

Transition-metal complexes with sulfur ligands

Part LXXXIV*. CH₃ complexes with [NiS] fragments as models for CO dehydrogenase. Synthesis and properties of [Ni('MeS₂')₂] and (NMe₄)[Ni(CH₃)('MeS₂')₂] ('MeS₂'⁻ = *o*-(methylthio)-thiophenolate(1-))

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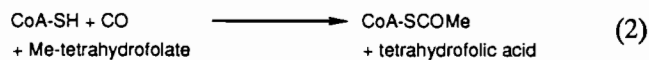
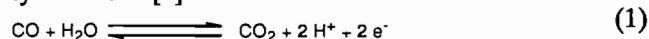
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Abstract

Reaction of [Ni('MeS₂')₂] (**1**) ('MeS₂'⁻ = *o*-(methylthio)thiophenolate(1-)) with methyl lithium yields the methyl complex anion [Ni(CH₃)('MeS₂')₂]⁻ which can be isolated as (NMe₄)[Ni(CH₃)('MeS₂')₂] (**2**). The molecular structures of **1** (monoclinic, *P*2₁/*c*, *Z* = 2, *a* = 791.5(5), *b* = 1083.1(8), *c* = 894.1(6) pm, β = 92.79(5)°, *R*/*R*_w = 0.063/0.049) and **2**·MeOH (monoclinic, *P*2₁/*c*, *Z* = 4, *a* = 1901.0(12), *b* = 830.3(9), *c* = 1716.1(14) pm, β = 113.84(5)°, *R*/*R*_w = 0.072/0.053) were elucidated by X-ray structure analysis. **1** contains a planar [NiS₄] core, **2**·MeOH exhibits a planar [NiS₃C] core, one thioether donor being decoordinates. **1** does not react with CO but **2** undergoes immediate reaction with CO. Monitoring the reaction by IR spectroscopy yields evidence for the intermediate formation of labile Ni-acetyl complexes. Reaction of **2** with protonic acids (HBF₄/Et₂O, HCl/THF) yields CH₄ and **1**. Thermolysis of **2** in solid state as well as in acetone solution at room temperature, however, gives C₂H₆, and **1** was identified as one of the resulting nickel species.

Introduction

Nickel complexes with alkyl ligands are important intermediates in various nickel-catalyzed organic reactions and are usually unstable at room temperature [2]. In a couple of complexes nickel-alkyl bonds are stabilized by σ-π coligands such as phosphines, CO or alkenes [3–5]; nickel-alkyl complexes with sulfur coligands are practically unknown [6]. Such species, however, are of interest as potential industrial catalysts and they are furthermore assumed as intermediates in carbon monoxide dehydrogenases (CODH) [7] which, for example, can be isolated from *Clostridium thermoaceticum* [8]. These CODHs catalyze the CO/CO₂ equilibrium according to eqn. (1) as well as the reaction of eqn. (2), such that CODHs also function as acetyl CoA synthetases [9].



*Dedicated to Professor Dr Wolfgang Beck on the occasion of his 60th birthday. For Part LXXXIII see ref. 1.

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EXAFS investigations of the CO-free, EPR-inactive form of CODH indicate planar coordination of the nickel centers being surrounded by either four sulfur donors (Ni-S = 216(3) pm) [10] or by two sulfur and two nitrogen donors (Ni-S = 221, Ni-N = 197 pm) [11]. It is furthermore assumed that acetyl CoA forms at these nickel centers and CO, CH₃ and COCH₃ groups are intermediary Ni ligands.

Model complexes that are wanted in order to gain a deeper insight into the function of CODH should accordingly contain, for example, planar [NiS₄] units and additional CO, CH₃, or COCH₃ ligands. A first approach to complexes of this kind are the amine-thioether complexes [Ni(L)(N(CH₂CH₂SR)₃)]⁺ (R = ⁱPr, ^tBu and L = Cl, H, CH₃, CO, C₂H₅ and COCH₃) with trigonal-bipyramidal nickel centers that were recently described by Holm and co-workers [12]. We report here on a planar Ni(II)-methyl complex with thioether and thiolate coligands.

Experimental

General

Unless stated otherwise, all operations were carried out at room temperature under N₂, dry solvents and

Schlenk techniques being used. Spectra were recorded on the following instruments: Zeiss IR spectrometer IMR 16 (solution spectra in CaF₂ cuvettes, solvent absorptions being compensated, solids as KBr pellets), Jeol NMR spectrometers FT-JNM-GX 270 and EX 270; Varian mass spectrometer MAT 212. A Phillips Pye Unicam PU 4500 capillary gas-chromatograph was used for gas chromatography.

o-Benzenedithiol (H₂'S₂') [13] was prepared as described in the literature; methyl iodide (MeI) and methyl lithium (LiMe) were purchased from Aldrich.

