Sulfur Site Adducts of Sulfur Dioxide in Nickel-Bound Thiolates and Their Conversion to Sulfate

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The formation of adducts of SO_2 at soft anionic ligand sites in metal-bound thiolates,[1] sulfides,[2–4] or iodides[5] has been well established by X-ray crystallography.[6,7] Hence the rapid uptake of SO_2 by the (*N,N'*-bis(mercaptoethyl)-1,5-diazacyclooctane)-nickel(II), (bme-daco)Ni^{II} or **1**, came as no surprise, particularly in view of the numerous examples of excellent nucleophilicity of the Ni–SR function in this complex.[8–11] A red microcrystalline solid analyzing[12] as (bme-daco)Ni^{II}·SO_2, or **1**·SO_2, precipitated immediately on bubbling SO_2 through a methanolic solution of **1** (100 mg of **1** in 5 mL of MeOH) and was isolated by filtration and air-dried in yields of ca. 60%. Slow evaporation of methanol solvent enlarged some of the crystals to a size suitable for X-ray crystallographic analysis.[13,14]

Cell parameters and a summary of the data collection are contained in Table 1. A full structure report is deposited as supplementary material. The molecular structure of **1**·SO_2 with numbering scheme is shown in Figure 1, and an alternate view is presented in Figure 2. In Table 2 selected bond lengths and angles are compared for **1**·SO_2 and **1**.[8] The nickel is rigorously square planar in **1**·SO_2, whereas in **1**, there is a slight (13.3°) tetrahedral twist in the N_2S_2 donor set. As was observed for **1**, in **1**·SO_2 the central carbon of one six-membered $NiNCH_2CH_2CH_2N$ ring, C(4), is disordered between two positions, C(4) and C(4′). The position of C(4) defines a six-membered metalladiazacyclohexane in the boat configuration whereas occupancy of C(4′) represents that ring in a chair configuration. The second metalladiazacyclohexane ring, reaching below the N_2S_2Ni plane, is fixed in a chair configuration. The fusing of the two rings thus results in two overall conformers of **1**·SO_2. The boat/chair conformer represented by the solid lines in Figure 1 (77% occupancy) is the more common in square planar (bme-daco)-Ni^{II} derivatives,[8–10,15] whereas the chair/chair form (23% occupancy) is always seen for six-coordinate, octahedral complexes based on diazacyclohexane.[11] In **1**, the disorder is accounted for by a 50/50 mixture of the two conformers.

Table 1. Summary of X-ray Crystal Structure Data for (bme-daco)Ni·SO_2, (**1**·SO_2)

chem formula	$C_{10}H_{20}N_2S_3O_2Ni$	*Z*	4
fw	355.2	ρ(calcd), g/cm^3	1.631
space group	$P2_1/c$ (No. 14)	temp, K	296
a, Å	8.933(4)	radiation (λ, Å)	Mo Kα (0.710 73)
b, Å	14.620(6)	abs coeff, mm^{-1}	1.758
c, Å	11.161(5)	min/max transm coeff	0.8265/0.9385
β, deg	97.04(4)	R^a	0.0553
V, Å^3	1446.720(0)	$R_w{}^a$	0.0467

[a] Residuals: $R = \sum|F_o - F_c|/\sum F_o$; $R_w = \{[\sum w(F_o - F_c)^2]/[\sum w(F_o)^2]\}^{1/2}$.

