follows the proposal for the biosynthesis made by Nandi and Shemin almost 30 years ago. In contrast to the published syntheses of **11**, the correctly functionalized side chains are introduced with the two starting materials used for the synthesis of the pyrrole ring; subsequent functionalization is therefore not necessary. The bonds formed in this synthetic scheme are the same as those formed in the biosynthesis catalyzed by porphobilinogen synthase. The overall yield starting from 5-phthalimidomethyllevulinate is 25%. The synthesis can be used to obtain selectively labeled porphobilinogen.

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[13] NMR data of the protected porphobilinogen **11**: ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 8.56$ (br. s, 1H, NH), 7.83–7.76 (m, 2H, $HC5^4$, $HC5^{4'}$), 7.73–7.67 (m, 2H, $HC5^5$, $HC5^{5'}$), 6.49 (d, $J = 2.7$ Hz, 1H, HC2), 4.80 (s, 2H, H_2C5^1), 3.67 (s, 3H, H_3C3^4), 3.65 (s, 3H, H_3C4^3), 3.64 (s, 2H, H_2C4^1), 2.72 (pseudo t, $J \approx 7.6$ Hz, 2H, H_2C3^1), 2.53 (pseudo triplet, $J \approx 7.3$ Hz, 1H, H_2C3^2); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 174.4$ (s, $C3^3$), 173.1 (s, $C4^2$), 169.0 (s, $C5^2$, $C5^{2'}$), 134.7 (d, $C5^5$, $C5^{5'}$), 132.7 (s, $C5^3$, $C5^{3'}$), 125.3 (s, C5), 124.0 (s, $C5^4$, $5^{4'}$), 122.2 (s, C4), 116.0 (d, C2), 113.7 (s, C3), 52.6 (q, $C3^4$), 52.1 (q, $C4^3$), 35.3 (t, $C3^2$), 33.0 (t, $C5^1$), 30.3 (t, $C4^1$), 21.2 (t, $C3^1$).

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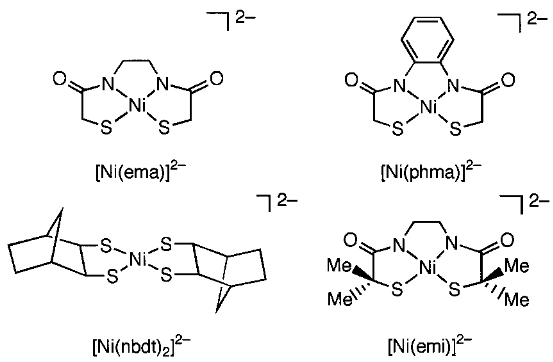
First Isolation and Structural Characterization of a Nickel(III) Complex Containing Aliphatic Thiolate Donors[**]

Jan Hanss and Hans-Jörg Krüger[*]

Dedicated to Professor Richard H. Holm
on occasion of his 65th birthday

The discovery of a nickel site with a thiolate-rich ligand environment in hydrogenases some 15 years ago stimulated considerable interest in nickel(II) thiolate complexes and their redox behavior.[1] Because of the recent crystal structure determination of the enzyme from the sulfate-reducing bacterium *Desulfovibrio gigas*, the initial description of the nickel site as a mononuclear metal center was revoked, and the heterobimetallic nature firmly established.[2] Efforts towards modeling the structure and reactivity of the active site in nickel-containing hydrogenases are now shifting from the synthesis of mononuclear nickel thiolate complexes towards the synthesis of thiolato-bridged iron–nickel complexes. However, one of the original tasks for inorganic chemists has, to our knowledge, never been accomplished: namely, the preparation *and* isolation of a stable mononuclear nickel(III) complex with aliphatic thiolate donors[3] in the coordination environment. Here we report on the first successful isolation and structural characterization of such a complex.

