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The *cis*-Bis(*cis*-2-mercaptostilbene-1-sulfinato)nickel(II) Dianion: A Product of the Irreversible Oxidation of the Bis(*cis*-stilbene-1,2-dithiolato)nickel(II) Dianion

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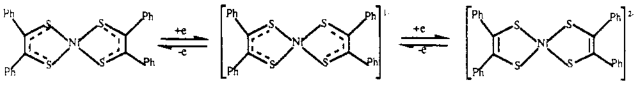
Received April 19, 1990

Whereas the reaction of molecular oxygen with the bis(*cis*-stilbene-1,2-dithiolato)nickel(II) dianion, $[Ni(S_2C_2Ph_2)_2]^{2-}$, in weakly alkaline or neutral solutions leads to the quantitative recovery of the neutral bis(*cis*-stilbene-1,2-dithiolato)nickel dithiolene, $Ni[(S_2C_2Ph_2)_2]$, an irreversible oxidation occurs in strongly alkaline solutions to yield the anion $[Ni(O_2S_2C_2Ph_2)_2]^{2-}$, which was isolated as the disodium salt. The complex represents the first example of a class of chelates of *cis*-2-mercaptostilbene-1-sulfinic acid. A solvate obtained from acetone/dimethyl sulfoxide of composition $Na_2[Ni(O_2S_2C_2Ph_2)_2](CH_3COCH_3)_2(DMSO)$ crystallizes in space group $P\bar{1}$ with unit cell dimensions at −100 °C of $a = 11.552$ (6) Å, $b = 12.494$ (5) Å, $\alpha = 112.56$ (3)°, $\beta = 91.42$ (4)°, $\gamma = 106.03$ (4)°, $Z = 2$, and $d_{calcd} = 1.447$ g cm^{-3}. The Ni(II) ion is coordinated to the sulfur atoms of two anions of *cis*-2-mercaptostilbene-1-sulfinic acid. The Ni(II) ion is in a nearly planar environment; the ligands are arranged in a cis configuration. The mean Ni–S bond distances are 2.158 (15) Å, the mean S–O bond lengths are 1.475 (8) Å, and the O–S–O angles are 109.1 and 112.5°, respectively. Two sodium ions are asymmetrically 5- and 6-coordinated, interacting with the two oxygen atoms of adjacent ligands and are solvated by DMSO and by terminal as well as bridging acetone molecules.

Introduction

The neutral bis(stilbene-1,2-dithiolato complex of nickel, $Ni[(S_2C_2Ph_2)_2]$ (**1**) ($Ph = C_6H_5$),[1] is a prototype of complexes with delocalized ground states[2] and is well-known to be reducible to mono- and dianionic species:



1 2 3

The electron-transfer reactions involving **1** and related compounds are generally regarded as fully reversible. While this is true in solvents such as dimethylformamide and has been well documented by polarographic studies,[3] using molecular oxygen as the electron acceptor, we have since observed the first example of an irreversible oxidation of **3**, giving rise to a new anionic nickel(II) complex whose structure was elucidated by chemical degradation studies and an X-ray crystallographic structure analysis of its disodium salt.

Results

Reversible and Irreversible Oxidations of $[Ni(S_2C_2Ph_2)_2]^{-,2-}$. Whereas **1** is quantitatively regenerated from solutions of the anion **2** on reaction with O_2, the corresponding reaction of **3** in strongly alkaline solutions produces a new complex, **4**, which on recrystallization from acetone/dimethyl sulfoxide was isolated in form of pink, diamagnetic crystals of composition $Na_2[Ni(O_2S_2C_2Ph_2)_2](CH_3COCH_3)_2(CH_3SOCH_3)$, mp 195 °C dec. On thermolysis, **4** decomposes into diphenylacetylene, SO_2, and Na_2NiS_2. The anion of **4** is stable in neutral and alkaline aqueous solutions. In acidic media, it decomposes rapidly with the formation of Ni(II), SO_2, H_2S, and diphenylacetylene, suggesting that it is an anionic chelate of *cis*-2-mercaptostilbene-1-sulfinic acid, PhC(SH)=C(SO$_2$H)Ph (**5**).

The formation of **4** from **3** requires alkaline conditions (0.2–0.3 M NaOH) and depends on the nature of oxidant; in mildly alkaline solutions, or with H_2O_2 instead of O_2, **3** is oxidized to **1** instead.

