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Inorganica Chimica Acta 300–302 (2000) 829–836

Inorganica Chimica Acta

Transition metal complexes with sulfur ligands Part CXLIV. Square planar nickel complexes with NiS_4 cores in three different oxidation states: synthesis, X-ray structural and spectroscopic studies☆

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Received 30 November 1999; accepted 10 December 1999

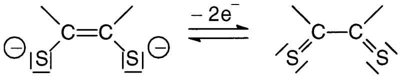
Abstract

The reaction of '$^{bu}S_2$'$^{2-}$ = 3,5-ditertiarybutyl-1,2-benzenedithiolate(2 −) with $Ni(ac)_2 \cdot 4H_2O$ and subsequently $AsPh_4Cl$, yielded $(AsPh_4)_2[Ni('^{bu}S_2')_2]$ (**1**). Complex **1** is extremely air sensitive and oxidized rapidly to give $(AsPh_4)[Ni('^{bu}S_2')_2]$ (**2**). The anion of **2** could be further oxidized by iodine to give neutral $[Ni('^{bu}S_2')_2]$ (**3**). Complexes **1**, **2** and **3** contain nickel in the formal oxidation states + 2, + 3 and + 4, and could be completely characterized by X-ray structure determination and spectroscopic methods. The results indicate that the oxidation of **1** → **2** → **3** concerns electrons residing in molecular orbitals having $[NiS_4]$ character. No evidence could be obtained for an involvement of the benzene rings or an electron delocalization beyond the $[NiS_4]$ core. This conclusion corresponds with the reactivity of **3** versus **2** and **1** towards protons and CO. While **3** is inert to the attack of H^+ and CO, **2** and **1** exhibit rapid reactions to give '$^{bu}S_2$'–H_2 and either nickel–chloro complexes or $Ni(CO)_4$. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Nickel thiolate complexes; High oxidation states

1. Introduction

Nickel complexes with sulfur coordination spheres have attracted considerable interest as model compounds for the active centers of nickel sulfur enzymes [2], e.g. NiFe hydrogenases, as homogeneous and heterogeneous hydrodesulfurization catalysts [3], and as compounds exhibiting unusual electronic properties when the ligands contain sulfur donors connected by unsaturated C_2 bridges. For the latter type of complexes, the nickel dithiolenes, the assignment of (formal) metal oxidation states and ligand charges has been as controversial as for other metal dithiolenes [4]. The ambiguity of these assignments is caused by the formal redox equilibrium converting an ene-dithiolate into a dithioketone according to Eq. (1).



(1)

Such a redox conversion has principally to be considered also for 1,2-benzenedithiolate(2 −) anions yielding cyclohexadiene-1,2-dithioketones when binding to high-oxidation state metal centers. The question is whether the very stable aromatic system of the benzene ring prevents such an oxidation, i.e. is 1,2-benzenedithiolate(2 −) an innocent or a so-called 'non-innocent' ligand [4c]. Here we address this question with X-ray structural and spectroscopic results on the series of $[Ni('^{bu}S_2')_2]^{n-}$ complexes ($n = 2, 1, 0$). These complexes contain '$^{bu}S_2$'$^{2-}$ = 3,5-ditertiarybutyl-1,2-benzenedithi-

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☆ For Part CXLIII see Ref. [1].

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PII: S0020-1693(99)00608-8

olate(2 −) ligands and nickel in the formal oxidation states of + 2, + 3 and + 4.

Changes in electron content between different oxidation states of transition metal complexes can cause significant changes in molecular structure. A detailed analysis of such changes is usually restricted to two adjacent oxidation states [5]. Completely characterized and strictly homologous complexes in three or more different oxidation states are extremely rare [6].

Analogous complexes containing the planar $[Ni(S_2C_6H_4)_2]^{n-}$, anions with $n = 2$ [7] and $n = 1$ [8] have been known for some time and could be characterized by X-ray structure determination. Our attempts to obtain also the neutral species $[Ni(S_2C_6H_4)_2]$ failed. Oxidation of the anionic species with various oxidizing reagents yielded grey–black products being insoluble and intractable. Attempts by others to synthesize neutral $[Ni(S_2C_6Cl_4)_2]$ by electrochemical oxidation of $(NBu_4)[Ni(S_2C_6Cl_4)_2]$ resulted only in a species described as $(NBu_4)_{0.15}[Ni(S_2C_6Cl_4)_2]$ [9].

