction is possible and the π-orbitals of CN^- make a contribution to frontier orbitals other than the HOMO. The HOMO for **3** (MO 57) is again found to be predominantly an antisymmetric combination of S p_z orbitals (approximately 83% S and 6% Ni). It is apparent from the comparison of the results for **1** and **3** that S−S interactions are of little importance in **1**.

The FMOs of the monosulfinates (**2** and **4**) are dominated by contributions from sulfinate O atoms rather than from either the sulfinate or thiolate S atoms. For example, in **2** the HOMO (MO 67) is dominated by O p orbitals (approximately 49% O, 10% S, and 26% Ni), and the thiolate S atom (S3) makes a negligible contribution. The next highest filled MOs (66-64) are also dominated by O p orbitals, although MO 65 has substantial S p_z components from the thiolate S atom. MOs 63 and 62 are the first orbitals dominated by contributions from the thiolate S atom. MOs 62 and 61 are predominantly in-plane S p orbitals roughly analogous to orbitals 57 and 55 in **1**. The LUMO of the monosulfinate complex is not very different from that of the *cis*-dithiolate and remains essentially a Ni p_z orbital. The unoccupied $d_{x^2-y^2}$ orbital makes a major contribution to MO 72.

The electronic structure of **4** is quite similar to **2**. The HOMO for **4** (MO 65 is also largely O in character (approximately 54% O, 10% S, and 18% Ni) and MOs 64−62 are dominated by contributions from O p orbitals, with MO 62 (HOMO-3) having a contribution from p_z orbitals on the thiolate S atom in analogy with MO 65 (HOMO-2) in **2**. MOs 61 and 60 are the highest energy orbitals dominated by contributions from the thiolate S-donor, and orbital 59 is the highest energy orbital dominated by contributions from the CN^- ligand. The LUMO is again largely a Ni p_z orbital. Orbitals with contributions from the Ni $d_{x^2-y^2}$ orbital lie above the mostly Ni p orbitals in this model as well.

B. Electronic Spectroscopy. Electronic absorption spectra were predicted by CIS calculations performed on each theoretical model. The results of these calculations are compiled in Table 1 and may be compared with experimental data taken from spectra of acetonitrile solutions of **1**−**4**. In general, the calculated values for the energy of the electronic transitions and their relative intensities are in reasonable agreement with the experimental data given the level of theory used and allow qualitative assignments of the observed electronic absorptions to be made. The low energy transitions correspond to largely d−d transitions of the planar Ni(II) centers and are found at

Table 1. Experimental Electronic Spectral Data and Assignments

complex	exptl ν_{max}, cm^{-1} (ϵ, M^{-1} cm^{-1})	calcd ν_{max}, cm^{-1}	calcd f	assignment
1	16 300 (sh)	12 100	0.0000	$d_{yz}, d_{xz}, d_{z^2} \rightarrow d_{x^2-y^2}$
	21 050 (110)	14 300	0.0001	$d_{xy} \rightarrow d_{x^2-y^2}$
	36 500 (12 600)	46 300	0.0099	LMCT: S $p_z \rightarrow$ Ni p_z
		53 700	0.0010,	
	41 000 (sh)	53 900	0.0688	LMCT: S p $\rightarrow$ Ni $p_{x,y}$
		54 300	0.0032	
2	23 000 (321)	18 000	0.0003	$d_{xy} \rightarrow d_{x^2-y^2}$
	31 900 (5054)	37 200	0.0135	LMCT: O p $\rightarrow$ Ni p_z
	34 700 (3630)	44 800	0.0151	LMCT: O p $\rightarrow$ Ni p_y
	38 300 (6050)	45 500	0.0248	LMCT: O p $\rightarrow$ Ni p_x
	43 700 (sh)	48 100	0.0586	LMCT: O p $\rightarrow$ Ni
3	17 500 (25.4)	17 000	0.0000	$d_{z^2} \rightarrow d_{x^20y^2}$
	23 800 (364)	18 400	0.0001	$d_{xy} \rightarrow d_{x^2-y^2}$
	32 200 (7070)	49 200	0.0028	LMCT: S $p_{x,z} \rightarrow$ Ni p_z
		52 200	0.0108	
	36 600 (19 700)	52 600	0.0762	LMCT: S $p_{x,z} \rightarrow$ Ni p
		53 100	0.0003	
4	25 600 (sh)	20 100	0.0003	$d_{xy} \rightarrow d_{x^2-y^2}$
	30 900 (13 000)	36 700	0.0193	LMCT: O p $\rightarrow$ Ni p_z
		43 400	0.0380	LMCT: O p $\rightarrow$ Ni p_y
	37 900 (20 500)	46 400	0.0100	LMCT: O p $\rightarrow$ Ni p_x
		48 700	0.0469	

