Volume 32

Number 26

December 22, 1993

Inorganic Chemistry

Communications

Variable Oxygenation Levels of Sulfur in Sterically Hindered Thiolates: Molecular Structure of [*N*-(2-Mercapto-2-methylpropyl)-*N'*-(2-sulfeno-2-methylpropyl)-1,5-diazacyclooctanato]nickel(II)

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Received August 20, 1993

Key to the understanding of the reaction of oxygen sources with nickel-activated thiolate sulfurs,[1-3] a reaction of possible significance to the deactivation of nickel-containing enzymes,[3] is whether a nickel sulfenate (NiS(=O)R) functionality has more than a fleeting existence. The few well-characterized metallosulfenates are limited primarily to Co(III) and Ir(III).[4-6] Efforts to prepare derivatives of other metals have been thwarted by further reactivity with oxygen atom sources (eq 1) or disproportionation (eq 2) producing the stable sulfinate ligand.[7,8] Herein we report a successful strategy for the isolation of the first nickel sulfenate.

$$\mathrm{MS({=}O)R} + [\mathrm{O}] \rightarrow \mathrm{MSO_2R} \qquad (1)$$

$$2\mathrm{MS({=}O)R} \rightarrow \mathrm{MSO_2R} + \mathrm{MSR} \qquad (2)$$

Sulfur oxygenates result from the reaction of [*N,N'*-bis(mercaptoethyl)-1,5-diazacyclooctanato]nickel(II), **1**, with both molecular oxygen and hydrogen peroxide: a monosulfinate, [*N*-(mercaptoethyl)-*N'*-(sulfinoethyl)-1,5-diazacyclooctanato]nickel(II), **2**, and a bis(sulfinate), [*N,N'*-bis(sulfinoethyl)-1,5-diazacyclooctanato]nickel(II), **3**.[1a] Observations of column chromatographic separations indicated that precursors might be present, but reactions of substoichiometric amounts of single O-atom sources were routinely unsuccessful in isolating the expected sulfenato complex(es). With the expectation that steric encumbrance about sulfur might inhibit addition of a second O-atom, the complex of nickel shown as 1* in Scheme I was synthesized.[9]

The X-ray crystal structure of [*N,N'*-bis(2-mercapto-2-methylpropyl)-1,5-diazacyclooctanato]nickel(II), 1*, shows a rigorously square planar array of N_2S_2Ni, with sulfur sites flanked by methyl groups on the C atoms α to thiolate sulfur.[9] Complex 1* is much less reactive with molecular O_2 than is its non-methylated analogue, **1**. However reaction with H_2O_2 is rapid in CH_3CN, producing mixtures of oxygenates which were separated by silica gel flash chromatography, with MeOH as eluant. With 4 equiv of H_2O_2 at 22 °C, the major products had IR spectra[10] and X-ray crystal structures[11] analogous to those obtained for oxygenates of **1**,[1a,12] i.e., a mono(sulfinate), 2*, and a bis(sulfinate), 3*.[14] By careful attention to temperature, dilution, and stoichiometry, the yields of additional products, including the title complex 4*, could be optimized.

Scheme I depicts the reaction of 2 equiv of H_2O_2 with 1* at −78 °C and in high dilution where only two product fractions were obtained; neither was a sulfinate. The first eluting, bright yellow component, 4*, had an intense IR absorption at 909 cm^{-1} in MeOH, assignable to ν(SO),[4-6] and displayed a ^1H NMR spectrum consisting of four singlets of equal intensity in the methyl region.[10] Orange component 5* had a similar band in the IR at

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(10) IR absorptions, KBr pellets, ν(SO) region (cm^{-1}): 2*, 1053, 1182; 3*, 1029, 1062, 1180, 1191, 4*, 909, 5*, 921. ^1H NMR, CD_3OD solvent, TMS standard, CH_3 region (all singlets of equal intensity (ppm)): 1*, 1.43; 2*, 1.37, 1.25; 3*, 1.27; 4*, 1.66, 1.56, 1.32, 1.22; 5*, 1.48; 1.51.