2. Experimental

Unless noted otherwise, all reactions were carried out under an atmosphere of argon at room temperature using standard Schlenk techniques. The argon atmosphere was required by the $[Ni('^{bu}S_2')_2]^{2-}$ anion, which is extremely sensitive towards oxidation and could not be handled under an atmosphere of dinitrogen. Solvents were dried, distilled and argon saturated before use. Physical measurements were carried out with the following instruments: IR, Perkin–Elmer 16 PC FTIR spectrometer; NMR spectra: Jeol JNM-GX 270 spectrometer with the protio-solvent signal used as internal reference. Chemical shifts are quoted on the δ scale (downfield shifts are positive) relative to tetramethylsilane. Spectra were recorded at 25°C. UV–Vis–NIR spectra: Shimadzu UV-3101 PC spectrometer; EPR spectra: Bruker ESP 300 spectrometer (X-band, 9.4 GHz). Spectra were recorded in DMF–$CHCl_3$ (1:1 by volume) solution at 293 or − 120 K, and referenced towards diphenylpicrylhydrazyl ($<g> = 2.0036(2)$) [10]. XPS measurements: Solutions of the probes were spread on gold plates, the solvents were removed in the pre-vacuum. Spectra were recorded with an AEI ES 200 B spectrometer (AEI, Manchester, UK), Al Kα radiation and referenced towards gold ($E_b(Au\ ^4f_{7/2}) = 84.0$ eV [11]). The measurements were repeated three times and yielded a reproducibility of 0.2 eV. Cyclic voltammograms were recorded with an EG&G PAR 264 A potentiostat, equipped with a ROTEL A three-electrode cell (glassy carbon working electrode, Pt counter-electrode and Ag/AgCl/KCl reference electrode). Conducting electrolyte: 0.1 M NBu_4PF_6; internal standard $Cp_2Fe^{0/+} = 0.40$ V versus NHE [12]. Elemental analyses: Carlo Erba EA 1106 or 1108 analyzer.

$'^{bu}S_2'–H_2$ was prepared as described in the literature [13]. $AsPh_4Cl·H_2O$ was purchased from Alfa. Nickel metal, 86.2% enriched in ^{61}Ni was purchased from Scientific and Production Association ALFA-LAB, Moscow, Russia.

2.1. Syntheses and reactions

2.1.1. Synthesis of $(AsPh_4)_2[Ni('^{bu}S_2')_2]$ (**1**)

Under stirring, $'^{bu}S_2'–H_2$ (1.61 g, 6.33 mmol) was dissolved in 12.7 ml of 1 N LiOMe in MeOH. After 20 min, solid $Ni(ac)_2·4H_2O$ (780 mg, 3.13 mmol) was added. A slightly purple solution resulted, which was cooled to − 30°C. In the course of 5 days, ocher crystals of $Li_2[Ni('^{bu}S_2')_2]$ precipitated, which were separated, washed with cold MeOH (− 90°C, 30 ml), and dried in vacuo. These crystals (250 mg, 0.43 mmol) were dissolved in MeOH (6 ml) and combined with $AsPh_4Cl·H_2O$ (380 mg, 0.87 mmol). A small amount of dark-green crystals of $(AsPh_4)[Ni('^{bu}S_2')_2]$ precipitated and was removed. The remaining dark-yellow solution was carefully layered with 11 ml of Et_2O. In the course of 8 days, red crystals of $(AsPh_4)_2[Ni('^{bu}S_2')_2]·2Et_2O$ precipitated which were separated, washed with 4 ml of a cold (− 90°C) 1:1 mixture of MeOH–Et_2O and 10 ml of cold (− 90°C) Et_2O. Drying these crystals at 60°C in vacuo (30 h, 10^{-3} mbar) yielded a brown powder of solvate free $(AsPh_4)_2[Ni('^{bu}S_2')_2]$. *Anal.* Calc. for $C_{76}H_{80}As_2NiS_4$ (1330.29): C, 68.62; H, 6.06; S, 9.64. Found: C, 68.92; H, 6.25; S, 9.61%. ^1H NMR (269.6 MHz, acetone-d_6, δ (ppm)): 7.34 (4H, br, C_6H_2), 1.95 (36H, br, CMe_3).

2.1.2. Synthesis of $(AsPh_4)[Ni('^{bu}S_2')_2]$ (**2**)

For 20 min, air was bubbled through a solution of $Li_2[Ni('^{bu}S_2')_2]$ (680 mg, 1.17 mmol) in MeOH (25 ml) yielding a deep green solution. A solution of $AsPh_4Cl·H_2O$ (525 mg, 1.20 mmol) in MeOH (10 ml) was added dropwise. Deep green crystals of $(AsPh_4)[Ni('^{bu}S_2')]$ precipitated, which were separated after 1 day, washed with 60 ml of MeOH and dried in vacuo for 1.5 days at 60°C. Yield: 940 mg (85%). *Anal.* Calc. for $C_{52}H_{60}AsNiS_4$ (946.95): C, 65.96; H, 6.39; S, 13.54. Found: C, 66.09; H, 6.46; S, 13.42%.