Structural Analysis. Single crystals of an acetone–dimethyl sulfoxide solvate of **4** of composition $Na_2[Ni(O_2S_2C_2Ph_2)_2](CH_3COCH_3)_2(CH_3SOCH_3)$ were obtained from acetone/dimethyl sulfoxide mixtures and were suitable for X-ray crystallographic analysis. Crystallographic and data collection parameters are given in Table I, positional parameters and their estimated standard deviations in Table II, selected bond distances and angles in Table III, and perspective views of the structure in Figures 1 and 2.

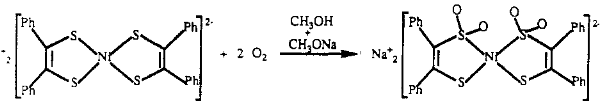
Table I. Crystallographic Data Collection Parameters of the Dianionic Complex **4**

formula	$C_{36}H_{38}Na_2$-NiO_7S_5	V, Å^3	1945.6 (14)
		Z	2
space group	$P\bar{1}$	fw	847.7
a, Å	11.552 (6)	ρ, g/cm^3 (calcd, measd)	1.447, 1.46
b, Å	12.494 (5)		
c, Å	15.494 (5)	μ, cm^{-1}	8.24
α, deg	112.56 (3)	λ, Å (Mo Kα)	0.71073
β, deg	91.42 (4)	T, K	173
γ, deg	106.02 (4)	$R(F_o)$, $R_w(F_o)$	0.059, 0.074

Discussion

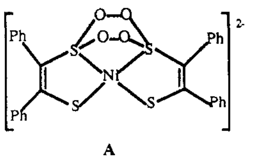
Oxidation reactions of anionic nickel dithiolenes have previously been conducted only under conditions leading to the recovery of the neutral dithiolenes. The present study demonstrates that irreversible oxidations of anionic metal dithiolenes are possible under appropriate reaction conditions.

The formation of **4** from **3** according to eq 1 is related to the oxidation of thiols to sulfinic acids, which is also known to require alkaline conditions.[4] The formation of sulfinato ligands has also been observed in complexes with other sulfur-containing ligands.[5] In most such cases, however, H_2O_2 was employed as the oxidant, which we have found converts **3** to **1** rather than to **4**.

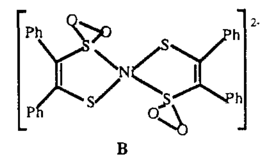


(1)

The oxidation of **3** may be assumed to proceed via a monooxygenated intermediate that reacts rapidly with a second molecule of O_2 to form a dioxygenated species for which structures A or B are possible.



A



B

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(1) Schrauzer, G. N.; Mayweg, V. *J. Am. Chem. Soc.* **1962**, *84*, 3321.

(2) (a) Schrauzer, G. N. *Transition Met. Chem.* **1968**, *4*, 299. (b) McCleverty, J. A. *Prog. Inorg. Chem.* **1968**, *10*, 49. (c) Hoyer, E.; Dietzsch, W.; Schroth, W. *Z. Chem.* **1971**, *11*, 41. (d) Burns, R. P.; McAuliffe, C. A. *Adv. Inorg. Chem. Radiochem.* **1979**, *22*, 303. (e) Mahadevan, J. *J. Cryst. Spectrosc. Res.* **1986**, *16*, 347. (f) Mueller-Westerhoff, U. T.; Vance, B. In *Comprehensive Coordination Chemistry*; Wilkinson, G., et al., Eds.; Pergamon: Oxford, England, 1987; Vol. 2, p 595. (g) Alvarez, S.; Vicente, R.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107*, 6253.

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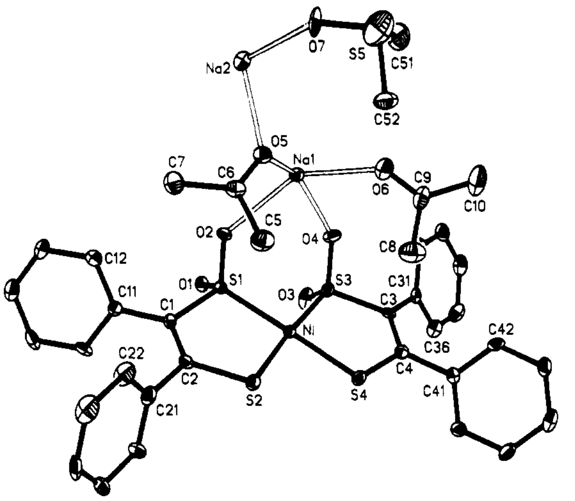


Figure 1. Numbering of atoms and perspective view of the structure of 4 (atoms drawn with 30% probability ellipsoids; hydrogen atoms not shown).

