4616 *Inorg. Chem.* **1997,** *36,* 4616−4617

A Unique Mononuclear Nickel Disulfonato Complex Obtained by Oxidation of a Mononuclear Nickel Dithiolate Complex

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Received June 12, 1997

There has been increasing interest in the study of the oxidation of nickel thiolate complexes in recent years owing to the known air sensitivity of thiols and nickel thiolates, in an attempt to further understand the behavior in air of some sulfur-rich nickel-containing enzymes such as [Ni−Fe] hydrogenases[1,2] and CO dehydrogenase.[3] Experimental studies of the oxidation products of nickel thiolate complexes to date have shown that the thiolate ligands are oxidized rather than the metal center itself. Oxidation products of nickel dithiolates have been characterized with the addition of up to four oxygens as shown schematically in Figure 1.[4,5] In all of these cases, the oxidation stopped before any of the Ni−S bonds were oxidized. The sulfenate (RSO) and sulfinate (RSO_2) groups remain coordinated to nickel via sulfur, with the nickel remaining in a square-planar coordination.[5]

The structural characterisation of the active site of the [Ni−Fe] hydrogenase enzyme, extracted from *Desulfovibrio Gigas*,[2] in which the catalytic site was revealed to contain a heterodimetallic nickel−iron cluster in a sulfur-rich environment has renewed interest in the chemical modeling of [Ni−Fe] hydrogenases. In view of this new structural information, the ligand H_2dsdm was considered useful in our synthetic modeling studies. The mononuclear [Ni(dsdm)] and trinuclear $[Ni_3(dsdm)_2]Cl_2$ complexes with this ligand have previously been reported from this laboratory.[6] The nickel monomer was reinvestigated as it contains two *cis* sulfur atoms from thiolate groups, which have potential in forming heterodimetallic complexes in which sulfur bridges to iron compounds. From one reaction with [Ni(dsdm)], some unexpected green crystals were isolated and they were shown by X-ray diffraction analysis to be an oxidation product in which the thiolate sulfurs were both oxidized to sulfonate. The sulfonate groups are coordinated to nickel via oxygen. The observed slow oxidation of the nickel dithiolate has been reproduced by deliberate oxidation of the mononuclear starting material with 6 equiv of hydrogen peroxide. To our knowledge, this is the first example of the oxidation of a nickel dithiolate complex resulting in a coordinated nickel disulfonate, of which the synthesis and X-ray structure are described below.

The ligand H_2dsdm was synthesized according to a literature procedure.[7] [Ni(dsdm)] was synthesized by modifying the published procedures.[6,8] To a solution of [Ni(dsdm)] (0.05 g, 1.94×10^{-4} mol) in 20 mL of DMF was added 6 equiv of hydrogen peroxide (1.16×10^{-3} mol, 0.12 mL) while stirring. The dark red solution turned to pale green within 1 min. Pale green crystals suitable for X-ray analysis were obtained in 60% yield, after slow evaporation of the solvent.

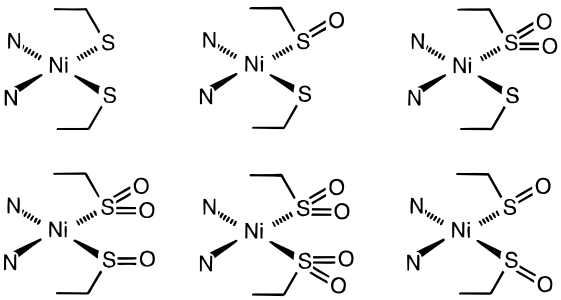

Figure 1. Schematic representation of a nickel dithiolate complex and its known oxidation products.[5]

The compound $[Ni(dsodm)(H_2O)_2]\cdot 2H_2O$ was characterized by IR and UV/vis spectroscopy and elemental analysis[9] and single-crystal X-ray crystallography.[10] A fully labeled representation of the molecular structure of the oxidized compound is given in Figure 2. The coordination around the nickel is octahedral, with the nickel sitting on a 2-fold axis. The ligand occupies four coordination sites with the amine nitrogens in *cis* positions and the two sulfonate oxygens in *trans* positions. Two water molecules *cis* to each other complete the octahedral coordination set. A tight hydrogen-bond network is formed by all available hydrogen atoms from the water molecules. Both the hydrogen atoms of the noncoordinated water molecule are hydrogen bonded to sulfonate oxygens. The distances of the acceptor oxygen to the hydrogen atoms are between 1.93(3) and 2.20(3) Å; the donor−acceptor distances are in the range 2.740(2)−2.948(2) Å. The nickel to nitrogen bond distances