2.1.3. Synthesis of $[Ni('^{bu}S_2')_2]$ (**3**)

An acetone solution of iodine (295 mg, 2.32 mmol, 25 ml) was added to an acetone solution of $(NMe_4)[Ni('^{bu}S_2')_2]$ (700 mg, 1.10 mmol, 20 ml). ($(NMe_4)[Ni('^{bu}S_2')_2]$ was prepared from $Li_2[Ni('^{bu}S_2')_2]$ and NMe_4Cl analogously to **2**.) A red–brown solution resulted, from which blue crystals of $[Ni('^{bu}S_2')_2]$ precipitated. They were separated after 2 days, washed with MeOH (60 ml) and Et_2O (5 ml), dried, and recrystallized from hot xylene. Yield: 565 mg (91%). *Anal.* Calc. for $C_{28}H_{40}NiS_4$ (563.60): C, 59.67; H, 7.15; S, 22.76.

Found: C, 59.75; H, 7.30; S, 22.62%. ^{1}H NMR (269.6 MHz, C_6D_6, δ (ppm)): 8.23 (2H, s, C_6H_2), 7.59 (2H, s, C_6H_2), 1.78 (18H, s, CMe_3), 1.14 (18H, s, CMe_3). $^{13}C\{^1H\}$ NMR (67.7 MHz, C_6D_6, δ (ppm)): 176.1, 167.9, 153.2, 150.7, 122.7 (C_6H_2), 38.2, 35.7 (CMe_3), 31.3, 30.9 (CMe_3).

*2.1.4. Acid hydrolysis of $(AsPh_4)_2[Ni(\text{'}^{bu}S_2\text{'})_2]$ (**1**) and $(AsPh_4)[Ni(\text{'}^{bu}S_2\text{'})_2]$ (**2**)*

The respective complexes (2 mmol) were stirred in a mixture of CH_2Cl_2 (20 ml) and concentrated hydrochloric acid (25 ml) for 30 min. The CH_2Cl_2 phase was separated, and the green aqueous phase was extracted with CH_2Cl_2 (20 ml). The CH_2Cl_2 phases were combined, washed with water, dried over Na_2SO_4, and evaporated. The remaining colorless oil was identified as '$^{bu}S_2$'–H_2 by ^{1}H NMR spectroscopy. $[Ni(\text{'}^{bu}S_2\text{'})_2]$ (**3**) remained unchanged under identical conditions for 24 h.

*2.1.5. Reaction of $(AsPh_4)_2[Ni(\text{'}^{bu}S_2\text{'})_2]$ (**1**) and $(AsPh_4)[Ni(\text{'}^{bu}S_2\text{'})_2]$ (**2**) with CO*

THF solutions (30 ml) of the respective complexes were treated with 120 bar CO in an autoclave for 24 h. The IR spectra of the resulting solutions showed a strong ν(CO) band at 2041 cm^{-1}, which was assigned to $Ni(CO)_4$. $[Ni(\text{'}^{bu}S_2\text{'})_2]$ remained unchanged for 72 h under analogous conditions, and no $Ni(CO)_4$ band could be detected in the IR spectrum.

*2.2. X-ray structure analyses of $(AsPh_4)_2[Ni(\text{'}^{bu}S_2\text{'})_2]\cdot 2Et_2O$ (**1**$\cdot 2Et_2O$), $(AsPh_4)[Ni(\text{'}^{bu}S_2\text{'})_2]$ (**2**) and $[Ni(^{bu}S_2)_2]$ (**3**)*

Single crystals were grown as follows: red cubes of **1**$\cdot 2Et_2O$ from an Et_2O solution which was layered with MeOH, dark green prisms of **2** from an acetone solution which was layered with Et_2O, and dark-blue cuboids of **3** from a toluene solution which was layered with MeOH. Suitable single crystals were sealed in glass capillaries. Data were collected with a Siemens P4 diffractometer using Mo Kα radiation ($\lambda = 71.073$ pm), a graphite monochromator and ω-scan technique (scan speed 3.0–30° min^{-1}). The structures were solved with direct methods (SHELXTL-PLUS) [14]. Full-matrix least-squares refinements on F^2 were carried out with SHELXTL-NT 5.1 [14]. Non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located in Fourier synthesis difference maps. For all hydrogen atoms both the positional parameters and a common isotropic displacement parameter were restricted during refinement. Complex **2** contains two independent molecules in the unit cell; in one molecule one tertiary butyl group is disordered. Two different orientations were refined (C231–C233 and C241–C243), with site occupancies of 0.83(1) and 0.17(1). The C atoms of the minor component (C241–C243) were refined isotropically, and no H-atoms were included for this alternative orientation. Table 1 lists selected crystallographic data.

3. Results

3.1. Syntheses and reactions

According to Scheme 1, the red Ni^{II}complex $(AsPh_4)_2[Ni(\text{'}^{bu}S_2\text{'})_2]$ (**1**) formed from $Ni(ac)_2\cdot 4H_2O$, the dilithium salt of the ligand and $AsPh_4Cl$. The yellow MeOH solution containing the $Li_2[Ni(\text{'}^{bu}S_2\text{'})_2]$ salt proved extremely air-sensitive, and even traces of air led to an immediate color change to light-green. When air was bubbled through such a solution, the color changed to dark green. Addition of $AsPh_4Cl$ yielded $(AsPh_4)[Ni(\text{'}^{bu}S_2\text{'})_2]$ (**2**). The further oxidation of **2** proved more difficult. A considerable number of unsuccessful experiments were carried out before we found that the analogous $(NMe_4)[Ni(\text{'}^{bu}S_2\text{'})_2]$ could be readily oxidized by iodine in acetone to give the neutral complex $[Ni(\text{'}^{bu}S_2\text{'})_2]$ (**3**). Complex **3** is deep blue and soluble in toluene.