X-ray structure determination of [Ni('MeS₂')₂] (1) and (NMe₄)[Ni(CH₃)('MeS₂')₂]·MeOH (2·MeOH)

Single crystals of [Ni('MeS₂')₂] (1) formed when a saturated CS₂ solution of 1 slowly evaporated at room temperature.

Single crystals of (NMe₄)[Ni(CH₃)('MeS₂')₂]·MeOH (2·MeOH) precipitated within 14 days when a saturated THF/MeOH (3:1) solution of 2 was layered with Et₂O at -40 °C and cooled to -78 °C. Suitable crystals were sealed in glass capillaries.

Non-hydrogen atoms were refined anisotropically, aromatic hydrogen atoms were placed at calculated positions and refined as rigid groups, hydrogen atoms of the methyl groups were placed at ideal tetrahedral positions and rotated around their central carbon atom during refinement. All hydrogen atoms were refined with a common isotropic temperature factor. The OH hydrogen atom H(1) in 2·MeOH was located by difference Fourier synthesis and fixed during refinement.

Table 1 contains selected crystallographic data; Tables 2 and 3 list the atomic coordinates for 1 and 2·MeOH.

Syntheses and reactions

[Ni('MeS₂')₂] (1)

A saturated solution of Ni(CH₃COO)₂·4 H₂O (1245 mg, 5 mmol) in MeOH was combined with a solution of H₂'S₂' (1420 mg, 10 mmol) and NaOMe (1080 mg, 20 mmol) in 50 ml of MeOH. When MeI (0.62 ml, 10 mmol) in 25 ml of MeOH was added dropwise to the brown solution orange-brown crystals of 1 precipitated (1.5 g, 83%). *Anal.* Calc. for C₁₄H₁₄NiS₄ (369.23): C, 45.83; H, 3.89. Found C, 45.55; H, 3.82%. MS(FD): *m/z* 368 (*M*⁺). ¹H NMR δ (acetone), ppm: 6.9–7.6 (m, 4 H, C₆H₄); 2.83 (s, 3 H, SCH₃). ¹³C{¹H} NMR δ (acetone), ppm: 151.6, 134.7, 130.6, 130.1, 129.2, 123.8, (C₆H₄); 26.6 (SCH₃).

(NMe₄)[Ni(CH₃)('MeS₂')₂] (2)

LiMe in Et₂O (2.1 mmol, 1.3 ml of a 1.6 M solution) was added to [Ni('MeS₂')₂] (770 mg, 2.1 mmol) in 60 ml of THF at -50 °C whereupon the color of the reaction mixture changed from orange to red. Addition

of NMe₄Cl (230 mg, 2.1 mmol) in 20 ml of MeOH at -60 °C and layering the solution with 60 ml of Et₂O yielded red crystals within two weeks at -78 °C. The crystals were separated and recrystallized by the same procedure. The isolated crystals were washed with a small quantity of MeOH/Et₂O (1:5) and dried in high-vacuum at -40 °C (600 mg, 62%). *Anal.* Calc. for C₁₉H₂₉NNiS₄ (458.41): C, 49.78; H, 6.38; N, 3.06. Found: C, 49.95; H, 6.49; N, 3.04%. ¹H NMR δ (acetone), ppm: 6.7–7.8 (m, 8 H, C₆H₄); 3.42 (s, 12 H, N(CH₃)₄); 3.30 (s, 3 H, OCH₃); 2.60 (s, 1 H, OH· · · S); 2.30 (s, 6 H, SCH₃); -0.33 (s, 3 H, NiCH₃); ¹³C{¹H} NMR δ (acetone), ppm: 153.4, 139.2, 136.9, 132.4, 125.5, 121.4 (C₆H₄); 55.0 (N(CH₃)₄); 48.8 (OCH₃); 18.7 (SCH₃); -9.0 (NiCH₃).

Reaction of (NMe₄)[Ni(CH₃)('MeS₂')₂] with protonic acids

Dropwise addition of an equimolar quantity of acid (HBF₄ in Et₂O or HCl in THF) to a suspension of (NMe₄)[Ni(CH₃)('MeS₂')₂] (230 mg, 0.5 mmol) in 30 ml of THF at -30 °C led to a brown solution and evolution of gas. The gas (9.5 ml) was collected in a gas burette and identified as methane by gas chromatography. A brown solid was isolated from the solution and characterized as [Ni('MeS₂')₂] by means of ¹H NMR spectroscopy.