Previous endeavors to synthesize mononuclear nickel(III) complexes with aliphatic thiolates utilized the nickel(II) complexes depicted in Scheme 1.[4] Although solutions of the relatively stable nickel(III) complexes $[Ni(nbdt)_2]^-$ and $[Ni(emi)]^-$ [4] could be electrochemically generated, no solid compounds were isolated. Recently, we showed that stable copper(II) and even copper(III) complexes can be prepared with the quadruply deprotonated ligand *N,N'*-1,2-phenylenebis(2-sulfanyl-2-methylpropionamide) (H_4phmi).[5] With respect to its donor-atom set, H_4phmi is related to some of the



Scheme 1. Nickel(II) complexes with aliphatic thiolate ligands which have been used to electrochemically generate nickel(III) complexes in solution.[4]

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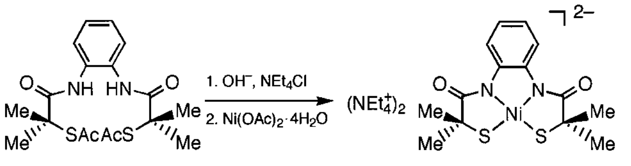
ligands depicted in Scheme 1. In general, nickel(III) complexes are more difficult to synthesize than copper(III) complexes, because Ni^{III}/Ni^{II} redox potentials are more positive than those of isostructural Cu^{III}/Cu^{II} redox pairs.[6] In addition, presumably due to the presence of an unpaired electron, nickel(III) complexes display a more pronounced tendency to decompose than the corresponding copper(III) complexes. One of the major obstacles to the synthesis of nickel(III) thiolate complexes is autoreduction of the metal ion by the coordinated thiolates with concomitant formation of disulfides.[7] This seems to be less of a problem when the thiolate-donor functionality is somewhat sterically protected, as in $[Ni(nbdt)_2]^-$ and $[Ni(emi)]^-$. For nickel(III) amidate complexes, a well-known decomposition pathway involves the presence of a hydrogen atom in an α position with respect to the amidato functionality.[8] Because no hydrogen atom is present in an α position to any donor functionalities in H_4phmi, in contrast to the amidethiol ligands used in previous studies, this ligand was deemed suitable for synthesizing nickel(III) complexes that are stable enough to be isolated.

The red nickel(II) complex $(NEt_4)_2[Ni(phmi)]$ (**1**) was prepared according to Equation (a). Based on the diamagnetism and electronic absorption spectrum of the complex, a square-planar coordination geometry is attributed to the nickel ion. Owing to severe disorders in the crystal lattice of **1**, a structure determination was carried out on a single crystal of $K(PPh_4)[Ni(phmi)]$ (**2**).[9] As expected, the nickel ion is coordinated to two deprotonated amide and two thiolate groups. In agreement with the results for **1**, the NiN_2S_2 coordination environment in **2** is essentially square planar, and the nickel ion deviates from the least-squares N_2S_2 plane by only 0.022 Å. The potassium ion bridges the two thiolate sulfur atoms (3.173–3.208 Å) and is further bound in a tetrahedral geometry to two amide oxygen atoms of adjacent $[Ni(phmi)]^{2-}$ moieties (2.559–2.672 Å). Despite the coordinated potassium ion, the average Ni–N and Ni–S bond lengths of 1.879 ± 0.005 and 2.171 ± 0.005 Å, respectively, (see legend of Figure 1) are very similar to those found in $[Ni(ema)]^{2-}$.[4b] Electrochemical data suggest that in solution the potassium ion is no longer bound to the complex anion $[Ni(phmi)]^{2-}$.



(a)

$(NEt_4)_2[Ni(phmi)]$ **1**

The cyclic voltammograms of complexes **1** and **2** in acetonitrile reveal an electrochemically reversible oxidation at −0.71 V (versus the ferrocene/ferrocenium redox potential; all following potentials are given with respect to this redox pair). Quantitative electrolysis at −0.51 V provides a blue solution after the passage of 0.98 electrons per complex anion; upon re-reduction of the solutions at −0.91 V, more than 95% of the original nickel(II) complex is recovered. Spectrophotometric examination of the stability of the dissolved oxidized complex over time reveals that even after 50 days under an atmosphere of nitrogen 90% of the complex $[Ni(phmi)]^-$ is still present. This observation warrants the claim that isolation of the oxidized species is feasible. Indeed, quantitative bulk electrolysis of **2** in acetonitrile results in analytically pure crystals of blue $(PPh_4)[Ni(phmi)]$ (**3**) after recrystallization from acetone/diethyl ether.