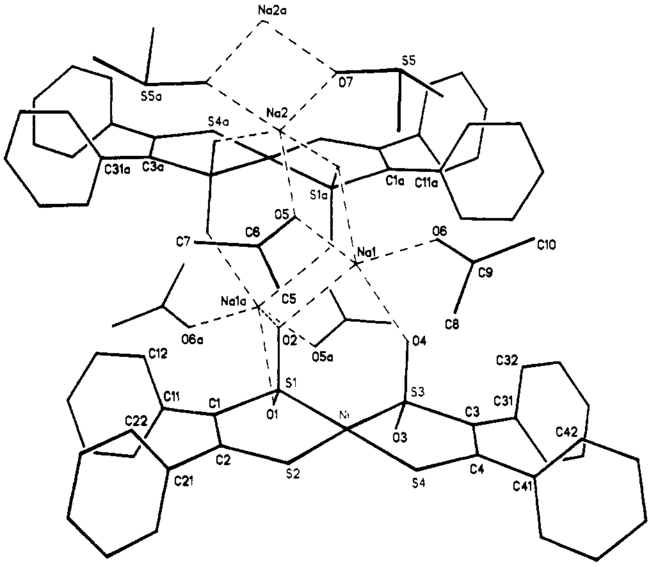
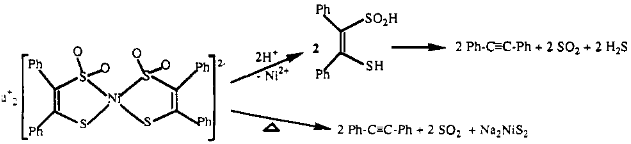


Figure 2. Schematic drawing of the structure of 4, emphasizing the coordination of the sodium ions.

Intermediate A, whose formation could be favored through a template effect, would account for the observed cis configuration of 4. The formation of 4 via intermediate B could also be possible by assuming a conversion of the initially formed trans isomer into the cis isomer, however.

Complex 4 is the first example of a complex of *cis*-2-mercaptostilbene-1-sulfinic acid. The acid itself could not be isolated and is unstable in the free state, as evidenced by the behavior of 4 on acid hydrolysis; the observed fragmentation of 4 on thermolysis is consistent with the presence of coordinated dianions of *cis*-2-mercaptostilbene-1-sulfinic acid (eq 2).



(2)

The structure of 4 reveals an idealized planar $Ni(S_2C_2)_2$ moiety and two pairs of symmetrically arranged oxygen atoms above and below the NiS_4 plane. Although one Ni–S bond appears to be significantly shorter than the other three, and the O(3)–S–O(4) angle is larger than O(1)–S–O(2), these distortions probably arise from packing effects and the presence of the chelated and solvated sodium ions. The two sodium ions are asymmetrically five- and six-coordinated, interacting with two oxygen atoms of adjacent ligands and solvated by dimethyl sulfoxide and by terminal as well as bridging acetone molecules. The bridging acetone ligands are nearly symmetrically bonded to the two sodium atoms; the Na(1)–O(5)–Na(2) bond angle is 99.3 (2)°, and the Na(1)–O(5) and Na(2)–O(5) bond lengths are 2.492 (7) and 2.346 (6) Å, respectively. The Na–O bond length to the terminal acetone molecule, Na(1)–O(6), of 2.371 (10) Å is slightly longer than that to the oxygen atom of the dimethyl sulfoxide molecule, Na(2)–O(7), of 2.270 (9) Å. The phenyl groups are tilted in positions that indicate the absence of significant electronic interactions with the NiS_4C_4 moiety; there is also no evidence for Ni···Ni interactions.

Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$)