Thermolysis of (NMe₄)[Ni(CH₃)('MeS₂')₂] (2) at room temperature

In solid state. (NMe₄)[Ni(CH₃)('MeS₂')₂] (50 mg, 0.11 mmol) was warmed to room temperature in a Schlenk tube sealed with a septum. Within 2 days the copper-colored crystals weathered to become a light-brown powder. Gas was removed with a microliter syringe from the Schlenk tube through the septum and identified as ethane by gas chromatography. The light-brown powder was recrystallized from CS₂ and ¹H NMR spectroscopically identified as [Ni('MeS₂')₂].

In solution. A solution of (NMe₄)[Ni(CH₃)('MeS₂')₂] (70 mg, 0.15 mmol) in 4 ml of acetone-d₆ was warmed to room temperature. ¹H NMR spectra of the solution were recorded every 30 min. Signals at 0.83, 2.83 and 6.9–7.6 ppm indicated formation of [Ni('MeS₂')₂] and ethane.

Reaction of Li[Ni(CH₃)('MeS₂')₂] with CO

An equimolar quantity of LiMe (0.5 mmol, 0.31 ml of a 1.6 M solution in Et₂O) was added to the brown solution of [Ni('MeS₂')₂] (185 mg, 0.5 mmol) in 20 ml of THF at -50 °C. When CO was bubbled through the solution its color quickly changed from red to red-yellow. The reaction was monitored by IR spectroscopy and completed after *c.* 1 h.

TABLE 1. Summary of crystallographic data and parameters for data collection and refinement of $[\text{Ni}(\text{MeS}_2)_2]$ (**1**) and $(\text{NMe}_4)[\text{Ni}(\text{CH}_3)(\text{MeS}_2)_2] \cdot \text{MeOH}$ (**2**·MeOH)

Compound	1	2 ·MeOH
M_r	369.23	490.40
Crystal size (mm^3)	$0.4 \times 0.15 \times 0.15$	$0.3 \times 0.3 \times 0.1$
Space group	$P2_1/c$	$P2_1/c$
Crystal system	monoclinic	monoclinic
a (pm)	791.5(5)	1901.0(12)
b (pm)	1083.1(8)	830.3(9)
c (pm)	894.1(6)	1716.1(14)
β (°)	92.79(5)	113.84(5)
V (nm^3)	0.765(1)	2.477(3)
Z	2	4
ρ_{calc} (g/cm^3)	1.60	1.32
μ (cm^{-1})	17.8	11.2
Temperature (K)	293	200
Diffractometer	Nicolet-R3m/V	Nicolet-R3m/V
Radiation	Mo $K\alpha$ ($\lambda = 71.073$ pm)	Mo- $K\alpha$ ($\lambda = 71.073$ pm)
Monochromator	graphite	graphite
Scan technique	ω -scan	ω -scan
Scan speed (°/min)	3.0–15	3.0–15
2θ range (°)	3–54	3–54
Absorption correction	none	none
Reflections collected	2332	6902
Independent reflections	1642	5450
Reflections observed	1060	2109
σ criterion	$F > 6\sigma(F)$	$F > 6\sigma(F)$
Structure solution	direct methods	direct methods
Program	SHELXTL-PLUS	SHELXTL-PLUS
R ; R_w	0.063; 0.049	0.072; 0.053
Parameters refined	89	245

 TABLE 2. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{pm}^2 \times 10^{-1}$) of $[\text{Ni}(\text{MeS}_2)_2]$ (**1**)

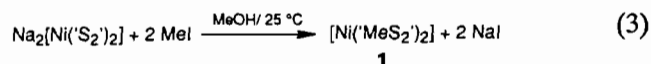
Atom	x	y	z	U_{eq}^a
Ni(1)	5000	0	0	38(1)
S(1)	3606(2)	422(2)	-2086(2)	50(1)
S(2)	3138(2)	-1364(2)	584(2)	42(1)
C(1)	3991(9)	-2821(6)	-35(8)	63(3)
C(15)	1432(9)	-1149(5)	-754(7)	40(2)
C(14)	-94(10)	-1729(6)	-620(8)	51(3)
C(13)	-1399(10)	-1551(6)	-1642(8)	55(3)
C(12)	-1203(10)	-738(6)	-2812(8)	54(3)
C(11)	307(9)	-133(6)	-2936(7)	49(2)
C(10)	1660(9)	-320(5)	-1923(6)	41(2)

^aEquivalent isotropic U defined as one third of the orthogonalized U_{ij} tensor.