Concerning the reactions of [NiFe] hydrogenases in different oxidation states, which are assumed to occur at the nickel centers [2], the reactivity of **1**, **2** and **3** towards protons and CO was of particular interest. Somewhat surprisingly, the neutral complex **3** proved completely inert towards protons and is stable for days even towards concentrated hydrochloric acid. A reaction with CO could neither be observed at 1 bar nor at 120 bar pressure in an autoclave. In contrast, and as observed with other anionic nickel thiolate complexes [15], **1** and **2** almost instantaneously dissociated when treated with hydrochloric acid to give '$^{bu}S_2$'–H_2 and nickel–chloro species. When treated with CO, complex **1** and **2** decomposed in THF to give $Ni(CO)_4$ and organosulfur compounds which were not characterized in detail. $Ni(CO)_4$ was detected by its IR band at 2041 cm^{-1}.

Hydride sources such as $LiBEt_3H$ reduced **3** to give successively the anions of **2** and **1**, which could be precipitated by addition of $AsPh_4Cl$. Monitoring these reactions by ^{1}H NMR spectroscopy did not yield any evidence for nickel–hydride species.

*3.2. X-ray structure determination of $(AsPh_4)_2[Ni(\text{'}^{bu}S_2\text{'})_2]\cdot 2Et_2O$ (**1**$\cdot 2Et_2O$), $(AsPh_4)[Ni(\text{'}^{bu}S_2\text{'})_2]$ (**2**) and $[Ni(\text{'}^{bu}S_2\text{'})_2]$ (**3**)*

All three complexes **1**, **2** and **3** yielded single crystals upon recrystallization. Complex **1** was obtained as the solvate **1**$\cdot 2Et_2O$. The X-ray crystal structure determinations showed that all three compounds contain discrete cations, anions or molecules. Intermolecular interac-

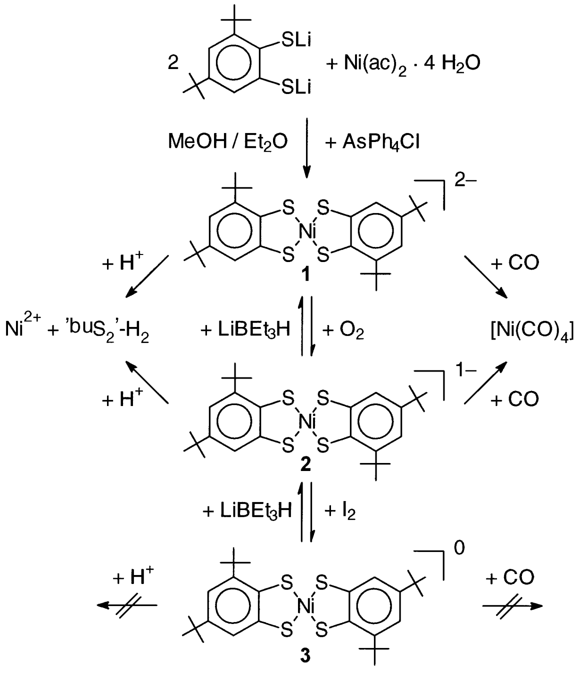
Table 1
Crystal and data collection [a] parameters of $(AsPh_4)_2[Ni(\text{'}^{bu}S_2\text{'})_2]\cdot 2Et_2O$ (**1**·2Et$_2$O), $(AsPh_4)[Ni(\text{'}^{bu}S_2\text{'})_2]$ (**2**) and $[Ni(\text{'}^{bu}S_2\text{'})_2]$ (**3**)

Compound	**1**·2 Et$_2$O	**2**	**3**
Chemical formula	$C_{84}H_{100}As_2NiO_2S_4$	$C_{52}H_{60}AsNiS_4$	$C_{28}H_{40}NiS_4$
Formula weight	1478.43	946.87	563.55
Crystal system	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (pm)	1001.4(2)	1314.8(3)	589.4(1)
b (pm)	1354.7(3)	1447.4(3)	938.5(3)
c (pm)	1617.6(3)	1537.1(3)	1399.5(4)
α (°)	71.34(2)	87.03(2)	70.56(2)
β (°)	87.21(2)	68.01(2)	85.65(2)
γ (°)	69.57(2)	64.81(2)	79.65(2)
V (nm^3)	1.943(1)	2.434(1)	0.718(1)
Z	1	2	1
D_{calc} (g cm^{-1})	1.25	1.29	1.30
μ (cm^{-1})	12.47	12.78	9.81
T (K)	293	293	293
Crystal size (mm)	0.7 × 0.5 × 0.4	0.6 × 0.4 × 0.3	0.7 × 0.4 × 0.4
θ Range (°)	1.7–27.1	1.6–27.1	1.5–27.1
Measured reflections	9980	12 991	4068
Independent reflections	8539	10 691	3161
Observed reflections [b]	5184	5325	2407
Reflection parameters	421	539	151
Goodness-of-fit	0.738	0.754	0.983
$\Delta\rho$ (e nm^{-3})	341/−300	900/−1103	365/−518
R_1 [b]; wR_2 (%)	3.3; 6.8	4.6; 10.9	3.5; 10.3