	x	*y*	*z*	*U*(eq)
Ni	2409 (1)	3452 (1)	511 (1)	19 (1)
S(1)	1805 (2)	2216 (2)	1198 (2)	19 (1)
S(2)	2462 (2)	4995 (2)	1823 (2)	27 (1)
S(3)	2427 (2)	2030 (2)	−815 (2)	21 (1)
S(4)	2946 (2)	4774 (2)	−108 (2)	27 (1)
S(5)	−4950 (4)	250 (3)	−1863 (3)	87 (2)
Na(1)	−651 (3)	575 (3)	−724 (2)	25 (1)
Na(2)	−3699 (3)	−460 (3)	−99 (2)	28 (2)
O(1)	2524 (5)	1385 (5)	1157 (4)	24 (3)
O(2)	501 (5)	1494 (5)	875 (4)	23 (3)
O(3)	3373 (6)	1470 (6)	−756 (4)	39 (3)
O(4)	1219 (5)	1121 (5)	−1228 (4)	33 (3)
O(5)	−2124 (5)	1373 (5)	295 (4)	31 (3)
O(6)	−1287 (6)	1265 (6)	−1837 (5)	49 (4)
O(7)	−4967 (6)	−92 (6)	−1026 (5)	40 (3)
C(1)	1943 (7)	3148 (7)	2440 (6)	19 (4)
C(2)	2203 (8)	4358 (8)	2662 (6)	24 (4)
C(3)	2853 (7)	2692 (7)	−1644 (6)	21 (4)
C(4)	3082 (8)	3923 (7)	−1291 (6)	24 (4)
C(5)	−1169 (10)	3486 (8)	1200 (8)	47 (5)
C(6)	−1763 (8)	2208 (8)	1080 (7)	30 (4)
C(7)	−1896 (10)	2004 (9)	1970 (7)	45 (5)
C(8)	−249 (10)	3369 (10)	−1374 (9)	60 (6)
C(9)	−965 (9)	2121 (10)	−2075 (8)	42 (5)
C(10)	−1339 (13)	2003 (11)	−3042 (8)	76 (7)
C(11)	1925 (5)	2591 (5)	3141 (3)	23 (4)
C(12)	919	1654	3125	33 (4)
C(13)	918	1189	3819	44 (5)
C(14)	1921	1662	4529	42 (5)
C(15)	2926	2599	4545	37 (5)
C(16)	2928	3064	3851	29 (4)
C(21)	2278 (6)	5275 (5)	3641 (3)	33 (4)
C(22)	1227	5362	4053	49 (5)
C(23)	1308	6260	4960	63 (6)
C(24)	2440	7072	5456	62 (6)
C(25)	3492	6985	5044	52 (5)
C(26)	3411	6087	4136	41 (5)
C(31)	3110 (5)	1892 (5)	−2585 (3)	23 (4)
C(32)	2254	768	−3136	33 (4)
C(33)	2506	5	−3997	38 (5)
C(34)	3615	365	−4306	42 (5)
C(35)	4472	1489	−3756	37 (5)
C(36)	4219	2252	−2895	31 (4)
C(41)	3384 (5)	4636 (4)	−1884 (3)	21 (4)
C(42)	2676	4246	−2762	29 (4)
C(43)	2957	4920	−3315	33 (4)
C(44)	3947	5984	−2990	40 (5)
C(45)	4655	6374	−2112	40 (5)
C(46)	4373	5700	−1559	28 (4)
C(51)	−4189 (12)	−472 (11)	−2633 (8)	76 (7)
C(52)	−3967 (9)	1787 (8)	−1317 (8)	45 (5)

Complex 4 represents the first member of a potentially large group of "oxodithiolenes", whose synthesis is now being attempted by various methods.

Experimental Section

Materials. All common laboratory chemicals were of reagent grade. The Grignard reagents and lithium borohydride were purchased from Aldrich Chemical Co. Complex **1** was synthesized by the method described in ref 6; the mono- and dianions **2** and **3** were generated in

Table III. Bond Distances and Bond Angles

(a) Anion of **4**

Bond Distances (Å)

Ni–S(1)	2.162 (3)	Ni–S(2)	2.174 (2)	S(5)–C(51)	1.630 (14)	S(5)–C(52)	1.787 (9)
Ni–S(3)	2.133 (2)	Ni–S(4)	2.164 (3)	O(6)–C(9)	1.226 (16)	O(5)–C(6)	1.218 (9)
S(1)–O(1)	1.483 (7)	S(1)–O(2)	1.483 (5)	C(1)–C(2)	1.357 (13)	C(1)–C(11)	1.486 (12)
S(1)–C(1)	1.789 (8)	S(1)–Na(1A)	3.147 (4)	C(2)–C(21)	1.482 (9)	C(3)–C(4)	1.363 (12)
S(2)–C(2)	1.747 (11)	S(3)–O(3)	1.468 (8)	C(3)–C(31)	1.501 (9)	C(4)–C(41)	1.487 (12)
S(3)–O(4)	1.473 (5)	S(3)–C(3)	1.778 (11)	C(5)–C(6)	1.490 (14)	C(6)–C(7)	1.486 (16)
S(4)–C(4)	1.755 (8)	S(5)–O(7)	1.501 (10)	C(8)–C(9)	1.493 (12)	C(9)–C(10)	1.476 (18)

Bond Angles (deg)