Results and discussion

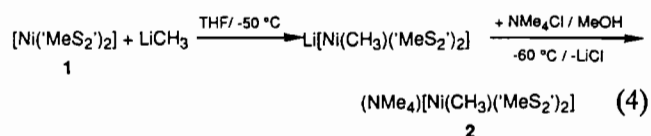
Syntheses

$[\text{Ni}(\text{MeS}_2)_2]$ (**1**), first described by Livingstone [14a], was synthesized by a new method via alkylation of $[\text{Ni}(\text{S}_2)_2]^{2-}$ by methyl iodide according to eqn. (3).



The ^1H NMR spectrum of orange **1** shows a characteristic singlet for the S-CH₃ groups in addition to a multiplet for the aromatic protons (see 'Experimental'). The S-CH₃ singlet proved that only one stereoisomer of **1** formed in the course of alkylation.

Reaction of **1** with LiCH₃ yielded the Ni-methyl complex $\text{Li}[\text{Ni}(\text{CH}_3)(\text{MeS}_2)_2]$ according to eqn. (4) [14b].



$\text{Li}[\text{Ni}(\text{CH}_3)(\text{MeS}_2)_2]$ is air-sensitive, thermolabile, and slowly decomposes already at room temperature. Addition of a methanol solution of NMe₄Cl rendered $(\text{NMe}_4)[\text{Ni}(\text{CH}_3)(\text{MeS}_2)_2]$ (**2**) that was isolated in crystalline form and completely characterized. **2** exhibits a characteristic singlet at -0.33 ppm in the ^1H NMR spectrum (in acetone-d₆) that is assigned to the [Ni-CH₃] group.

TABLE 3. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{pm}^2 \times 10^{-1}$) of $(\text{NMe}_4)[\text{Ni}(\text{CH}_3)(\text{MeS}_2)_2] \cdot \text{MeOH}$ ($2 \cdot \text{MeOH}$)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} ^a
Ni(1)	7767(1)	31(2)	415(1)	33(1)
S(1)	7617(2)	1854(4)	1225(2)	48(1)
S(2)	6512(1)	-128(4)	-312(2)	38(1)
S(3)	8093(1)	-1704(4)	-354(2)	40(1)
S(4)	7640(2)	-1706(4)	-2292(2)	47(1)
C(1)	8855(4)	87(13)	1188(5)	47(4)
C(10)	6620(5)	2165(11)	858(6)	30(4)
C(11)	6313(6)	3200(14)	1274(7)	51(5)
C(12)	5543(6)	3471(14)	977(7)	56(6)
C(13)	5056(7)	2725(12)	226(7)	51(6)
C(14)	5329(5)	1689(13)	-194(7)	44(5)
C(15)	6111(5)	1382(12)	123(6)	35(4)
C(20)	7318(5)	-2947(12)	-1009(6)	33(4)
C(21)	6911(6)	-3924(12)	-680(7)	42(5)
C(22)	6327(6)	-4921(16)	-1210(7)	56(6)
C(23)	6155(6)	-4993(17)	-2056(7)	65(6)
C(24)	6552(6)	-4032(13)	-2400(6)	47(5)
C(25)	7122(5)	-2971(11)	-1890(6)	36(4)
C(16)	6197(5)	528(12)	-1410(6)	57(5)
C(26)	7191(6)	-2070(14)	-3409(5)	74(6)
N(1)	8802(5)	1979(11)	3885(5)	40(4)
C(2)	9337(6)	2169(14)	4781(6)	75(7)
C(3)	8876(6)	371(12)	3561(6)	56(5)
C(4)	7992(6)	2232(13)	3789(8)	73(7)
C(5)	8996(5)	3185(13)	3385(6)	60(5)
O(1)	9291(4)	-4055(9)	1012(5)	60(4)
C(6)	9155(6)	-4557(14)	1708(7)	77(7)

^aEquivalent isotropic *U* defined as one third of the orthogonalized *U*_{*ij*} tensor.

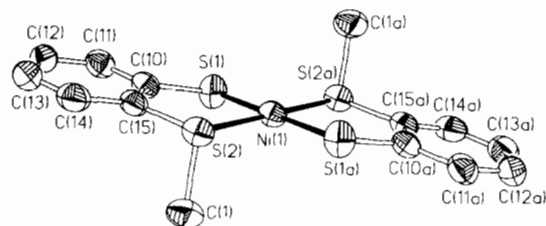


Fig. 1. Molecular structure of $[\text{Ni}(\text{MeS}_2)_2]$ (**1**) (H atoms omitted).

X-ray structure determination of $[\text{Ni}(\text{MeS}_2)_2]$ and $(\text{NMe}_4)[\text{Ni}(\text{CH}_3)(\text{MeS}_2)_2] \cdot \text{MeOH}$

Occurrence of the $[\text{Ni}-\text{CH}_3]$ entity in **2** was further verified by X-ray structure determination. For the purpose of comparison, the molecular structure of **1** (see Fig. 1) was also determined. Table 4 summarizes selected distances and angles.