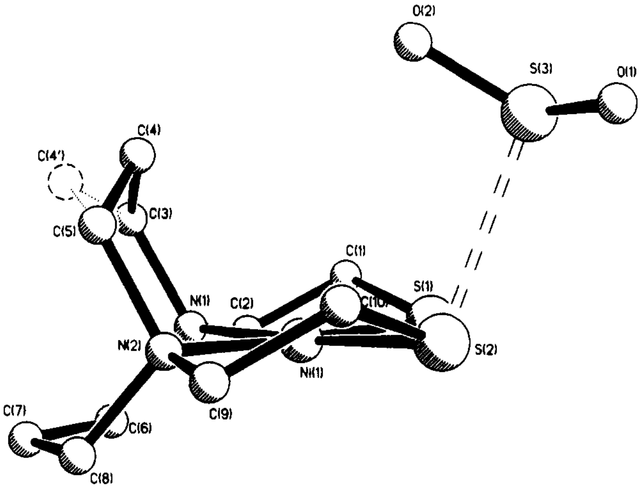

Figure 1. Molecular structure of (bme-daco)Ni·SO_2, **1**·SO_2. Atoms labeled **a** are generated by a C_2 axis from refined atoms; hydrogen atoms have been omitted for clarity. Site occupancy for C(4) was refined to 77%, and C(4′) to 23%.

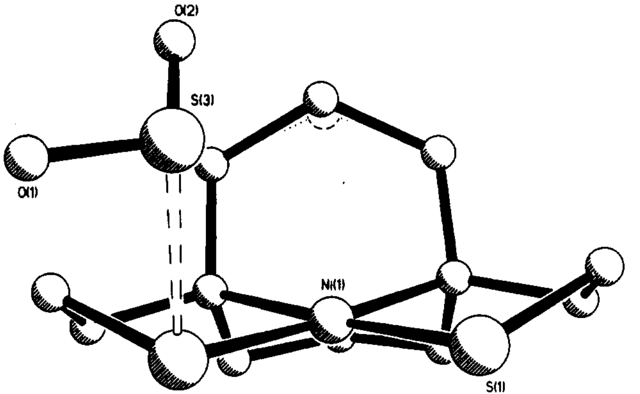

Figure 2. Alternate view of the molecular structure of **1**·SO_2.

A difference in the two compounds is the relative orientation of the ethylene linkages between N and S. In **1**·SO_2 they eclipse each other across the N_2S_2 plane whereas in **1** they are staggered. A second obvious difference is the presence of a pyramidal SO_2 unit bound to S(2) in **1**·SO_2 at a S--S distance of 2.597(2) Å, larger than the covalent radii sum (2.06 Å) and comparable to

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(11) (a) Goodman, D. C.; Tuntulani, T.; Farmer, P. J.; Darensbourg, M. Y.; Reibenspies, J. H. *Angew. Chem., Int. Ed. Engl.* **1992**, *32*, 116. (b) Darensbourg, M. Y.; Font, I.; Mills, D. K.; Pala, M.; Reibenspies, J. H. *Inorg. Chem.* **1992**, *31*, 4965.

(12) Elemental analysis by Galbraith Labs. Anal. Calcd for $NiC_{10}H_{20}N_2S_3O_2$ (found): C, 33.8 (33.5); H, 5.68 (5.17); N, 7.89 (7.96).

(13) A dark red crystal of **1**·SO_2 was mounted on a glass fiber with epoxy cement at room temperature. Preliminary examination and data collection were performed on a Nicolet R3m/V X-ray diffractometer. Lorentz and polarization corrections were applied to 2807 reflections. A semiempirical absorption correction[14] was applied (T_{max} = 0.9385; T_{min} = 0.8265). The molecular structures were solved by direct methods[14] and refined anisotropically for all non-hydrogen atoms with a full-matrix least-squares method.

(14) All crystallographic calculations were performed with SHELXTL-PLUS rev 3.4 (G. M. Sheldrick, Institut fur Anorganishe Chemie die Universitat, Tammannstrass 4, D-3400, Gottingen, Federal Republic of Germany).