S(1)–Ni–S(2)	90.6 (1)	S(1)–Ni–S(3)	93.4 (1)	S(2)–C(2)–C(1)	123.7 (6)	S(2)–C(2)–C(21)	113.0 (6)
S(2)–Ni–S(3)	175.9 (1)	S(1)–Ni–S(4)	175.8 (1)	C(1)–C(2)–C(21)	123.3 (8)	S(3)–C(3)–C(4)	115.0 (7)
S(2)–Ni–S(4)	85.8 (1)	S(3)–Ni–S(4)	90.2 (1)	S(3)–C(3)–C(31)	117.3 (6)	C(4)–C(3)–C(31)	126.9 (8)
Ni–S(1)–O(1)	117.3 (3)	Ni–S(1)–O(2)	112.2 (3)	S(4)–C(4)–C(3)	121.9 (8)	S(4)–C(4)–C(41)	114.8 (6)
O(1)–S(1)–O(2)	109.1 (3)	Ni–S(1)–C(1)	106.3 (3)	C(3)–C(4)–C(41)	123.2 (7)	O(5)–C(6)–C(5)	121.9 (10)
O(1)–S(1)–C(1)	104.6 (4)	O(2)–S(1)–C(1)	106.6 (4)	O(5)–C(6)–C(7)	121.7 (9)	C(5)–C(6)–C(7)	116.4 (7)
Ni–S(2)–C(2)	103.6 (3)	Ni–S(3)–O(3)	112.4 (3)	O(6)–C(9)–C(8)	121.3 (11)	O(6)–C(9)–C(10)	122.2 (8)
Ni–S(3)–O(4)	112.7 (3)	O(3)–S(3)–O(4)	112.5 (4)	C(8)–C(9)–C(10)	116.3 (11)	C(1)–C(11)–C(12)	121.7 (3)
Ni–S(3)–C(3)	108.0 (3)	O(3)–S(3)–C(3)	104.4 (4)	C(1)–C(11)–C(16)	118.2 (3)	C(2)–C(21)–C(22)	120.6 (4)
O(4)–S(3)–C(3)	106.3 (4)	Ni–S(4)–C(4)	104.9 (3)	C(2)–C(21)–C(26)	119.3 (4)	C(3)–C(31)–C(32)	119.8 (3)
O(7)–S(5)–C(51)	109.8 (7)	O(7)–S(5)–C(52)	100.0 (5)	C(3)–C(31)–C(36)	120.2 (3)	C(4)–C(41)–C(42)	120.1 (3)
C(51)–S(5)–C(52)	104.6 (6)	S(1)–C(1)–C(2)	114.8 (7)	C(4)–C(41)–C(46)	119.9 (3)		
S(1)–C(1)–C(11)	119.3 (6)	C(2)–C(1)–C(11)	125.4 (7)				

(b) Solvated Sodium Ions

Bond Distances (Å)

S(5)–Na(2A)	3.381 (6)	Na(1)–O(2)	2.440 (6)	Na(2)–O(7)	2.270 (9)	Na(2)–S(5A)	3.381 (6)
Na(1)–O(4)	2.325 (7)	Na(1)–O(5)	2.492 (7)	Na(2)–O(1A)	2.314 (7)	Na(2)–O(3A)	2.229 (10)
Na(1)–O(6)	2.371 (10)	Na(1)–S(1A)	3.147 (4)	Na(2)–O(7A)	2.374 (8)	O(1)–Na(1A)	2.622 (6)
Na(1)–Na(1A)	3.570 (8)	Na(1)–O(1A)	2.622 (6)	O(1)–Na(2B)	2.314 (7)	O(2)–Na(1A)	2.560 (8)
Na(1)–O(2A)	2.560 (8)	Na(2)–O(5)	2.346 (6)	O(3)–Na(2B)	2.229 (10)	O(7)–Na(2A)	2.374 (8)

Bond Angles (deg)