The crystal structure of **1** consists of discrete molecules exhibiting crystallographic centrosymmetry and planar $[\text{NiS}_4]$ cores. Two mutually *trans* thiolate-S and two thioether-S atoms coordinate the Ni center of **1**. Despite the different covalent radii of thiolate-S and thioether-S atoms, the Ni-S distances of **1** (216.9(2)) are identical and differ only slightly from those found in other

TABLE 4. Selected distances and angles of $[\text{Ni}(\text{MeS}_2)_2]$ (**1**)

Distances (pm)		Angles ($^\circ$)	
Ni(1)-S(1)	216.9(2)	S(1)-Ni(1)-S(2)	91.6(1)
Ni(1)-S(2)	216.9(2)	S(2)-Ni(1)-S(1A)	88.4(1)
S(1)-C(10)	175.0(7)	S(2)-Ni(1)-S(2A)	180.0(0)
S(2)-C(1)	181.3(7)	Ni(1)-S(1)-C(10)	104.2(2)
S(2)-C(15)	177.5(7)	Ni(1)-S(2)-C(1)	104.6(2)
S(1)-S(2)	310.9	Ni(1)-S(2)-C(15)	104.6(2)

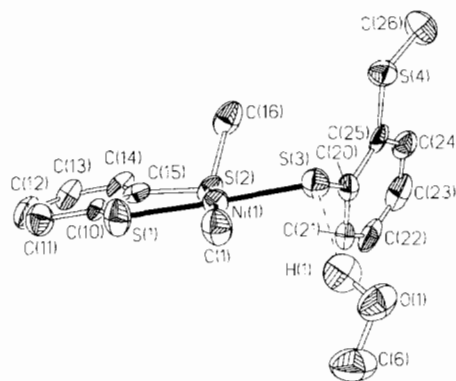


Fig. 2. Structure of the solvated anion of $(\text{NMe}_4)[\text{Ni}(\text{CH}_3)(\text{MeS}_2)_2] \cdot \text{MeOH}$ ($2 \cdot \text{MeOH}$) (H atoms omitted, except for H(1)).

$\text{Ni}(\text{II})$ -thiolato or $\text{Ni}(\text{II})$ -thioether complexes [15], e.g. $[\text{Ni}(\text{OS}_4)]_2$ (217.8 pm) ($\text{OS}_4^{2-} = 2,2'$ -bis-(2-mercaptophenylthio)diethylether(2-)), $[\text{Ni}(\text{S}_4-\text{C}_5)]_2$ (217.3 pm) ($\text{S}_4-\text{C}_5^{2-} = 1,5$ -bis-(2-mercaptophenylthio)pentane(2-)), $[\text{Ni}(\text{S}_4-\text{C}_3)]$ (217.0 pm) ($\text{S}_4-\text{C}_3^{2-} = 1,3$ -bis-(2-mercaptophenylthio)propane(2-)) [16], $[\text{Ni}(\text{14}-\text{S}_4)]^{2+}$ (217.6 pm) ($\text{S}_4 = 1,5,8,12$ -tetrathia-cyclotetradecane) [17] or $[\text{Ni}_2(\text{SC}_2\text{H}_4\text{SC}_2\text{H}_4\text{S})_2]$ (217.6 pm) [18].

The crystal lattice of **2** consists of discrete cations, anions and MeOH solvate molecules. Figure 2 shows the structure of the anion of $2 \cdot \text{MeOH}$; Table 5 lists selected distances and angles.

The Ni centers of the anions are surrounded by one C and three S atoms in a plane. The average Ni-S distance of 218.7 pm only slightly exceeds the Ni-S distances of **1** but the individual Ni-S distances are either considerably smaller (Ni-S(1): 215.0(4) pm) or larger (Ni-S(2): 220.5(3), Ni-S(3): 220.6(4) pm). The MeOH solvate is hydrogen bridged to the S(3) thiolate-S atom. Hydrogen bridging is concluded from the S(3)-O(1) distance (319.0 pm) that is less than the sum of the van der Waals' radii (325-332 pm) [19, 20]. It is also indicated by the short S(3)-H(1) distance of 218.2 pm.