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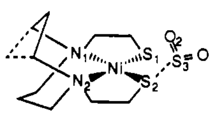
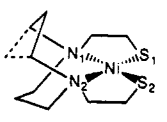
Table 2. Selected Bond Distances (Å) and Angles (deg) for (bme-daco)Ni·SO$_2$ (**1·SO$_2$**) and (bme-daco)Ni^{II} (**1**)

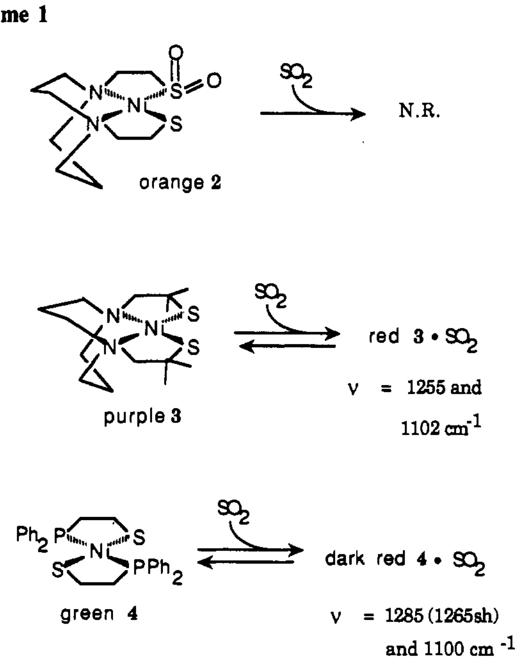
	 **1·SO$_2$**	 **1**
Ni–S(1)	2.167(2)	2.159(2)
Ni–S(2)	2.173(2)	2.159(2)
Ni–N(1)	1.991(4)	1.985(6)
Ni–N(2)	1.995(4)	1.985(6)
S(2)–S(3)	2.597(2)	
S(3)–O(1)	1.443(5)	
S(3)–O(2)	1.448(5)	
N(1)–Ni–N(2)	89.9(2)	89.8(3)
S(1)–Ni–S(2)	88.4(1)	89.5(1)
S(3)–S(2)–Ni	104.6(1)	
N(1)–Ni–S(1)	90.8(1)	91.4(2)
N(2)–Ni–S(2)	90.7(1)	91.4(2)
O(1)–S(3)–O(2)	114.3(3)	
O(1)–S(3)–S(2)	98.7(2)	
O(2)–S(3)–S(2)	99.8(2)	

SO$_2$ adducts at thiolate sulfur in (Ph$_3$P)$_3$Cu(SPh) (2.530(5) Å) and at μ-sulfide in (Cp*MoS$_2$)$_2$ (2.601(8) Å).[1,2] Likewise the S-O distance of 1.44 Å is typical of sulfur-bound pyramidal SO$_2$ units.[6] The average O–S(3)–S(2) angle of 99° further emphasizes the pyramidal nature of the sulfur-bound SO$_2$, Figure 2. The SO$_2$ addendum has no effect on the Ni–S bond distance: within the N$_2$S$_2$ plane there are no statistically significant differences between the two Ni–S bond distances of **1·SO$_2$**, nor between those in **1**, Table 2.

The solid-state (KBr pellet) infrared spectrum of **1·SO$_2$** finds bands at 1217 and 1076 cm^{-1}, which are assigned to ν(SO). In acetonitrile the bands are slightly shifted to 1225 and 1086 cm^{-1} (distinctly different from free SO$_2$ dissolved in acetonitrile, 1310 and 1150 cm^{-1}).[16] These values are at the lower end of the ν(SO) range for known ligand-bound SO$_2$ adducts, all of which contain reversibly bound SO$_2$.[6] Indeed, in CH$_3$CN solution over the course of 30 min a purge of N$_2$ or Ar serves to completely remove the SO$_2$. Nevertheless, as obtained crystalline from methanol, solid **1·SO$_2$** is stable even to vacuum as low as 0.5 mmHg. The vis/UV spectrum of red solutions of **1·SO$_2$** in CH$_3$CN shows a single and intense absorption at 362 nm (ϵ = 1570 M^{-1} cm^{-1}). In comparison, **1**, which forms purple CH$_3$CN solutions, has three absorptions at 350, 500, and 600 nm.[8] A sample for ^{1}H NMR was prepared from the crystalline **1·SO$_2$** dissolved in CD$_3$CN solvent and placed under an SO$_2$ atmosphere. The positions and pattern of the ^{1}H NMR spectrum are almost identical to those of **1**,[8] indicating little perturbation of the nearest protons by the loosely bound SO$_2$ group.