Ni–S(1)–Na(1A)	141.3 (1)	O(1)–S(1)–Na(1A)	55.9 (2)	O(7)–Na(2)–S(5A)	104.4 (2)	O(5)–Na(2)–S(5A)	107.5 (2)
O(2)–S(1)–Na(1A)	53.5 (3)	C(1)–S(1)–Na(1A)	112.3 (3)	O(5)–Na(2)–O(1A)	86.7 (2)	Na(1)–Na(2)–O(1A)	45.0 (1)
C(51)–S(5)–Na(2A)	146.1 (6)	O(7)–S(5)–Na(2A)	37.6 (3)	S(5A)–Na(2)–O(1A)	147.2 (3)	O(7)–Na(2)–O(1A)	103.3 (3)
O(2)–Na(1)–O(4)	85.8 (2)	C(52)–S(5)–Na(2A)	93.4 (4)	O(7)–Na(2)–O(3A)	150.8 (3)	O(5)–Na(2)–O(3A)	111.8 (3)
O(4)–Na(1)–O(5)	144.4 (2)	O(2)–Na(1)–O(5)	77.5 (2)	O(1A)–Na(2)–O(3A)	87.8 (3)	S(5A)–Na(2)–O(3A)	59.6 (2)
O(4)–Na(1)–O(6)	82.4 (3)	O(2)–Na(1)–O(6)	136.9 (2)	O(7)–Na(2)–O(7A)	82.8 (3)	O(5)–Na(2)–O(7A)	103.3 (2)
O(2)–Na(1)–S(1A)	106.3 (2)	O(5)–Na(1)–O(6)	88.7 (3)	O(1A)–Na(2)–O(7A)	167.8 (3)	S(5A)–Na(2)–O(7A)	22.7 (2)
O(5)–Na(1)–S(1A)	99.0 (2)	O(4)–Na(1)–S(1A)	115.9 (2)	S(1)–O(1)–Na(1A)	96.1 (3)	O(3A)–Na(2)–O(7A)	82.0 (3)
Na(2)–Na(1)–O(1A)	38.6 (1)	O(6)–Na(1)–S(1A)	116.2 (2)	Na(1A)–O(1)–Na(2B)	96.5 (2)	S(1)–O(1)–Na(2B)	135.4 (4)
O(4)–Na(1)–O(1A)	137.9 (2)	O(2)–Na(1)–O(1A)	117.8 (3)	S(1)–O(2)–Na(1A)	98.7 (3)	S(1)–O(2)–Na(1)	128.9 (4)
O(6)–Na(1)–O(1A)	97.9 (2)	O(5)–Na(1)–O(1A)	77.4 (2)	S(3)–O(3)–Na(2B)	132.8 (4)	Na(1)–O(2)–Na(1A)	91.1 (2)
O(2)–Na(1)–O(2A)	88.9 (2)	S(1A)–Na(1)–O(1A)	27.9 (2)	Na(1)–O(5)–Na(2)	99.3 (2)	S(3)–O(4)–Na(1)	137.5 (4)
O(5)–Na(1)–O(2A)	116.8 (3)	O(4)–Na(1)–O(2A)	93.8 (2)	Na(2)–O(5)–C(6)	127.2 (7)	Na(1)–O(5)–C(6)	120.4 (6)
S(1A)–Na(1)–O(2A)	27.8 (1)	O(6)–Na(1)–O(2A)	133.0 (2)	S(5)–O(7)–Na(2)	139.2 (5)	Na(1)–O(6)–C(9)	140.2 (6)
O(5)–Na(2)–O(7)	95.9 (3)	O(1A)–Na(1)–O(2A)	55.6 (2)	Na(2)–O(7)–Na(2A)	97.2 (3)	S(5)–O(7)–Na(2A)	119.8 (5)

solution by the reduction of **1** with stoichiometric amounts of sodium borohydride in methanol. Pure compressed oxygen was obtained from a local supplier and was used as received. Infrared spectra were recorded on an Perkin-Elmer 1330 infrared spectrometer; ^{1}H NMR spectra were recorded on a GE QE-300 instrument at 300 MHz; UV–vis absorption spectra were recorded on a Beckman DU-50 Instrument.

Alkaline Oxidation of 3 to 4. Complex **1**, 1.0 g (1.84 mmol) was suspended in 30 mL of methanol in a Schlenk tube of 250-mL capacity. Under nitrogen gas flow, 0.25 g (6.25 mmol) of NaOH and, subsequently, 0.080 g (2.10 mmol) of $NaBH_4$ were added. The black suspension was heated to 60 °C and maintained at this temperature for 90 min, resulting in a red-brown homogeneous solution. After the mixture was cooled to room temperature, 5 mL of acetone was added to destroy excess $NaBH_4$. After 10 min, the N_2 flow was replaced by a flow of oxygen gas, which was maintained for 8 h, during which the reaction solution was stirred vigorously. A yellow precipitate formed, which was isolated by filtration and washed with water, methylene chloride, and finally hexane, affording 0.87 g of product. Recrystallization from acetone/dimethyl sulfoxide afforded 1.09 g (1.28 mmol) of pink crystals, yield 70% based on **3**, mp 195 °C dec. Anal. Calcd for $Na[Ni(O_2S_2C_2Ph_2)_2](CH_3COCH_3)_2(CH_3SOCH_3) = C_{36}H_{38}Na_2NiO_7S_5$: C, 51.01; H, 4.52; S, 18.91. Found: C, 50.90; H, 4.40; S, 18.70. Mass spectra [*m/z* (relative intensity, assignment)]: 178 (100, PhCCPh), 64 (SO_2). ^{1}H NMR spectrum in CD_3COCD_3 [ppm (assignment)]: 7.10–7.30 (br) (Ph H). IR $\nu_{S=O}$ (cm^{-1}) in Nujol: 1038, 1100. UV-vis absorption spectrum in dimethyl sulfoxide [λ, nm (ε)]: 339 (32 000), 298 (28 000), d–d transitions obscured.