X-ray structure determination of $2 \cdot \text{MeOH}$ thus confirms formation of a Ni-C bond in the reaction according to eqn. (4). Since one of the two MeS_2^- ligands coordinates only via its thiolate-S donor, the complex

TABLE 5. Selected distances and angles of $(\text{NMe}_4)[\text{Ni}(\text{CH}_3)(\text{MeS}_2)_2] \cdot \text{MeOH} (2 \cdot \text{MeOH})$

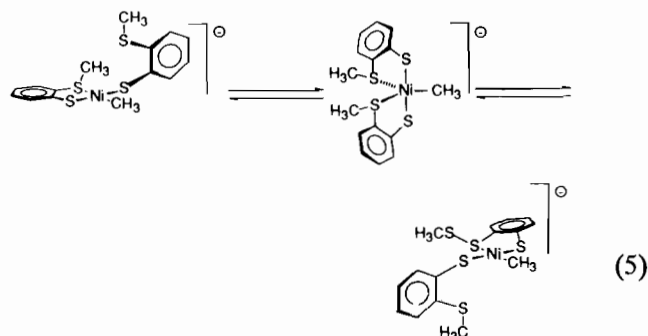
Distances (pm)		Angles ($^\circ$)	
Ni(1)–S(1)	215.0(4)	S(1)–Ni(1)–S(2)	90.7(1)
Ni(1)–S(2)	220.5(3)	S(2)–Ni(1)–S(3)	97.1(1)
Ni(1)–S(3)	220.6(4)	S(1)–Ni(1)–C(1)	85.7(3)
Ni(1)–C(1)	195.4(7)	S(3)–Ni(1)–C(1)	86.9(3)
S(1)–C(10)	175.9(10)	Ni(1)–S(1)–C(10)	106.1(3)
S(2)–C(15)	178.0(11)	Ni(1)–S(2)–C(15)	105.6(3)
S(2)–C(16)	181.4(10)	Ni(1)–S(2)–C(16)	113.4(4)
S(3)–C(20)	177.8(9)	Ni(1)–S(3)–C(20)	113.3(4)
S(3)–O(1)	319.0	Ni(1)–H(1)–O(1)	148.0
S(3)–H(1)	218.2	C(15)–S(2)–C(16)	101.9(5)
S(4)–C(25)	175.9(12)	C(25)–S(4)–C(26)	102.7(5)
S(4)–C(26)	178.1(9)	S(1)–C(10)–C(11)	121.6(6)
O(1)–C(6)	138.5(16)	S(1)–C(10)–C(15)	120.4(8)
S(1)–S(2)	309.8	S(3)–C(20)–C(21)	122.5(7)
S(3)–S(4)	308.0	S(3)–C(20)–C(25)	118.7(8)
Ni(1)–S(4)	477.6	S(2)–C(15)–C(10)	116.6(7)

anion possesses C_1 symmetry. The thioether-S atom S(4) is located so far off the Ni center (477.6 pm) that interaction with the Ni atom and a Ni–S(4) bond, respectively, can be excluded. The Ni–C distance (195.4(7) pm) of the $[\text{Ni}-\text{CH}_3]$ unit is similar to the one in the above-mentioned $[\text{Ni}(\text{CH}_3)(\text{N}(\text{CH}_2\text{CH}_2\text{S}^i\text{Pr})_3)]^+$ ion (Ni–C = 194(2) pm) [12].

NMR spectra

NMR spectra of **2** indicate that the anion of **2** possesses higher symmetry in solution than in solid state. 17 signals are to be expected in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum for the structure of $2 \cdot \text{MeOH}$ determined by X-ray structure determination; only ten signals, however, could be observed in acetone- d_6 . Six signals can be assigned to the aromatic protons and one each to the S–methyl, the MeOH, the NMe_4^+ and the Ni–methyl C atoms. The chemical shift of the C atom of the $[\text{Ni}-\text{CH}_3]$ group at -9.0 ppm lies within the same range as in other Ni–alkyl complexes, e.g. $[\text{Ni}(\text{CH}_3)(\text{C}_2\text{H}_4)_2]^-$ (-12.2 ppm), $[\text{Ni}(\text{CH}_3)(\text{CDT})]^-$ (-4.6 ppm) (CDT = 1,5,9-cyclododecatriene) or $[\text{Ni}(\text{CH}_3)(\text{CO})_3]^-$ (-24.7 ppm) [21]. Thus, the number of signals shows that the ‘ MeS_2 ’-C atoms are pairwise magnetically equivalent indicating C_2 , C_i or C_s symmetry of the anion of $2 \cdot \text{MeOH}$ in solution. This is even more evident in the ^1H NMR spectrum of **2**: it shows one signal only for the S–methyl protons. MeOH hydroxyl and methyl, NMe_4 methyl, and the metal-bound methyl groups each also give rise to singlets. The chemical shift of the $[\text{Ni}-\text{CH}_3]$ protons (-0.33 ppm) is again comparable with other $[\text{Ni}-\text{CH}_3]$ complexes, e.g. $[\text{Ni}(\text{PMe}_3)_4(\text{CH}_3)]^-$ (-0.3 ppm) [4], $[\text{Ni}(\text{CH}_3)(\text{C}_2\text{H}_4)_2]^-$ (-0.58 ppm) [21] or $[\text{Ni}(\text{CH}_3)(\text{N}(\text{C}_2\text{H}_4\text{S}^i\text{Pr})_3)]^+$ (-0.71 ppm) [12].