energies similar to experimentally measured values (*e.g.* bis(maleonitrile)nickelate(2−): $d_{xy} \rightarrow d_{x^2-y^2} = 11\,690$ cm^{-1}, $\epsilon = 30$ M^{-1} cm^{-1}; $d_{xz} \rightarrow d_{x^2-y^2} = 17\,500$ cm^{-1}; $\epsilon = 570$ M^{-1} cm^{-1}.[15]) High energy transitions are dominated by LMCT transitions that arise from MOs that can be described as filled S p-orbitals in the dithiolate complexes, but are predicted to be sulfinate O-orbitals in the oxidation products.

Discussion

The qualitatively accurate *ab initio* theoretical models for the dithiolate complexes (**1** and **3**) in this study indicate that the filled FMOs are largely S p orbitals and that Ni d orbitals make only small contributions to the HOMO and filled FMOs. This is the origin of the nucleophilicity of the thiolate ligands in the Ni(II) complexes and is consistent with the experimental observation that oxidation by O_2 occurs at the S-donor atoms. The nucleophilicity of thiolate ligands is well known, and is partly responsible for the fact that nickel thiolates tend to form oligomers,[7,16−19] that the thiolate S atoms are readily alkylated,[19] and that many of the reported oxidation products of nickel thiolate complexes are Ni(II) complexes with oxidized thiolate ligands.[6−10]

The HOMOs of the dithiolate complexes are essentially p-orbitals on the S-donor atoms, similar to the HOMO found in nickel bis(dithiolene) complexes, which is ca. 80% S in character (20% from each of four S-donor atoms).[20] It is interesting to note that nickel bis(dithiolene) complexes are another group of compounds that show the oxidation of one of the thiolate S-donor atoms to a sulfinate S-donor ligand in the presence of O_2.[21] In analogy with the oxidation of the dithiolates, the dithiolenes undergo oxidation at only one of the two S-donors in each ligand.

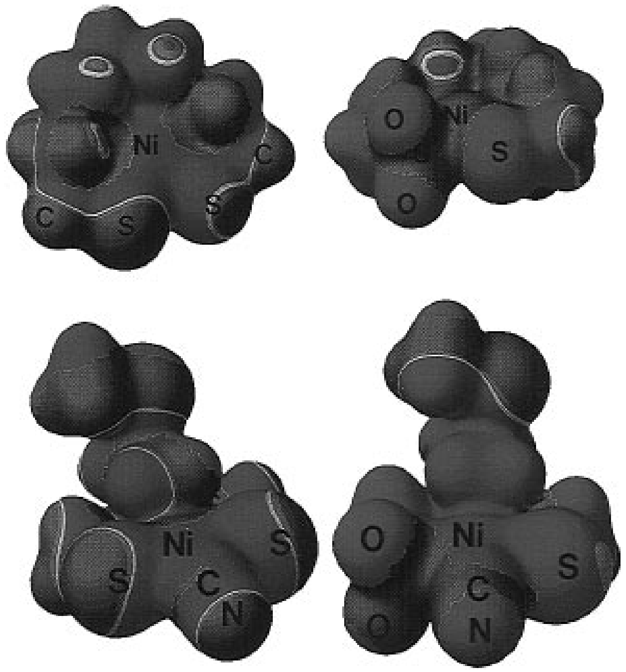

Figure 2. Electrostatic potentials and electron density diagrams: (A, top left) **1**; (B, top right) **2**; (C, bottom left) **3**; (D, bottom right) **4**. Colors indicate the electrostatic potential surface of the molecule calculated using a positive probe charge. Dark blue indicates the most nucleophilic regions and red the least nucleophilic regions (dark blue/light blue = 0.090 esu, light blue/pink = 0.030 esu, pink/dark green = 0.010 esu, dark green/light green = 0 esu, light green/yellow = −0.010 esu, yellow/orange = −0.030 esu, orange/red = −0.060 esu). The sizes of the spheres represent relative electron density.