Oxidation of 3 with O_2 under Neutral and Acidic Conditions. Complex **1**, 1.0 g (1.84 mmol) was reduced to the dianion **3** as described above. To the solution of **3** was added 1 mL of glacial acetic acid, which effected its neutralization. The solution was vigorously stirred while a flow of oxygen gas was maintained for 2 h. During this period a dark green precipitate of **1** formed, which was identified by IR and UV–vis spectroscopy.

Oxidation of 3 with H_2O_2. To neutral and alkaline solutions of **3**, prepared as described above from **1**, were added stoichiometric amounts of 10% aqueous H_2O_2. In all cases, **1** formed rapidly and quantitatively and was identified by its IR spectrum.

Reaction of 2 with O_2 in Alkaline Solution. Complex **1**, 1 g (1.48 mmol) was suspended in 50 mL of ethyl alcohol containing 0.060 g (1.5 mmol) of NaOH and reduced with 0.080 (1.5 mmol) of $NaBH_4$ at 60 °C. Through the red solution of **2** was passed a stream of oxygen for 3 h, resulting in no apparent change. Upon acidification with 20 mL of 1 M HCl, a dark green solid formed, which was identified as **1** by its infrared and UV–vis absorption spectra.

Thermolysis of 4. Complex **4**, 0.2 g (0.24 mmol), was briefly heated to 250 °C in an argon-filled test tube. The gas phase contained SO_2; the solid organic volatile product of melting point 60–61 °C was identified as diphenylacetylene, lit.[7] mp 61.5–62.5 °C, by its ^{13}C NMR spectrum. The black, nonvolatile residue contained sodium, nickel, and sulfur. Anal. Calcd for Na_2NiS_2: S, 37.95. Found: S, 38.25.

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Acid Degradation of 4. Complex **4**, 0.5 g (0.59 mmol) was dissolved in 50 mL of ethanol at 40 °C. To this solution was added 50 mL of 1 N aqueous HCl. A stream of N_2 was blown through the solution to remove the evolving H_2S and SO_2. Analysis of the gas phase by GC–MS revealed m/z 64 (SO_2) and 34 (H_2S). The aqueous phase was diluted and extracted with hexane to yield a colorless solid, mp 60–62 °C, identified by ^{13}C NMR spectroscopy as diphenylacetylene.

X-ray Crystallographic Structure Analysis. A crystal of **4** was obtained from acetone/dimethyl sulfoxide and was sealed in a capillary and mounted on a Nicholet R3m/V diffractometer for X-ray data collection. Since crystal decomposition occurred, probably due to loss of solvent trapped in the lattice, the data were collected at −100 °C. The intensities of monitored reflections decreased by approximately 1% during 39 h of X-ray exposure. No absorption correction was applied because of the low value of μ. The cell parameters were obtained from 20 reflections in the 2θ range 15–25°; the space group was identified as $P\bar{1}$. The positions of the nickel and sulfur atoms were obtained from automatic direct methods routine of the program SHELXTL plus. The positions of the remaining non-hydrogen atoms were determined from a difference Fourier map. All atoms were refined anisotropically. Hydrogen atoms were included in ideal positions with U fixed at 0.08 Å. Refinements gave final values of R and R_w that are given in Table I. The final difference map had no feature of any chemical significance, though it had a few residual peaks with intensity 0.63 e Å^{-3}. No evidence for secondary extinctions was found. Positional and thermal parameters are given as supplementary material. Perspective drawings of **4** are given in Figures 1 and 2. Table II lists the atomic coordinates and equivalent isotropic displacement coefficients. A summary of interatomic distances and bond angles is given in Table III.

Acknowledgment. This work was supported by the National Science Foundation.