It is emphasized that the two ‘ MeS_2 ’-methyl groups of **2** give rise to one singlet in the ^1H NMR as well as the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum. This is only possible if the free thioether donor in **2** becomes bound to the nickel center and a species with two-fold symmetry and five-coordinate nickel results. This can occur in a dynamic equilibrium, for example, according to eqn. (5).



NMR spectra recorded at variable temperatures showed that this equilibrium cannot be frozen in the range of -10 to -80 $^\circ\text{C}$.

Reactions

Whereas **1** does not react with CO, **2** rapidly reacts with CO. Monitoring the reaction by IR spectroscopy (Fig. 3) shows the initial formation of a compound with an IR $\nu(\text{CO})$ band at 1602 cm^{-1} . When the reaction proceeds, this band disappears again and is replaced by a band at 1725 cm^{-1} having a shoulder at 1700 cm^{-1} . In addition, a complex pattern of $\nu(\text{CO})$ bands between 2040 and 1890 cm^{-1} appears. After 1 h, only four $\nu(\text{CO})$ bands are left at 2040 , 1950 , 1725 and 1720 cm^{-1} that do not change any more.

Unambiguous assignment of these bands to individual species has so far not been possible. Tentatively, the $\nu(\text{CO})$ band at 1602 cm^{-1} can be assigned to a nickel–acetyl species that forms only as intermediate. This assumption is supported by the $\nu(\text{CO})$ bands of related complexes, e.g. $[\text{Ni}(\text{COCH}_2\text{SiMe}_3)(\text{S}_2\text{CNMe})(\text{PMe}_3)]$ ($\nu(\text{CO}) = 1610$ cm^{-1}) that appear in the same region [22]. The bands at 1725 and 1720 cm^{-1} indicate the formation of organic carbonyl compounds. These can be ketones [23], resulting from the reaction of the nickel–acetyl species with $[\text{Ni}(\text{CH}_3)(\text{MeS}_2)_2]^-$ or thioesters, $\text{RS}-\text{COCH}_3$ [12], that result when acetyl groups are transferred from the nickel–acetyl species to thiolate donors of the ‘ MeS_2 ’-ligands. The $\nu(\text{CO})$ bands in the range between 2040 and 1950 cm^{-1} certainly stem from nickel carbonyl complexes.

Precipitation of $[\text{Ni}(\text{CH}_3)(\text{MeS}_2)_2]^-$ as NMe_4 salt **2** in MeOH according to eqn. (4) shows that the anion is surprisingly stable towards protic solvents like MeOH.

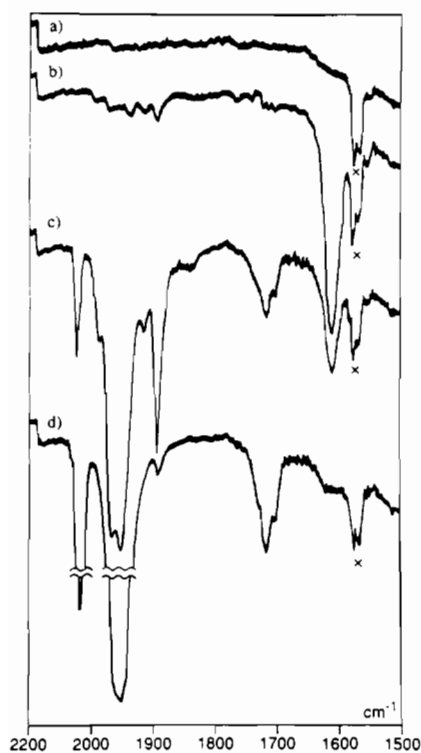
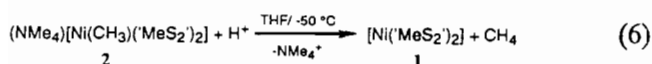
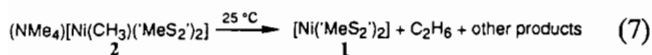


Fig. 3. Monitoring of the reaction of $\text{Li}[\text{Ni}(\text{CH}_3)(\text{MeS}_2)_2]$ with CO in THF at -50°C by IR spectroscopy: (a) start, (b) after 10 min, (c) after 30 min, (d) after 1 h of reaction with CO; x=bands of the 'MeS₂' ligands.