[a] All data collected with graphite-monochromatized Mo Kα radiation ($\lambda = 71.073$ pm).
[b] $[I > 2\sigma(I)]$.

tions or stacking phenomena as found with other nickel dithiolenes were not observed.

The nickel complexes of **1**, **2** and **3** contain centrosymmetric planar $[Ni(\text{'}^{bu}S_2\text{'})_2]$ entities. Crystallographically required, $(AsPh_4)[Ni(\text{'}^{bu}S_2\text{'})_2]$ (**2**) has two independent molecules (1) and (2) in the unit cell. One of the two tertiary butyl groups of the anion (2) is disordered with site occupancies of two possible sites being refined to 0.83(1) and 0.17(1). Fig. 1 depicts the molecular structure of the $[Ni(\text{'}^{bu}S_2\text{'})_2]$ entities found in all three compounds **1**, **2** and **3**, Table 2 lists and compares relevant distances and angles of the individual complexes.



Scheme 1. Syntheses and reactions of **1**, **2** and **3**.

Table 1 shows that the Ni–S distances decrease in the order **1** > **2** > **3** with the formal increase of the nickel oxidation states from +2 to +4. Likewise, the C–S distances decrease. However, the decrease of Ni–S and C–S distances covers only a very small range. In all three complexes the Ni–S distances are relatively short, in particular, when compared with the Ni–S distances

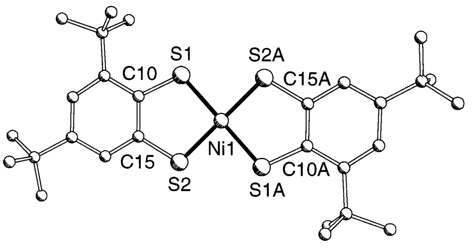


Fig. 1. Molecular structure of the $[Ni(\text{'}^{bu}S_2\text{'})_2]$ entities in $(AsPh_4)_2[Ni(\text{'}^{bu}S_2\text{'})_2]\cdot 2Et_2O$, (**1**·2Et$_2$O), $(AsPh_4)[Ni(\text{'}^{bu}S_2\text{'})_2]$ (**2**) and $[Ni(\text{'}^{bu}S_2\text{'})_2]$ (**3**) (H atoms omitted).

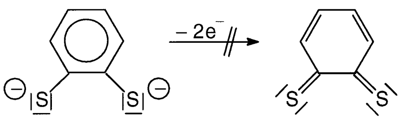
Table 2
Selected distances (pm) and angles (°) of **1**, **2** and **3**

Compound	Ni(II)	Ni(III) (1) [a]	Ni(III) (2) [a]	Ni(IV)	Trend [b]
Ni(1)–S(1)	217.50(8)	214.37(11)	214.46(12)	212.40(8)	↓
Ni(1)–S(2)	217.15(9)	213.53(11)	214.46(12)	212.67(8)	↓
S(1)–C(10)	177.0(2)	175.4(4)	175.1(4)	173.1(2)	↓
S(2)–C(15)	175.5(2)	174.5(4)	174.3(4)	172.3(2)	↓
C(15)–C(10)	140.1(3)	140.7(5)	140.7(5)	141.9(3)	o
C(11)–C(10)	142.6(3)	142.5(5)	143.4(5)	142.9(3)	o
C(15)–C(14)	140.2(3)	139.1(5)	139.1(5)	140.9(3)	o
C(12)–C(11)	139.8(3)	138.7(5)	137.8(5)	137.5(3)	n
C(14)–C(13)	138.3(3)	136.7(5)	138.9(5)	137.3(3)	n
C(13)–C(12)	139.0(3)	141.2(5)	140.1(5)	142.2(3)	n
$d_{CC(Aryl)}$	140.0(3)	139.8(5)	140.0(5)	140.5(3)	o
S(1)–Ni(1)–S(2)	89.63(3)	91.01(4)	90.96(4)	91.57(3)	↑
S(1)–Ni(1)–S(2a)	90.37(3)	88.99(4)	89.04(5)	88.43(3)	↓
S(1)–C(10)–C(15)	116.2(2)	116.3(3)	117.0(3)	116.3(2)	o
S(2)–C(15)–C(10)	119.9(2)	119.8(3)	119.3(3)	119.9(2)	o
S(1)–C(10)–C(11)	125.2(2)	125.4(3)	124.6(3)	124.3(2)	n
C(11)–C(10)–C(15)	118.6(2)	118.3(3)	118.4(3)	119.3(2)	n
S(2)–C(15)–C(14)	119.2(2)	118.7(3)	119.2(3)	118.8(2)	o
C(14)–C(15)–C(10)	120.8(2)	121.5(3)	121.5(4)	121.3(2)	o

[a] Two independent molecules in the unit cell.