We have examined SO$_2$ adducts of other nickel thiolates prepared in our laboratory, selected for their variation in electronic and steric properties, Scheme 1. The sulfinato ligand is known to decrease the nucleophilicity of the thiolate sulfur in complex **2**.[15] The methyl substituents on the α-C in **3** are expected to sterically encumber the sulfur sites, at the same time enhancing S-nucleophilicity.[17] The sulfur sites of complex **4** are less nucleophilic due to the electronic effect of the phosphine ligands, i.e., the Ni(d$_\pi$)–SR(lone pair) 4-electron destabilizing or π* interaction which heightens the electron donating ability of sulfur in thiolate, is less in the presence of *trans* phosphines.[18] There is no indication of SO$_2$ binding to complex **2**; however, in acetonitrile solution, **3** and **4** rapidly and reversibly form adducts. Qualitatively, as determined from the persistence (or lack thereof) of the SO$_2$ adducts in open, agitated CH$_3$CN solutions, the stability varies as follows: **4·SO$_2$** < **3·SO$_2$** < **1·SO$_2$**. This stability order correlates inversely with the ν(SO) infrared values (KBr pellets, Scheme 1). Lower values of ν(SO) are evidence of increased donor ability of the thiolate sulfur resulting in an increase of the repulsion of the lone pair electrons on S of SO$_2$ with the π electron density in the S=O bond. Evidently, the steric hindrance in **3** overrides the electronic effect, producing a more weakly bound adduct.

Scheme 1



Solid state stabilities of **1·SO$_2$**, **3·SO$_2$**, and **4·SO$_2$** vary dramatically. Although precipitates of **3·SO$_2$** and **4·SO$_2$** form immediately on reacting methanolic solutions of **3** and **4** with SO$_2$, attempts to collect the solids from methanol resulted in loss of SO$_2$ whenever the filtration process produced dry solid. *Thus **3·SO$_2$** and **4·SO$_2$** are particularly effective as reversible SO$_2$ binding agents, releasing SO$_2$ as dry solids, whereas **1·SO$_2$** serves as a store for SO$_2$ in the solid state.* Long term exposure to air was found to degrade CH$_3$CN solutions of the **1·SO$_2$** and (to a lesser extent) the **3·SO$_2$** adduct. The reaction of O$_2$ with **1·SO$_2$** is explored below.

When placed under 1 atm O$_2$, a blood red/black precipitate falls out of CH$_3$CN solutions of **1·SO$_2$** within 1 h. This solid is soluble in MeOH and has intense vis/UV absorptions at λ_{max} (ϵ) 410, 480, and 560 nm, characteristic of the NiS$_4$ donor set in the well-known trimetallic, [(bme-daco)Ni]$_2$Ni^{2+}.[10] In addition, IR bands in the ν(SO) region suggested the presence of sulfate ion, which was confirmed by quantitative precipitation as its barium salt.[19] On the basis of the stoichiometry in eq 1, i.e., three (bme-daco)Ni units per sulfate, a 70% yield of the trimetallic sulfate was obtained.

A previous study of monomeric (bme-daco)Ni^{II} established that, in the presence of one-electron oxidants such as Ce^{IV} or iodine, there was quantitative conversion of **1** to the trimetallic [(bme-daco)Ni]$_2$Ni^{2+}, following ligand oxidation, release of Ni^{2+}, and rapid scavenging by the parent thiolate, **1**.[10] We were,

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(16) The acetonitrile solution IR spectrum was recorded (in a sealed CaF$_2$ cell) promptly (<1 min) on dissolving the solid **1·SO$_2$** adduct obtained from methanol.