(11) X-ray diffraction data were collected on a Siemens R3m/V X-ray diffractometer at 296 and 193 K for 3* and 4*, respectively, and at 296 K on a Rigaku AFC5R X-ray diffractometer for 2*. Structures were solved by standard procedures; semiempirical absorption corrections were applied. Crystallographic data are given as follows: a, b, c; β; space group, Z, 2θ range, unique observed reflections, R (R_w) (%). [*N*-(2-mercapto-2-methylpropyl)-*N'*-(2-sulfeno-2-methylpropyl)-1,5-diazacyclooctanato]nickel(II), 4*: 10.643(4), 22.047(12), 7.912(3) Å; 109.58(3)°, $P2_1/c$ (No. 14), 4, 4.0°/50.0°, 1744 ($I > 2\sigma(I)$), 6.14 (6.08). [*N*-(2-mercapto-2-methylpropyl)-*N'*-(2-sulfino-2-methylpropyl)-1,5-diazacyclooctanato]nickel(II), 2*: 13.655(5), 13.004(4), 19.128(4) Å; *Pbca* (No. 61), 8, 5.0°/50.0°, 1324 ($I > 2\sigma$(I)), 6.8 (7.1). [*N,N'*-bis(2-sulfino-2-methylpropyl)-1,5-diazacyclooctanato]nickel(II), 3*: 8.066(2), 10.159(3), 14.231(5) Å; 105.70(3)°, P_1 (No. 2), 2, 4.0°/50.0°, 1305 ($I > 2\sigma(I)$), 5.4 (3.9).

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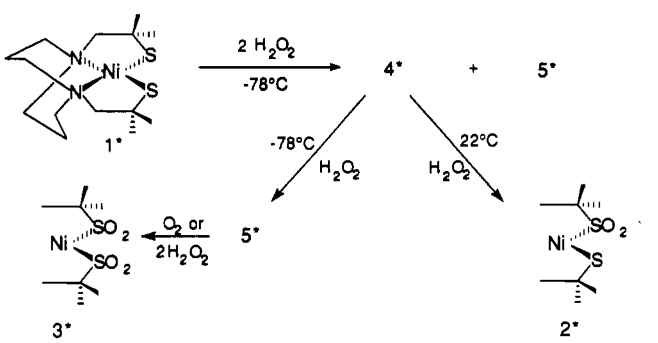
(13) Elemental analysis (Galbraith Laboratories): (a) Calc (obsd) for 2*, $C_{14}H_{28}N_2S_2O_2Ni$: C, 44.36 (44.23); H, 7.39 (7.74); N, 7.39 (6.87) (mp (with dec) 260–262 °C). (b) Calc (obsd) for 4*·H_2O, $C_{14}H_{30}N_2S_2O_2Ni$: C, 44.09 (43.75); H, 7.87 (7.75), N, 7.34 (7.05) (mp (with dec) 163–165 °C).

(14) A full report of the properties and structures of all oxygenates of 1* is in preparation.

0020-1669/93/1332-5897$04.00/0

Scheme I



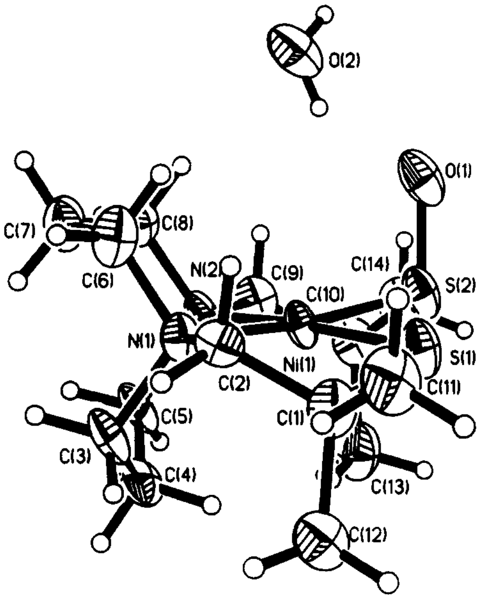
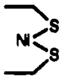
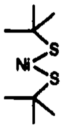
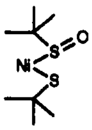
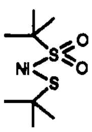
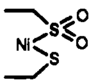


Figure 1. Thermal ellipsoid plot (50% level) of [*N*-(2-mercapto-2-methylpropyl)-*N'*-(2-sulfeno-2-methylpropyl)-1,5-diazacyclooctanato]nickel(II)·H_2O, **4***. Selected bond lengths (Å): Ni–S(1) = 2.148(3); Ni–S(2) = 2.162(3); Ni–N(1) = 1.998(7); Ni–N(2) = 2.016(9); S(2)–O(1) = 1.548(8); O(1)–O(2) = 2.820(5). Selected bond angles (deg): S(1)–Ni–S(2) = 88.3(1); N(1)–Ni–N(2) = 90.4(3); N(1)–Ni–S(1) = 91.3(3); N(1)–Ni–S(2) = 172.8(2); Ni–S(2)–O(1) = 105.9(3).