[b] ↓ = decreasing value, ↑ = increasing value, o = identical within three e.s.d., n = not identical, but no clear trend.

of up to 240 pm in paramagnetic nickel thiolate complexes which have electrons in antibonding nickel–ligand molecular orbitals [16]. The C–C distances within the benzene rings do not show any significant changes. However, the individual C–C distances exhibit rather large deviations from the mean C–C distance value. This is certainly caused by the bulky tertiary butyl ring substituents introducing considerable asymmetry in the benzene system. The main point is that the C–C benzene distances do not yield any evidence for an oxidative formation of *o*-quinoid or 1,2-dithiocyclohexadiketone structures according to Eq. (2), when $[Ni(‘^{bu}S_2’)_2]^{2-}$ is oxidized to $[Ni(‘^{bu}S_2’)_2]^0$.



(2)

The Ni–S distances of **1** and **2** correspond with those in the parent complexes $(NMe_4)_2[Ni(S_2C_6H_4)_2]$ [8] and $(NMe_4)[Ni(S_2C_6H_4)_2]$ [7]. The short Ni–S distances in **3** compare with those in neutral ‘typical’ dithiolene complexes, for example, $[Ni(S_2C_2Ph_2)_2]$ (210.1(2) pm) [17] or $[Ni(S_2C_2(H)C_6H_4C_8H_{17})_2]$ (213.0(1) and 211.6(1) pm) [18].

In summary, the X-ray structural results do not show a ligand centered oxidation of **1** via **2** to **3** in the sense that the ‘^{bu}S$_2$’ ligands behave as ‘non-innocent’ ligands. The (slight) decrease of the $[NiS_4]$ core distances rather suggests that the relevant electrons being removed reside in molecular orbitals having mainly $[NiS_4]$ character.

3.3. Electrochemistry, NMR, EPR and UV–Vis spectra

Corresponding to the chemical redox transformations of **1** to **3**, the cyclic voltammograms (CV) of **1**, **2** and **3** are identical and each exhibits one quasi-reversible redox wave in the anodic and one in the cathodic region. They can be assigned to the $[Ni(‘^{bu}S_2’)_2]^{-/0}$ and the $[Ni(‘^{bu}S_2’)_2]^{1-/2-}$ couples. As an example, Fig. 2 shows the CV of $(AsPh_4)[Ni(‘^{bu}S_2’)_2]$ (**2**).

The redox potentials of the $[Ni(‘^{bu}S_2’)_2]$ couples lie in the same range as observed for other planar nickel complexes with four sulfur donors, irrespective of the question whether the bidentate sulfur ligands are considered dithiolene type ligands or rather ‘normal’ dithiolates, e.g. $[Ni(S_2C_2(4\text{-}ClC_6H_4)_2]^{0/1-}$ [4], $[Ni(S_2C_6H_4)_2]^{2-/1-}$ [8], or $[Ni(S_2\text{-norbornane})_2]^{2-/1-}$ [19].

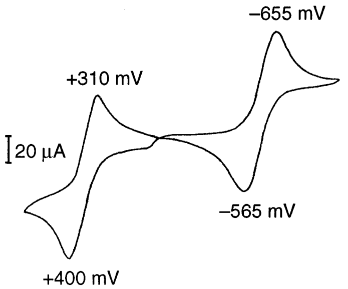


Fig. 2. Cyclic voltammogram of $(AsPh_4)[Ni(‘^{bu}S_2’)_2]$ (**2**) in THF (20°C, $v = 20$ mV s^{-1}, potentials vs. NHE).

Complexes **1** and **3** are diamagnetic as evidenced by their high-resolution NMR spectra. The ^{1}H NMR spectrum of [Ni(‘^{bu}S$_2$’)$_2$] (**3**) in C_6D_6 at 25°C shows two sharp tertiary butyl singlets at 1.15 and 1.77 ppm and two broadened signals at 7.6 and 8.2 ppm for the aromatic protons. Interestingly, in the ^{1}H NMR spectrum of (AsPh$_4$)$_2$[Ni(‘^{bu}S$_2$’)$_2$] (**1**) in $(CD_3)_2CO$ only one broad tertiary-butyl signal at 1.95 ppm and one singlet for the four ‘^{bu}S$_2$’ benzene ring protons appeared. These signals could not be resolved by lowering the temperature, because (AsPh$_4$)$_2$[Ni(‘^{bu}S$_2$’)$_2$] precipitated from the solution. The number of ^{1}H NMR signals could indicate that the anion of **1** forms isomers in solution, and upon crystallization only the centrosymmetric species characterized by X-ray structure analysis precipitates. Complex **2** is paramagnetic and did not yield a ^{1}H NMR spectrum, but an EPR spectrum (Fig. 3).