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(9) Infrared spectrum (KBr pellet): 1652 (s), 1475 (m), 1466 (m), 1448 (m), 1264 (m), 1233 (s), 1208 (s), 1178 (s), 1157 (s), 1041 (s), 935 (m), 754 (s), 556 (m) cm^{-1}. Vis−NIR (solid-state reflectance, D_2 lamp): bands at 9100, 15 300, 25 900 cm^{-1}. Microanalysis (Microanalysis Laboratory, University College Dublin): Found (calcd) for $[C_8H_{18}N_2NiO_6S_2(H_2O)_2]\cdot 2H_2O$, C = 22.50 (22.20), H = 6.01 (6.05), N = 6.42 (6.47), S = 14.50 (14.81), Ni = 13.25 (13.55).

(10) Crystal data for $[C_8H_{18}N_2NiO_6S_2(H_2O)_2]\cdot 2H_2O$: $M = 433.14$, blue-green transparent crystal ($0.25 \times 0.35 \times 0.50$ mm), monoclinic, space group $C2/c$ with $a = 14.4780(8)$ Å, $b = 9.4442(5)$ Å, $c = 12.5055(7)$ Å, $\beta = 100.907(4)°$, $V = 1679.03(16)$ Å^3, $Z = 4$, $D_c = 1.713$ g·cm^{-3}, $F(000) = 912$, μ(Mo Kα) = 14.5 cm^{-1}, 4249 reflections measured, 1925 independent ($R_{av} = 0.019$), Mo Kα radiation, graphite monochromator, $\lambda = 0.710\,73$ Å, $\theta_{max} = 27.5°$, $T = 250$ K, CAD4T diffractometer on rotating anode. Data were corrected with the DIFABS option in PLATON.[11] The structure was solved by Patterson techniques and refined on F^2 using SHELXL96. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were located in a difference map and their positions refined with individual isotropic displacement parameters. Convergence was reached at $R_1 = 0.0257$ (for 1687 reflections with $I > 2\sigma(I)$) and $wR_2 = 0.0656$ ($S = 1.07$). A final difference map did not show any features outside $-0.46 < \Delta\rho < 0.53$ e·A^{-3}.

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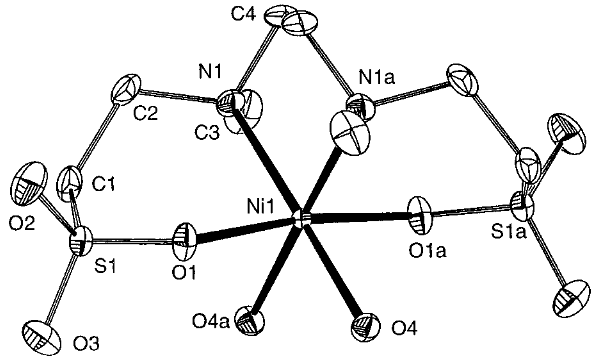

Figure 2. ORTEP view at 50% probability level of the molecular structure of [Ni(dsodm)(H$_2$O)$_2$]$\cdot$2H$_2$O (noncoordinating waters are omitted). Selected bond lengths (Å) and angles (deg): Ni1−O1 2.044(1), Ni1−O4 2.084(1), Ni1−N1 2.143(2), S1−O1 1.468(1), S1−O2 1.444(2), S1−O3 1.454(1); O1−Ni1−O4 85.03(5), O1−Ni1−N1 91.15(5), O1−Ni1−O1a 172.44(5), O1−Ni1−O4a 89.66(5), O4−Ni1−N1 175.19(5), O4−Ni1−N1a 89.66(5).

of 2.143(2) Å in [Ni(dsodm)(H$_2$O)$_2$]$\cdot$2H$_2$O, which are in the expected range for octahedrally coordinated nickel,[12] are significantly longer than those in the square planar nickel complexes.[5,6] The nickel to oxygen bonds in [Ni(dsodm)(H$_2$O)$_2$]$\cdot$2H$_2$O are 2.044(1) and 2.084(1) Å for the sulfoxide and the water molecule, respectively. These distances are in the expected range 2.03−2.13 Å found in similar complexes.[12−14]

There are only a few known cases of structurally characterized nickel complexes with coordinated sulfonato groups. The complex Na[Ni(tes)(H$_2$O)]$\cdot$5H$_2$O[12] was synthesized from the isolated ligand tes [tes = 1,4,7-triazacyclononane-*N*,*N*′,*N*″-tris(2-ethanesulfonate)] and is not the result of the oxidation of a thiolate complex. Second, there is a nickel triflate complex in which the triflate is coordinated to nickel, aqua(*N*,*N*-bis(2-(2-pyridyl)ethyl)benzylamine)bis(trifluoromethanesulfonato)nickel(II).[13] Finally, there is *cis*-bis(sulfanilato)bis(oxamide oxime)nickel(II) dihydrate,[14] in which one sulfanilato group coordinates to nickel via the sulfonate and the second coordinates via the amine group. In all of these structures, the nickel to sulfonato-oxygen distances are comparable to those in our new compound.

