Nickel(II) complexes bound to an [Fe_4S_4] cluster *via* bridging thiolates: synthesis and crystal structures of model compounds for the active site of nickel CO dehydrogenase

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[NiL] [L = $^{-}SCH_2CH_2N(Et)CH_2CH_2CH_2N(Et)CH_2CH_2S^{-}$] 1 reacts with [$Fe_4S_4I_4$]$^{2-}$ 2 to afford [$(NiL)_2Fe_4S_4I_2$] 3; in 3 the two fragments of 1 are doubly bridged *via* μ-sulfur of L to iron atoms of the [Fe_4S_4] core.

The attachment of transition-metal centres to [Fe_4S_4] units *via* bridging thiolate-S (from cysteine) or sulfide-S atoms is an interesting structural feature in certain oxidoreductases.[1] While an [Fe_4S_4] cluster and a sirohaem connected by a cysteinyl sulfur are revealed by the X-ray structure of *Escherichia coli* sulfite reductase,[2] indications of a related [Fe_4S_4]–X–Ni motif in nickel CO dehydrogenase[3] (CODH) and some NiFe–H_2 ases[4] come from spectroscopic data (for the first crystal structure of the [NiFe] hydrogenase from *Desulfovibrio gigas*, see Volbeda *et al.*[4]).

According to a current mechanistic proposal for CODH it is the close interaction of the [Fe_4S_4] core and the nickel ion that enables rapid substrate conversion.[5]

When stoichiometric mixtures of the neutral nickel aminothiolate **1** and the tetraiodo cluster anion **2** in acetonitrile are kept at ambient temperature substitution of two iodides leads to the novel [$Ni_2Fe_4S_4$] cluster **3** [eqn. (1)] which can be isolated after 24 hours as black needles.

$$\underset{\mathbf{1}}{2[\mathrm{NiL}]} + \underset{\mathbf{2}}{[\mathrm{Fe_4S_4I_4}]^{2-}} \longrightarrow \underset{\mathbf{3}}{[(\mathrm{NiL})_2\mathrm{Fe_4S_4I_2}]} + 2\ \mathrm{I^-} \qquad (1)$$

The neutral cluster contains formally two Ni^{II}, two Fe^{II} and two Fe^{III} ions and was characterized by CV, IR, UV–VIS, elemental and crystal-structure analysis.†

Although examples of substitution reactions of anionic ligands by uncharged molecules are rare in the chemistry of iron–sulfur clusters, reaction (1) can easily be rationalized in terms of reactivity schemes exhibited by related nickel(II) thiolates.[6] The coordinated thiolate-S atoms undergo alkylation reactions with MeI and form μ-S-bridged oligomeric transition-metal complexes from additional metal halogenides. This demonstrates the nucleophilicity of nickel(II)-bound thiolate-S functions.

In dichloromethane solution, **3** exhibits a quasi-reversible oxidation wave, at 150 mV *vs.* SCE; this value lies between those of [$Fe_4S_4(SBu^t)_4$]$^{2-}$ (−110 mV *vs.* SCE in Me_2SO)[8a] and [$Fe_4S_4I_4$]$^{2-}$ clusters (550 mV *vs.* SCE in CH_2Cl_2).[8b]

Metathesis of iodide in **3** with thiolate using KSPh in CH_2Cl_2 solution yields [$(NiL)_2Fe_4S_4(SPh)_2$] **4** and KI. After filtration and addition of tetrahydrofuran, black crystals of **4** separate after 24 h, which were characterized by IR, UV–VIS and elemental analysis.‡

The corresponding monosubstituted cluster anion [$NiLFe_4S_4I_3$]$^-$ has also been obtained but so far only from dichloromethane with the trinuclear counter ion [NiLNiLNi]$^{2+}$ as salt **5** with very low solubility. By-products as well as the formation of the cation of **5** indicate that the poor reliability of the synthesis of **5** is due to reaction of the solvent with thiolates of the nickel complex *before* substitution at the Fe–S cluster (**3** is stable in CH_2Cl_2 solution). A crystal structure analysis of **5** with poor quality data revealed similar structural features to those observed in **3** (see below).

Compound **3** crystallizes as an acetonitrile solvate, **3**·2 MeCN. The neutral cluster exhibits crystallographic C_2 symmetry (Fig. 1). The [Fe_4S_4] core is significantly distorted with the longest Fe···Fe distance between Fe(2) and Fe(2a) [3.113(2) Å]. Both the fivefold coordination of these atoms and the Fe···Ni contacts [2.827(1) Å] seem to weaken the bonds between these iron atoms.