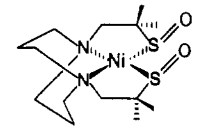
920 cm^{-1} but only two singlets in the methyl region of the ^{1}H NMR.[10] In contrast, both sulfinates, **2*** and **3***, display ν(SO) bands of lower intensity in the 1030–1200-cm^{-1} region and NMR patterns consistent with the symmetry of the complexes. That is, both **3*** and the parent dithiolate, **1***, show a single ^{1}H NMR resonance for four equivalent methyl groups,[10] while two singlets characterize **2***.

Elemental analysis[13] and X-ray crystal structure analysis[11,14] confirmed **4*** to be [*N*-(2-mercapto-2-methylpropyl)-*N'*-(2-sulfeno-2-methylpropyl)-1,5-diazacyclooctanato]nickel(II)·H_2O (Figure 1). In **4*** as well as **2*** and **3***,[14] the fused nickelladiazacyclohexane rings are in the chair/boat conformation, with the boat conformer on the same side of the N_2S_2 plane as the axial methyl groups of the pendant thiolate arms. The included water molecule of **4*** is involved in weak H-bonding interactions with sulfenato oxygens, bridging two adjacent complexes in the solid state. Metric parameters of significance in this series of sulfur oxygenates are given in Table I. The Ni–SR distances in **1** and **1*** suggest that the methyl substituents have no effect on the S-binding ability and do not enlarge the ligand cavity; indeed, there is a contraction of Ni–S bonds in going from **2** to **2***. These data find that Ni–SO_2R bonds are shorter than Ni–SR bonds, accountable to the smaller size of S^{2+} in the sulfinate,[1,3] as well as the elimination of the destabilizing effect of filled Ni-dπ/S-lone pair interaction in the Ni–SR bond, factors which apparently overwhelm the diminishing S-donor ability on going from SR^- to SO_2R^-. Hence the observed lengthening of the nickel-sulfur bond in the NiS(=O)R ligand points to a combination of electronic factors which compromises the Ni–S bond of NiS(=O)R, as compared to NiSR and $NiSO_2R$. The S–O distance in **4*** is ca. 0.1 Å longer than that for the sulfinates, as is also seen in the sulfenato/sulfinato complexes of Co(III).[4a,d]

Table I. Selected Bond Distances

compd	structure	Ni–S (Å)	S=O (Å)	ref
1		2.159(3) 2.159(3)		15
1*		2.152(1) 2.152(1)		9
4*		2.162(3) 2.148(3)	1.548(8)	this work
2*		2.109(4) 2.132(4)	1.46(1) 1.47(1)	this work
2		2.140(1) 2.163(1)	1.463(2) 1.456(3)	1a

The steric protection which evidently permits isolation of this rare sulfenate also limits its reactivity. Sulfenate **4*** is nonreactive with Me_2S and PPh_3, expected to be O-atom abstracting agents. Furthermore **4*** is thermally stable in the absence of air, withstanding long periods of reflux in CH_3CN solvent. Compound **4*** is however reactive with O_2 as well as H_2O_2 yielding higher oxygenates. With 1 equiv of H_2O_2 at 22 °C, the predominant product is **2***, whereas, at −78 °C, the product has the same spectral properties as compound **5***, Scheme I. That **5*** is along the reaction path to the fully oxygenated species is demonstrated by further reactivity with either H_2O_2 or molecular O_2, yielding the well-characterized **3***, Scheme I. This reactivity as well as the IR and NMR data[10] lead to the presumption that **5*** is yet another sulfenato complex, a *cis*-disulfenate. Work continues to establish its identity, unambiguously, as well as its role in oxygenations by molecular O_2.


5*

Note Added in Proof. Complex **5*** has recently been obtained in crystalline form and its structure determined by X-ray crystallography to be precisely as intimated above, a *cis*-disulfenate, with oxygens syn to the NiN_2S_2 plane. The average Ni–S and S=O bond distances are 2.17 and 1.54 Å, respectively.

Acknowledgment. The National Institutes of Health is acknowledged for the funding of this work (Grant RO1 GM44865-01), and the National Science Foundation, for the X-ray diffractometer and crystallographic computing system (Grant CHE-8513273). Appreciation is extended to Drs. P. J. Farmer and M. Maguire for their help.

Supplementary Material Available: Tables of atomic coordinates and equivalent isotropic displacement parameters for **1***, **2***, and **3*** (4 pages). Ordering information is given on any current masthead page.

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