The effects of the change in electronic structure of the FMOs from S-centered to O-centered on the reactivity of the complexes is also illustrated by electrostatic potentials. The results of such calculations for **1** and **3** using a positive charge as a probe is shown by the colors in Figure 2. These calculations reveal that the sites expected to be the most nucleophilic are the thiolate S-donor atoms (blue). The Ni center (red) is found to be among the least nucleophilic sites in both complexes. A Mulliken analysis of the atomic charges indicates that the S atoms are the most negatively charged centers in both complexes (−0.22 for **1** and −0.36 for **3**). Despite the approximate nature of this analysis, the charges obtained are in line with expectations based on the relative electron affinity of S and are consistent with the fact that **3** is an anionic complex and therefore has the greater charge density on S.

Upon exposure to O_2, the dithiolates are quantitatively converted to monosulfinate complexes **2** and **4**. The mechanisms that have been proposed for this reaction involve nucleophilic attack by the thiolate ligand on an O_2 molecule to form a thiadioxirane-like intermediate, in analogy with the oxidation of thioethers by $^1O_2$.[8] The theoretical models support this view, since the S atoms are predicted to be the most nucleophilic centers and the complex with the most negatively charged S-donor atoms also has the faster oxidation rate.[8] Nucleophilic reactions are generally envisioned as involving the HOMO of the nucleophile and the LUMO of the electrophile. Examination of the HOMOs of **1** and **3** predicts that nucleophilic attack involving the S p_z orbitals will come from a direction above or below the plane of the complexes. This prediction is supported by the structure reported for an SO_2 adduct of a nickel(II) *cis*-dithiolate complex.[22] This structure reveals that

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the SO_2 molecule is positioned so as to place the S atom above the plane of the molecule over one of the two thiolate ligands at a distance of 2.597(2) Å.

Another interesting feature of the O_2 oxidations is that they stop completely after the oxidation of one of the two thiolate ligands.[8] This has been attributed to an "inductive effect".[23] The analysis of the electrostatic potentials for **2** and **4** (Figure 2) do indicate that the remaining thiolate S-donor is no longer nucleophilic in the monosulfinates. However, from an FMO viewpoint, the reason for the loss of reactivity observed for the remaining thiolate ligand is due to the fact that the FMOs of **2** and **4** are mostly localized on O atoms of the sulfinate ligands. Examination of the electron density surfaces in Figure 2 reveals little change in electron density at the remaining thiolate S-donor, suggesting that changes in electron density at this sulfur are not important. This is supported by a Mulliken population analysis for both monosulfinates, which indicates qualitatively that while the sulfinato S-donor bears now bears a positive charge (1.1 and 1.0, respectively), the negative charge residing on the thiolate S-donor is largely unchanged from the corresponding dithiolates (−0.24 and −0.36, respectively).

The CIS calculations predict electronic transitions for **2** and **4** that are somewhat surprising. Thiolate complexes are known to exhibit S → M LMCT transitions in the near-UV region of the spectrum, and this is what is predicted by the theoretical models for **1** and **3**. All known nickel(II) monosulfinate complexes exhibit two intense transitions in the near UV region of their spectra.[8] These bands are apparently diagnostic for nickel(II) *S*-sulfinato complexes. The CIS calculations predict that these electronic transitions are due to primarily to sulfinate → Ni LMCT, rather than to thiolate → Ni LMCT.

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Supporting Information Available: Table of approximate orbital character for the FMOs of **1**−**4**, table of atomic charges for **1**−**4** derived from a Mulliken population analysis, table of CIS calculated transition energies and oscillator strengths, and tables of Gaussian archive output for the calculations on **1**−**4** (27 pages). Ordering information is given on any current masthead page.

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