With acids as HBF_4 or HCl , however, the CH_3 ligand is cleaved off, and **2** releases approximately stoichiometric quantities of methane according to eqn. (6).



Cleavage of the $\text{Ni}-\text{CH}_3$ bond of **2** is also thermally possible and occurs already at room temperature. Then, however, the resulting gaseous product is not methane but ethane in approximately equimolar amounts with respect to **2** according to eqn. (7).



This thermolysis takes place in solid state as well as in acetone solution. The released C_2H_6 was identified by gas chromatography and ^1H NMR spectroscopy. Both in reaction (6) and (7) **1** was isolated and characterized as one of the other products.

Conclusions

Methylation of $[\text{Ni}(\text{S}_2)_2]^{2-}$ by CH_3I yields $[\text{Ni}(\text{MeS}_2)_2]$ (**1**). **1** easily adds LiCH_3 and forms the

$[\text{Ni}(\text{CH}_3)(\text{MeS}_2)_2]^-$ anion exhibiting a $[\text{Ni}-\text{CH}_3]$ group and a thioether donor that has become decoordinated. Intermediates in this reaction presumably are square-pyramidal or trigonal-bipyramidal adducts with five-coordinate nickel centers that are typical of substitution reactions of planar d^8 metal complexes. Intermediate formation of five-coordinate nickel species is also to be concluded from the NMR spectra of **2**. The number of observed ^1H and ^{13}C signals is only compatible with structures of an anion that exhibit at least two-fold symmetry.

Nickel-methyl complexes are usually unstable [2, 24], but stabilization of $\text{Ni}-\text{CH}_3$ bonds was achieved in a few cases by $\sigma-\pi$ coligands, e.g. in $\text{Li}(\text{TMEDA})_2\text{-}[\text{Ni}(\text{CH}_3)(\text{CO})_3]$ [21], $[\text{Ni}(\text{CH}_3)_2(\text{PMe}_3)_3]$ [4] or $[\text{Ni}(\text{CH}_3)_2(\text{PMe}_3)_2]$ [5]. $\text{Ni}-\text{CH}_3$ complexes with $[\text{NiS}]$ that exhibit model character for CODH are extraordinarily rare, and the $[\text{Ni}(\text{CH}_3)(\text{N}(\text{CH}_2\text{CH}_2\text{S}^i\text{Pr})_3)]^+$ -type complexes [12] cited above seem to represent the only examples known so far. They possess five-coordinate nickel centers in trigonal-bipyramidal ligand spheres. In contrast, **2** represents the first planar $[\text{Ni}-\text{CH}_3]$ complex with a sulfur-dominated coordination sphere.

The reactivity of **2** towards CO is of special interest with regard to reactions catalyzed by CODH. Unlike the precursor complex **1**, the methyl complex **2** reacts quickly with CO. $\nu(\text{CO})$ bands that appear and disappear in the IR spectra of the reaction solution indicate the primary formation of $[\text{Ni}-\text{COCH}_3]$ species that, due to their high reactivity, continue to react in order to finally yield ketones and/or thioesters, and nickel-carbonyl complexes as metal species.

Such reactions resulting in the formation of C-C bonds can tentatively be discussed as model reactions for the acetyl-CoA synthesis from C_1 precursors taking place at the $[\text{NiS}]$ centers of CODH. As is shown above, reversible decoordination reactions of S donors in planar $[\text{NiS}_4]$ cores may render possible or support these C-C bond making processes.

The $\text{Ni}-\text{CH}_3$ bond in **2** is surprisingly stable towards weak acids like MeOH but can easily be cleaved by strong acids. The resulting formation of methane is of interest with regard to the methane formation from CO in methanogenic bacteria catalyzed by enzymes with $[\text{NiS}]$ centers [25]. The question remains open whether formation of methane in the course of the reaction of **2** with H^+ is initiated by addition of protons to the thiolate-S donors or to the four-coordinate Ni center. It is, however, remarkable that thermolysis of **2** yields ethane instead of methane, and that the quantity of ethane released (1 mmol per mmol of **2**) suggests that thioether-S-methyl groups of **2** are involved in the formation of ethane. Elucidation of this question is currently investigated.

Supplementary material

Further details of the crystal structure analyses can be obtained from the Fachinformationszentrum Karlsruhe GmbH, D-7514 Eggenstein-Leopoldshafen 2, citing the deposition nos. CSD-320347 (1) and CSD-320348 (2·MeOH), the authors and the reference.

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