The structure determination of **3** (Figure 1)[9] demonstrates that the coordination environment and the square-planar coordination geometry around the nickel ion are preserved upon oxidation (the nickel ion deviates from the least-squares N_2S_2 plane by 0.007 Å). Within a distance of 6 Å there are no axial donor atoms at the nickel ion. With respect to **2**, the average Ni–N and Ni–S bond lengths in **3** are reduced to 1.856 ± 0.007 Å and 2.114 ± 0.005 Å, respectively. A comparison of the C–C and C–N bond lengths of the phenylenediamide moieties of **2** and **3** indicates essentially no change within the 3σ criterion. In addition, these bond lengths are very different from those reported for an oxidized cobalt complex,[10] in which oxidation does take place at the phenylenediamide portion of the ligand (Table 1). Although the interatomic S–S distance substantially decreases from 3.224 Å in **2** to 3.069 Å in **3**, there is no bonding interaction between the two sulfur atoms. These structural results serve as the first piece of evidence that the oxidation is mainly metal-centered. A substantial shortening of the Ni–N and Ni–S bonds is not expected to occur, since the electron is not removed from a strongly σ-antibonding orbital during the oxidation of the nickel(II) complex. The rather modest decrease of 0.023 Å for the Ni–N bonds is related to the stronger electrostatic interactions between the more electro-

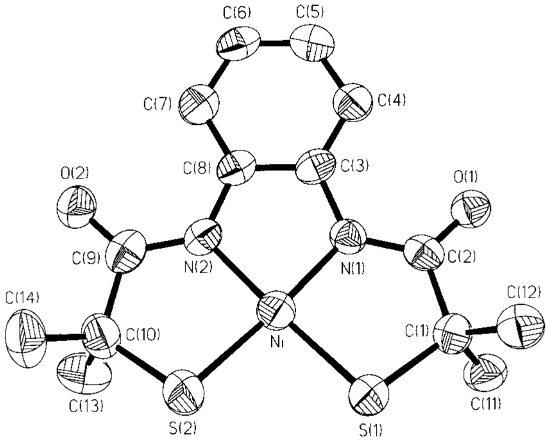


Figure 1. Perspective view of the structure of the $[Ni(phmi)]^-$ ion in **3** (thermal ellipsoids at the 50% probability level) and the atom-numbering scheme. Selected bond lengths [Å] and angles [°] in the $[Ni(phmi)]^-$ ion [in the two crystallographically independent $[Ni(phmi)]^{2-}$ ions in the crystal lattice of **2**]: Ni–S(1) 2.119(3) [2.168(1), 2.174(1)], Ni–S(2) 2.109(3) [2.166(1), 2.174(1)], Ni–N(1) 1.849(6) [1.878(2), 1.874(2)], Ni–N(2) 1.863(7) [1.882(2), 1.880(2)]; S(1)-Ni-S(2) 93.11(11) [96.09(3), 96.10(3)], S(1)-Ni-N(1) 90.40(22) [89.35(6), 89.20(6)], S(1)-Ni-N(2) 176.19(24) [175.18(6), 174.89(6)], S(2)-Ni-N(1) 175.59(23) [174.07(6), 174.66(6)], S(2)-Ni-N(2) 90.27(23) [88.73(6), 88.96(6)], N(1)-Ni-N(2) 86.31(30) [85.85(8), 85.74(8)].

Table 1. Bond lengths [Å] in the phenylenediamide moieties of $[Ni(phmi)]^{2-}$, $[Ni(phmi)]^-$, $[Co^{III}(L)]^-$, and $[Co^{II}(L)]$.

	$[Ni(phmi)]^{2-}$[a]	$[Ni(phmi)]^-$	$[Co^{III}(L)]^-$[b]	$[Co^{II}(L)]$[b]
N(1)–C(3)	1.420(3)	1.419(9)	1.415(3)	1.353(6)
N(2)–C(8)	1.414(3)	1.412(10)	1.406(3)	1.353(6)
C(3)–C(4)	1.399(3)	1.389(11)	1.376(4)	1.398(7)
C(4)–C(5)	1.396(4)	1.390(11)	1.387(4)	1.350(8)
C(5)–C(6)	1.382(4)	1.361(12)	1.380(4)	1.428(10)
C(6)–C(7)	1.399(4)	1.387(11)	1.386(4)	1.350(8)
C(7)–C(8)	1.401(3)	1.401(11)	1.387(4)	1.398(7)
C(3)–C(8)	1.422(3)	1.414(11)	1.411(4)	1.432(9)

[a] Averaged bond lengths from the two crystallographically distinct complex anions. [b] From ref. [10], with the numbering schemes adapted to those of complexes **2** and **3**.

positive central ion and the negatively charged ligand donor atoms. The slightly greater decrease in the Ni–S bond length by 0.057 Å may be explained by the lack of a potassium ion bridging the two sulfur atoms in **3**.