At 293 K, (AsPh$_4$)[Ni(‘^{bu}S$_2$’)$_2$] (**2**) dissolved in $CHCl_3$–DMF shows an isotropic signal with $<g> = 2.08$. This signal is split into a rhombic signal at 120 K with $g_1 = 2.18$, $g_2 = 2.04$ and $g_3 = 2.01$. In order to get more detailed information on the metal character of the SOMO, a ^{61}Ni enriched sample of (AsPh$_4$)[Ni(‘^{bu}S$_2$’)$_2$] (**2**) was prepared with an enrichment of 86.2%. This sample showed at 120 K an EPR spectrum with identical *g* values as unlabelled **2**. In addition, a strong hyperfine coupling of the unpaired electron with the magnetically active ^{61}Ni nucleus ($I = 3/2$) was observed, with $A_1(^{61}\mathrm{Ni}) = 131(15)$, $A_2(^{61}\mathrm{Ni}) < 17$ and $A_1(^{61}\mathrm{Ni}) = 57(10)$ mT. This observation clearly demonstrates a considerable metal contribution to the SOMO. Similar *g* and *A* values were observed for (NR$_4$)[Ni(S$_2$C$_2$(CN)$_2$)$_2$] [20] and (NR$_4$)[Ni(xylene-1,2-dithiolate)$_2$] [21]. They were controversially interpreted to indicate an unpaired electron occupying a nickel centered SOMO with some sulfur character [20] or a ligand centered SOMO with some nickel character [21]. Thus the question remained open, whether such complexes must be described as Ni^{III} complexes or rather radical ligand complexes stabilized by Ni^{II} centers. The same would hold true for (AsPh$_4$)[Ni(‘^{bu}S$_2$’)$_2$] (**2**). It is noted, however, that the $<g> = 2.0103(1)$ value of the 2,4,6-tritertiarybutyl-benzene-thiyl radical [22] is clearly different from the *g* values observed for the nickel complexes.

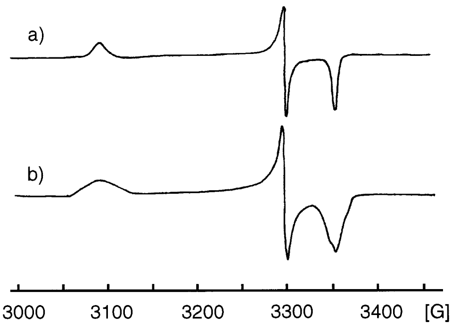


Fig. 3. EPR spectra of (AsPh$_4$)[Ni(‘^{bu}S$_2$’)$_2$] (**2**) in CHCl$_3$/DMF at 120 K (9.43 GHz, 100 kHz sweep width, 20.1 W (a) and 63.5 mW (b): (a) with natural abundance of ^{61}Ni; (b) with 86.2% of ^{61}Ni).

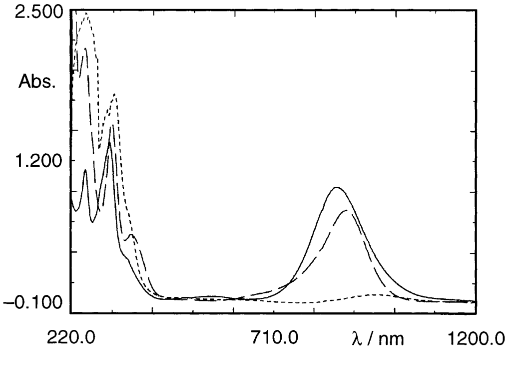


Fig. 4. UV–Vis–NIR spectra of (AsPh$_4$)$_2$[Ni(‘^{bu}S$_2$’)$_2$] (**1**), (AsPh$_4$)[Ni(‘^{bu}S$_2$’)$_2$] (**2**) and [Ni(‘^{bu}S$_2$’)$_2$] (**3**), (10^{-4} M in THF).

Fig. 4 shows the UV–Vis spectra of **1**, **2** and **3** in THF (10^{-4} M). They exhibit the typical π–π* benzene ring absorptions at 300 nm, **2** and **3** show additional intensive absorptions at 860 and 880 nm, respectively.

For nickel dithiolene complexes, bands in this region have been assigned to ligand→metal CT bands of the type $\pi(L) \rightarrow \pi_1$ [23], which are impossible in complexes having formally d^8 Ni^{II} centers, because π_1 is fully occupied.