This is confirmed by crystal structures with anionic bidentate dithiocarbamates (dtc) as ligands [$Fe_4S_4(dtc)_2X_2$] (X = Cl^-, PhS^-) where a similar coordination leads to Fe···Fe distances not longer than 3.053 Å.[9] In mixed terminal ligand iron–sulfur cubane clusters with cyclopentadienyl and dithiolene coordination, even longer Fe···Fe distances than found in **3** are observed.[11] However, due to the quite different electronic properties of these ligands, the structures are not comparable with **3**.

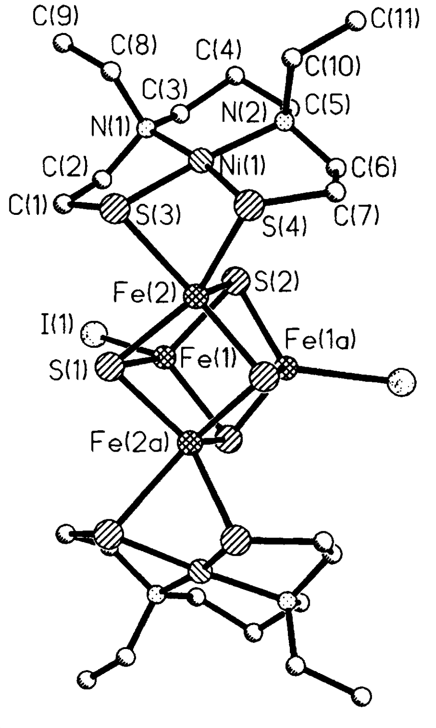

Fig. 1 Molecular structure of **3** (crystallographic C_2 symmetry) with atom numbering scheme (hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Fe(1)–S(1) 2.219(2), Fe(1)–S(2) 2.300(2), Fe(1)···Fe(1a) 2.804(2), Fe(1)···Fe(2) 2.784(1), Fe(2)···Fe(2a) 3.113(2), Fe(1)–I(1) 2.564(1), Fe(2)–S(1) 2.356(2), Fe(2)–S(2) 2.282(2), Fe(2)–S(3) 2.464(2), Fe(2)–S(4) 2.533(2), Fe(2)···Ni(1) 2.827(1), Ni(1)–S(3) 2.158(2), Ni(1)–S(4) 2.178(2), Ni(1)–N(1) 2.000(7), Ni(1)–N(2) 1.982(6), S(3)–Fe(2)–S(4) 69.39(7), S(4)–Ni(1)–S(3) 82.00(9), Ni(1)–S(3)–Fe(2) 75.08(7), Fe(2)–S(4)–Ni(1) 73.32(7), Ni(1)···S(2) 3.176(2).

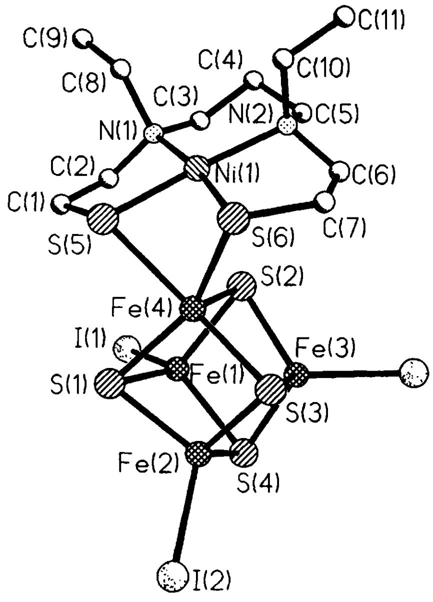

Fig. 2 Molecular structure of the monoanionic cluster of **5** with atom numbering scheme (hydrogen atoms omitted for clarity). Selected bond lengths (Å): Fe(1)···Fe(2) 2.740(5), Fe(1)···Fe(3) 2.753(5), Fe(1)···Fe(4) 2.820(5), Fe(2)···Fe(3) 2.718(5), Fe(2)···Fe(4) 2.952(5), Fe(3)···Fe(4) 2.826(5), Fe(4)···Ni(1) 2.806(5), Fe(4)–S(1) 2.363(8), Fe(4)–S(3) 234.7(8), Fe(4)–S(5) 2.519(8), Fe(4)–S(6) 2.536(9), Ni(1)···S(2) 3.179(8).

Coordination geometries with open sites like those found in **3** at Ni(1) and Fe(2) (see Fig. 1) are structural prerequisites for reaction with substrates at the active centres.