The magnetic moment of **3** is 1.78 μ_B, which corresponds to a low-spin complex. As with $[Ni(emi)]^-$,[4b] no ESR spectrum is observed for **3** at room temperature or at 100 K. However, at 10 K a spectrum of solid **3** doped into the isomorphous crystal lattice of the diamagnetic complex $(PPh_4)[Cu(phmi)]$ reveals a very broad rhombic signal with apparent g values at 2.55, 2.14, and 2.00. This indicates a short electron spin relaxation time due to a relatively small energy separation between the electronic ground and excited states. This conclusion is also supported by the observation that the NIR region of the electronic absorption spectrum of **3** contains a d–d transition at rather low energy (5120 cm^{-1}). In the presence of excess pyridine (py) in the solution of **3**, the powder spectrum of the frozen solution at 100 K (Figure 2) shows a nearly axial signal with g values at 2.313, 2.281, and 2.000. The splitting of the g_z component into three lines of equal intensities due to superhyperfine coupling ($A_z^N = 25$ G) with the nuclear spin ($I_N = 1$) of a single nitrogen donor atom is consistent with the formation of the monoadduct $[Ni(phmi)(py)]^-$. The formation of a similar monoadduct upon addition of pyridine to a solution containing the complex $[Ni(emi)]^-$ was reported.[4b] The large anisotropy and the average g values of 2.23 and 2.20 for $[Ni(phmi)]^-$ and $[Ni(phmi)(py)]^-$, respectively, indicate that the unpaired electron mainly resides in a metal-based orbital. The fact that g_x and g_y are larger than g_z and that g_z is 2.00, together with the observation of a superhyperfine splitting of the g_z component, clearly establish a $\ldots(d_{z^2})^1$ electron configuration for the ground state of $[Ni(phmi)(py)]^-$. The observation of an ESR spectrum at 100 K only after addition of pyridine is interpreted to mean that axial coordination of a pyridine molecule raises the energy of the d_{z^2} orbital enough to cause less mixing between the ground and the excited states and, therefore, an increase of the electron spin relaxation time.

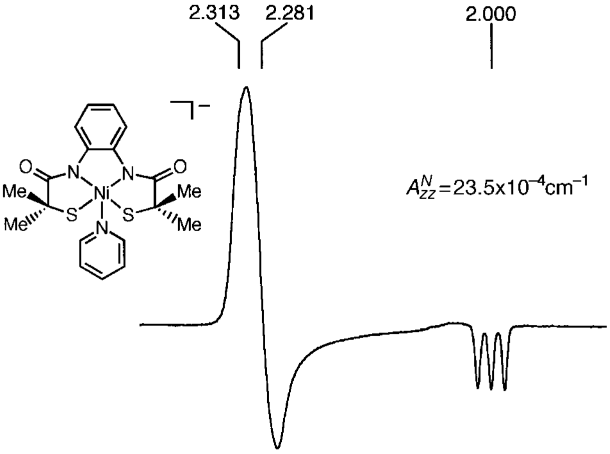


Figure 2. X-band ESR spectrum of a frozen solution of $[Ni(phmi)(py)]^-$ ions in dimethylformamide containing excess pyridine at 100 K (the g values are indicated).

The results presented here reveal that the oxidized species contains an authentic nickel(III) ion coordinated to aliphatic thiolate groups. In dimethylformamide, the Ni^{III}/Ni^{II} redox potential of **1** (−0.78 V) is about 120 mV more positive than that of $[Ni(emi)]^{2-}$, although the stability of the oxidized complex $[Ni(emi)]^-$ is inferior to that of **3**. Therefore, our investigation demonstrates that the stability of nickel(III) thiolate complexes is determined only to a certain extent by the lowest possible redox potential; abolishing or at least retarding possible decomposition pathways (e.g. by introducing steric hindrance around the thiolate donors or by avoiding the presence of any hydrogen atoms in an α position to the donor functionalities in the ligand) plays a larger role, at least for the currently discussed amidato–thiolato nickel complexes.

The original challenge for inorganic chemists to prepare *and* isolate stable nickel(III) complexes with aliphatic thiolates in the coordination sphere has finally been met. However, as with the recently reported copper complexes, the stabilization of the high oxidation state of the nickel ion is only achieved because the highly polarizable, negatively charged nitrogen donor atoms of the deprotonated amide functionalities can supply the electropositive metal ion with sufficient electron density to avoid autoreduction of the nickel(III) ion by the coordinated aliphatic thiolates.