3.4. XPS investigations

In order to determine the influence of the overall charge upon the nickel oxidation state in **1**, **2** and **3**, XPS measurements were also carried out for the Ni 2p$_{3/2}$ and S 2p binding energies (E_b). It is to be noted that the calibration of XPS data can be difficult because the reported E_b values tend to be severely influenced by secondary effects, the preparation of the probes, and the standards. For example, three different E_b (Ni 2p$_{3/2}$) values have been reported for (NBu$_4$)[Ni(S$_2$C$_2$(CN)$_2$)$_2$] (853.1 eV [24], 856.6 eV [25] and 857.3 eV [26]). E_b (Ni 2p$_{3/2}$) values for square planar Ni complexes with [NiS$_4$] cores range from 852.8 eV [24] to 859.7 eV [27]. The latter value is close to that of K$_2$NiF$_6$ (861.2 eV) [28] which is considered to contain ‘genuine’ Ni^{IV} centers. The only investigation on three different oxidation states of square planar NiS$_4$ species was reported for (NBu$_4$)$_n$[Ni(dmit)$_2$], $n = 2, 1, 0$ (dmit^{2-} = dimercapto-isotrithione(2−)) [29], in which no significant change was found for the E_b (Ni 2p$_{3/2}$) values. The E_b (S 2p) value of the thiolate sulfur donors showed a slight trend from 163.9 eV in (NBu$_4$)$_2$[Ni(dmit)$_2$] to 162.8 eV in neutral [Ni(dmit)$_2$]. The oxidation was interpreted as strictly ligand centered.

For these reasons, the XPS spectra of **1**, **2**, **3** were recorded under strictly identical conditions. Table 3

Table 3
Binding energies E_b, FWHM [a] (eV) of $1 \cdot 2Et_2O$, **2** and **3**

Compound	Ni(II)	Ni(III)	Ni(IV)
E_b (Ni $2p_{3/2}$)	858.1(1.3)	859.7(1.7)	860.5(1.8)
E_b (S 2p)	not measured	162.4(2.2)	163.4(2.5)

[a] Full-width at half maximum.

lists the results. The data show a clear trend for both the E_b (Ni $2p_{3/2}$) and E_b (S 2p) values, which both increase with formally increasing Ni oxidation states.

The E_b (Ni $2p_{3/2}$) increase of 2.4 eV lies in the same range as the difference of 3.3 eV between NiF_2 (857.5 eV) and K_2NiF_6 (860.8 eV) [28], and it contrasts the $[Ni(dmit)_2]^{2-/1-/0}$ series, which shows no significant E_b (Ni $2p_{3/2}$) changes. Thus, the XPS data also support the conclusion that the oxidation of **1** to **3** is neither ligand nor metal-centered but instead concerns electrons in molecular orbitals of $[NiS_4]$ character.

4. Conclusions

Square-planar nickel thiolate complexes with $[NiS_4]$ cores in three different oxidation states have been synthesized and unambiguously characterized. The $[Ni(\text{'}^{bu}S_2\text{'})_2]^{n-}$ species with $n = 2, 1, 0$ can be converted into each other by redox reactions, and the redox potentials lie in the range observed also for alkane–dithiolate complexes. The Ni–S distances slightly, but significantly, decrease when the nickel oxidation state formally increases from +2 via +3 to +4 in **1**, **2** and **3**. The formal oxidation state increase corresponds with the 2.4 eV increase of Ni $2p_{3/2}$ binding energies observed by XPS. The E_b (Ni $2p_{3/2}$) difference between **1** and **3** is of the same order as the difference of 3.3 eV between NiF_2 and K_2NiF_6, which are taken as standard Ni^{II} and Ni^{IV} complexes. The increasing E_b (S 2p) values of **1**, **2** and **3** demonstrate that the oxidation **1** → **3** also influences the sulfur electrons. Thus, the X-ray structural and XPS data suggest that the oxidation of **1**–**3** concerns electrons which reside in orbitals having $[NiS_4]$ character. This is in accord with the chemical properties of **1**, **2** and **3**, whose $[Ni(\text{'}^{bu}S_2\text{'})_2]$ species behave as typical covalent metal complexes.

No evidence could be obtained that the electronic changes in **1**, **2** and **3** extend beyond the nickel sulfur core into the benzene rings. The observed hyperfine interaction with the nickel center in the EPR spectrum of **2** demonstrates considerable nickel contribution to the SOMO. All results considered together suggest that 1,2-benzenedithiolate(2−) and its $\text{'}^{bu}S_2\text{'}^{2-}$ derivatives are normal 1,2-dithiolate ligands. A similar conclusion had previously been drawn for iron 1,2-benzenedithiolate complexes [30]. A significant nickel character of the frontier orbitals in $[Ni(\text{'}^{bu}S_2\text{'})_2]$ complexes may finally be concluded from the reactivity of **1** and **2** and the remarkable inertness of **3** towards CO.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-137423 ($\mathbf{1} \cdot 2Et_2O$), 137424 (**2**), 137425 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

Support of this work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged. We wish to thank Dr M. Moll for the recording of NMR spectra and W. Donaubauer for technical assistance in the X-ray diffraction studies. We are also indebted to Dr A. Elvers and Dr M. Meth for recording the EPR spectra.

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