The infrared spectrum of [Ni(dsodm)(H$_2$O)$_2$]$\cdot$2H$_2$O contains four strong bands at 1157−1233 cm^{-1} which can be assigned to the ν(SO) stretches. These four bands are approximately 100 cm^{-1} higher than the Ni−SO$_2$ bands observed by both Darensbourg[5] and Maroney.[4] The solid-state ligand-field spectrum of the oxidized compound is characteristic for an octahedral geometry; the calculated *Dq* value of 910 cm^{-1} of the high-spin nickel(II) ion is in good agreement with an N$_2$O$_4$ coordination sphere around nickel.[15] The change of the spin state and geometry of the nickel(II) ion from low-spin square-planar toward high-spin octahedral is not surprising as such, because of the changes of the donor groups from N/S to N/O.

The use of 6 equiv of dihydrogen peroxide leads to a clean conversion of the dithiolate complex to the disulfonate compound.[16] Earlier studies on oxidation of nickel thiolates[4,5] showed that oxidations with dioxygen stop at monosulfinates. A recent theoretical study of the oxidation of a nickel dithiolate complex has been carried out by Maroney *et al.*[17]

The complex used in that study was [*N*,*N*′-dimethyl-*N*,*N*′-bis(mercaptoethyl)propylenediamine]nickel(II), which is very similar to the starting compound used in this work but with a propyl group bridging the nitrogens. His study supported the view that thiolate oxidation using dioxygen will stop at monosulfinate formation. However, further oxidation leading to the disulfinates can be achieved using dihydrogen peroxide. Several research teams have studied the oxidation of thiolate groups coordinated to cobalt or chromium.[18−21] Various oxidants have been used, among which are hydrogen peroxide, hexaquacobalt(III), and neptunium(VI). Most of these studies report the formation of sulfenates and sulfinates. A proposed minor product of hydrogen peroxide oxidation may have been a sulfonate,[19] but in most cases even with an excess of peroxide only the formation of sulfinate has been observed.[20,21] Clear evidence for the formation of a sulfonate in good yield from cobalt thiolate has only been given when the oxidation was performed with chlorine in water.[18] In conclusion, so far oxidations of nickel thiolates resulting in sulfonates have not been reported. It is the first time that a nickel thiolate complex has undergone a conversion from a low-spin square planar compound to a high-spin octahedral complex, and thereby it is also the first time that cleavage of a nickel−sulfur bond has occurred. In the oxidation reactions leading to sulfenates and sulfinates,[4,5] the RSO$_x$ groups remain bound to the nickel through the sulfur atom, and the nickel ion thereby remains low-spin, in a square planar geometry. In the case of the Darensbourg bicyclic ligand,[5] this may be due to the more rigid nature of this ligand. However, the ligand used by Maroney *et al.*[4] is similar to our ligand in its flexibility, but so far oxidation of the thiolate groups of this ligand to sulfoxides has not been reported.

Our observation and the characterization of the first chelating bis(sulfonato)nickel complex formed from the direct oxidation of a mononuclear nickel dithiolate may also provide new insight into the behavior of sulfur-rich nickel-containing enzymes. Further electrochemical studies and oxidation studies to gain insight into the mechanistic pathways leading to the formation of these unprecedented sulfonates will be undertaken.

Acknowledgment. Financial support for this project has been provided by a Biotech grant (Contract No. BIO2-CT94-2041) from the European Union. The research of E.B. has been made possible by a Fellowship of the Royal Netherlands Academy of Arts and Sciences. The work was in part (A.L.S.) supported by The Netherlands Foundation of Chemical Research (SON) with financial aid from the Netherlands Foundation for Scientific Research (NWO). Appreciation is expressed to Dr. M. J. Maroney and Dr. M. Y. Darensbourg for useful comments.

Supporting Information Available: X-ray crystallographic files, in CIF format, are available on the Internet only. Access information is given on any current masthead page.

IC9707218

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