Supplementary Material Available: A unit cell packing diagram and tables of equivalent positions, scattering factors, positional parameters, anisotropic displacement coefficients, bond distances and bond angles, H-atom coordinates, and isotropic displacement coefficients (9 pages); a listing of observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

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Transition-Metal Complexes with Sulfur Ligands. 52.[1] Synthesis, X-ray Structure Characterization, and Reactions of [Fe(CO)(μ-“S$_4$”)]$_2$, a Novel Type of Chiral Complex with Relevance to Iron Oxidoreductases (“S$_4$”$^{2-}$ = 1,2-Bis((2-mercaptophenyl)thio)ethanato(2−))

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Received December 21, 1989

Searching for model complexes of hydrogenases and nitrogenases with chirotopic iron centers, we found that the thermal decarbonylation of [Fe(CO)$_2$(“S$_4$”)] (**1**) leads to [Fe(CO)(μ-“S$_4$”)]$_2$ (**2**) (“S$_4$”$^{2-}$ = 1,2-bis((2-mercaptophenyl)thio)ethanato(2−)). **2** results from the connection of two homochiral [Fe(CO)(“S$_4$”)] fragments and represents a new type of chiral complex. An analysis of theoretically possible isomers of **2** is given. One pair of enantiomers of **2** as well as **1** were characterized by X-ray structure determinations. **1**: monoclinic, $P2_1/c$, a = 1293.3 (6) pm, b = 1258.2 (6) pm, c = 1151.9 (4) pm, β = 111.88 (4)°, Z = 4, d_{calcd} = 1.60 g/cm^3, R (R_w) = 0.068 (0.054). **2**: monoclinic, $P2_1/c$, a = 1272.8 (5) pm, b = 1534.1 (23) pm, c = 1633.6 (16) pm, β = 104.76 (8)°, Z = 4, d_{calcd} = 1.69 g/cm^3, R (R_w) = 0.078 (0.065). The iron center of **1** is pseudooctahedrally coordinated by four sulfur and two carbon atoms. In **2**, the iron centers are coordinated pseudooctahedrally by five sulfur and one carbon atom and bridged via two thiolato-S atoms. The trans coordination of the thiolato-S atoms in **1** is retained in **2**. The chirotopic iron centers of **2** possess latent coordination sites and low-valent Fe centers capable of binding σ–π donors. In order to substitute or to transform the CO ligands, **2** was reacted with NO$^+$, NO, PMe$_3$, and MeLi. With NOPF$_6$, a CO/NO$^+$ substitution took place, yielding [Fe$_2$(CO)(NO)(μ-“S$_4$”)$_2$]PF$_6$ (**3**), which is isoelectronic to **2**. Treatment of **2** with NO gas or PMe$_3$ led to cleavage of Fe–thiolato-S bridges and formation of mononuclear [Fe(NO)$_2$(“S$_4$”)] (**4**) and [Fe(CO)(PMe$_3$)(“S$_4$”)] (**5**), respectively. The reaction between **2** and MeLi caused the elimination of the C_2H_4 bridge from the tetradentate “S$_4$”$^{2-}$ ligand under formation of [Fe(“S$_2$”)$_2$]$_2$$^{2-}$ (**6**) (“S$_2$”$^{2-}$ = 1,2-benzenedithiolate), which could be isolated as a AsPh$_4$$^+$ salt. The mutual influence of the Fe centers in **2** and **3** was investigated by Mössbauer spectroscopy.

Introduction

Iron atoms in a coordination sphere of sulfur form the active sites of numerous oxidoreductases, e.g., nitrogenases and hydrogenases. The structures of the polynuclear centers of these enzymes as well as the molecular mechanisms of the catalyzed reactions, however, are largely unknown.[2] Model compounds for such centers are all of the structural type; i.e., they are built up from iron, sulfide, and thiolate ligands, usually possess high symmetry, and do not react with relevant substrates, e.g., CO, N_2, or H_2.[3] The metal centers in oxidoreductases, however, must be expected to be chirotopic[4] due to the protein environment, even when they catalyze only reactions of achiral substrates and form highly symmetrical building blocks like the iron centers of [Fe$_4$S$_4$(SR)$_4$] clusters[2a] in ferredoxines. Further, such metal centers must have vacant or latently vacant sites for the coordination of substrates. In this context, we probed the formation of polynuclear complexes starting with [Fe(CO)$_2$(“S$_4$”)] (**1**) as chiral synthon. Our investigations yielded [Fe(CO)(μ-“S$_4$”)]$_2$ (**2**) (“S$_4$”$^{2-}$ = 1,2-bis((2-mercaptophenyl)thio)ethanato(2−)), which represents a new type of chiral complex. **2** consists of two homochiral fragments with chirotopic iron centers that have low-valent character and bind σ–π ligands.[5] Synthesis, structural

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