(17) The compound (*N,N'*-bis(2-mercapto-2-methylpropyl)-1,5-diazacyclooctane)nickel(II) has been prepared in our laboratories and characterized as an analogue to **1** by X-ray crystallography. Darensbourg, M. Y.; Font, I.; Pala, M.; Reibenspies, J. H. *J. Coord. Chem.*, in press.

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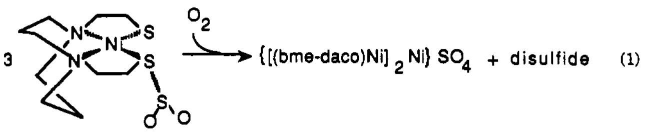
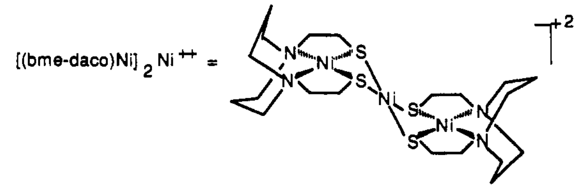
(19) A 100 mg sample of **1·SO$_2$** was placed in 20 mL of dry acetonitrile under 1 atm of O$_2$ and stirred for 2 days. The red-black solid, characterized by spectroscopy as {[(bme-daco)Ni]$_2$Ni}[SO$_4$],[10] was isolated by filtration, oven dried and weighed: 48 mg. Weighed samples of trimetallic sulfate were dissolved in water and an excess of Ba(NO$_3$)$_2$ added producing acid insoluble, white precipitates of BaSO$_4$ which were recovered, oven dried, and weighed.





$$SO_2 + O_2 \xrightarrow{2e^-} SO_4^{=} \qquad (2)$$

however, unable to unambiguously identify the oxidized ligand product as an inter- or intramolecular disulfide. The "sulfate" reaction, eq 2, has been well-established for SO_2 adducts of oxidizable metals, such as Ir^{I}, resulting in sulfate bound in a bidentate manner to Ir^{III}.[20] The overall reaction given by eq 1 is, to our knowledge, the first report of the oxidation of SO_2 in a ligand-bound adduct, and we suggest that it uses the ligand as the source of electrons.

There is no evidence to argue that the sulfate reaction in this case involves the intact (bme-daco)Ni·SO_2 adduct. Since nickel is well known to activate thiolates towards nucleophilic behavior,[8-11] as well as to promote oxygenation activity,[10,21] a role for nickel as catalyst (perhaps circumventing the spin-forbidden nature of this reaction) for the sulfate reaction is expected, but not yet established.[22] [Control experiments find that, when exposed to SO_2 and stirred under O_2 overnight, methanolic solutions of the sodium salt of the free bme-daco ligand, as well as simplier thiolates such as SEt^- and $SC(H)Me_2^-$, do not produce sulfate.][22]

This interesting reaction unfortunately consumes an equivalent of a quite expensive ligand. Attempts to develop (bme-daco)Ni^{II} as a catalyst for the sulfate reaction, eq 2, making use of more common thiolates as sacrificial electron source, are being made as mechanistic investigations continue.

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Supplementary Material Available: Tables of crystallographic data collection parameters, atomic coordinates and equivalent isotropic displacement parameters, complete bond lengths and bond angles, anisotropic displacement parameters, and H-atom coordinates and isotropic displacement parameters, and a packing diagram (7 pages). Ordering information is given on any current masthead page.

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(22) It is noteworthy that complex **4** which does not react with O_2 also does not convert SO_2/O_2 mixtures to SO_4^{2-}. In contrast, complex **3**, which reacts slowly with O_2, has been shown to undergo sulfate reaction with SO_2/O_2. From that reaction, an ether extraction has isolated an organic compound whose mass spectrum and ^1H NMR is entirely consistent with an intramolecular disulfide as implicated in eq 1.