Experimental Section

1: Under strictly anaerobic conditions, a solution of *N,N'*-1,2-phenylenebis(*S*-acetyl-2-sulfanyl-2-methylpropionamide) (200 mg, 0.5 mmol), KOH (140 mg, 2.5 mmol), and NEt_4Cl (166 mg, 1.0 mmol) in absolute EtOH (40 mL) was stirred for 0.5 h before a suspension of $Ni(OAc)_2 \cdot 4H_2O$ (124 mg, 0.5 mmol) in absolute EtOH (30 mL) was added. After the reaction mixture was heated at reflux for a short time, the solvent was completely removed in vacuo. The residue was treated with CH_3CN (40 mL), and the resulting red solution filtered. Slow diffusion of Et_2O into the solution in CH_3CN afforded a red crystalline material, which was collected, washed with Et_2O, and dried in vacuo to yield analytically pure **1** (235 mg, 75 % yield). Elemental analysis calcd for $C_{30}H_{56}N_4NiO_2S_2$: C 57.41, H 8.99, N 8.93; found: C 57.18, H 8.85, N 8.90; absorption spectrum (CH_3CN): λ_{max} (ε_M) = 550 (85.6), 439 (280), 359 (7020), 248 (36900), 232 nm (37600); ^1H NMR (360 MHz, CD_3CN, anion): δ = 8.64 (dd, 2H), 6.46 (dd, 2H), 1.23 (s, 12H).

Complex **2** was synthesized analogously with PPh_4Cl. However, based on the elemental analysis and the NMR spectrum, **2** is contaminated with $(PPh_4)_2[Ni(phmi)]$.

3: In a glove box, a mixture of $K(PPh_4)[Ni(phmi)]$ and $(PPh_4)_2[Ni(phmi)]$ (0.336 mmol based on the passed charge) in CH_3CN (10 mL) containing

0.05 M PPh_4Cl as supporting electrolyte was exhaustively oxidized at −0.51 V. The electrolysis was carried out at a platinum-net electrode with a PAR Model 273A Potentiostat/Galvanostat controlled by the PAR Model 270 Research Electrochemistry Software. After the oxidation was completed, the electrolyte PPh_4Cl was precipitated by diffusion of Et_2O into the resulting blue solution. Removal of the solvent from the filtered solution yielded a dark blue solid, which was redissolved in acetone (10 mL) under nitrogen. Diffusion of Et_2O into this solution afforded analytically pure **3** as dark blue, leafletlike crystals (128 mg, 54 % yield). Elemental analysis calcd for $C_{38}H_{36}N_2NiO_2PS_2$: C 64.60, H 5.14, N 3.97; found: C 64.63, H 5.12, N 4.12; absorption spectrum (CH_3CN): λ_{max} (ε_M) = 1953 (54.5), 940 (sh, 3410), 843 (3970), 573 (1330), 388 (3070), 337 (sh, 3710), 274 (sh, 21400), 266 (sh, 25700), 253 (sh, 28700), 230 nm (60600).

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[9] Crystallographic data for **2**: triclinic, space group $P\bar{1}$, $a = 13.149(2)$, $b = 14.778(3)$, $c = 19.541(6)$ Å, $\alpha = 88.00(2)$, $\beta = 72.99(1)$, $\gamma = 77.96(1)^\circ$, $V = 3550(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.395$ g cm^{-3}; $T = 153$ K; 2θ range $4.6^\circ < 2\theta < 50^\circ$; 12577 unique reflections (9891 with $F_o > 4\sigma(F_o)$), $\mu(Mo_{K\alpha}) = 8.63$ cm^{-1}; 853 parameters; $R = 0.0333$ ($F_o > 4\sigma(F_o)$). Crystallographical data for **3**: monoclinic, space group $P2_1/n$, $a = 14.157(7)$, $b = 11.342(4)$, $c = 21.032(5)$ Å, $\beta = 98.92(2)^\circ$, $V = 3336(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.407$ g cm^{-3}; $T = 153$ K; 2θ range $7^\circ < 2\theta < 120^\circ$; 4954 unique reflections (2546 with $F_o > 4\sigma(F_o)$), $\mu(Cu_{K\alpha}) = 27.54$ cm^{-1}; 418 parameters; $R = 0.0678$ ($F_o > 4\sigma(F_o)$). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100465. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. code + (49) 1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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