Another interesting structural detail is the weak interaction between Ni(1) and S(2) at 3.176(2) Å (see Fig. 1). The reinforcement of this contact would lead not only to a square-pyramidal coordination but also to a different electronic ground state of nickel.

Cluster **3** supplies the first proof of the existence of thiolate-bridged Ni–μ-S–Fe_4S_4 assemblies, which until now were only postulated from spectroscopic data obtained from the enzymes mentioned above and which is in reasonable agreement with EXAFS data.[10]

The preliminary crystal structure of **5** shows that, compared to **3**, the arrangement of the coordinated nickel complexes is very similar (Fig. 2), as are the Ni···Fe distances [**5**: Ni(1)···Fe(4) 2.806(5) Å]. As only one of the Fe atoms is five-coordinate in **5** the longest Fe···Fe distance [Fe(2)···Fe(4) 2.952(5) Å] is significantly shorter than in **3**.

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Footnotes

† The nickel complex **1** was synthesized by the same method as for the *N,N′*-dimethyl derivative.[7] Cluster **2** was used as its benzyltributylammonium salt,[8b] and the reaction was carried out under a nitrogen atmosphere in dried and degassed solvents. Cluster **3** was isolated in 82% yield. Anal. Calc. for **3**·2 MeCN ($C_{26}H_{54}Fe_4I_2N_6Ni_2S_8$): C, 23.99; H, 4.18; N, 6.46; S, 19.70. Found: C, 24.10; H, 4.24; N, 6.57; S, 20.02%. λ_{max} (CH_2Cl_2) 260, 385, 510 nm. IR (KBr): 2967m, 2928m, 2891m, 2863m, 2245w (MeCN), 1460m, 1435s, 1404w, 1381m, 1364m, 1296s, 1275m, 1244w, 1219w, 1198w, 1109s, 1051w, 1038m, 1007s, 990m, 972m, 955w, 936w, 868w, 791w, 741s, 721s, 683w, 569m, 544m, 380s, 361m, 280s cm^{-1}.

‡ *Compound* **4**: λ_{max} (CH_2Cl_2) 245, 455 nm. IR (KBr): 3065w, 3042w, 2965w, 2924w, 1574s, 1470s, 1433s, 1408w, 1379m, 1362w, 1298m, 1275w, 1240w, 1219w, 1196w, 1109m, 1082m, 1063m, 1040w, 1022m, 1005m, 986w, 974w, 909w, 870w, 783w, 739s, 719s, 696s, 567w, 544w, 476w, 424w, 388s, 368s, 351s, 287m cm^{-1}. Anal. Calc. for **4** ($C_{34}H_{58}N_4S_{10}Fe_4Ni_2$): C 34.48, H 4.94, N 4.73, S 27.07. Found: C 34.80, H 4.76, N 4.72, S 27.51%.

§ *Crystal data* for **3**·2MeCN, $C_{26}H_{54}Fe_4I_2N_6Ni_2S_8$, M = 1301.81, tetragonal, space group $I4_1cd$, a = 20.888(1), c = 20.532(1) Å, U = 8958.3(7) $Å^3$, T = 296 K, Z = 8, D_c = 1.931 g cm^{-3}, μ(Mo-Kα) = 3.864 mm^{-1}. A suitable crystal was mounted on a AED2 Siemens four-circle diffractometer. Data collection using Mo-Kα radiation (λ = 0.71073 Å) and ω–2θ scans gave 2273 independent reflections (θ_{max} 26°), of which 1870 with $I > 2\sigma(I)$ were used in all calculations. The structure was solved by direct methods and the solution developed using full-matrix least-squares refinement on F^2 and difference Fourier synthesis. Displacement parameters were refined for non-H atoms, H atoms were included in fixed calculated positions.[12] At convergence, R = 0.0353, $wR2$ = 0.0966, GOF = 1.067 for 217 parameters. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/3.

Preliminary crystal data for **5**·CH_2Cl_2, $C_{23}H_{50}Cl_2Fe_4I_3N_4Ni_{2.5}S_8$: M = 1460.93, monoclinic, space group $P2_1/n$, a = 12.405(4), b = 31.144(12), c = 12.541(4) Å, β = 110.09(4)°, U = 4550(3) $Å^3$, T = 296 K, Z = 4, D_c = 2.133 g cm^{-3}, μ(Mo-Kα) = 4.796 mm^{-1}, data collection, refinement and solution as above, 4225 independent reflections (θ_{max} 20°), R = 0.0767, $wR2$ = 0.1637, GOF = 1.028 for 303 parameters (displacement parameters isotropic for C and H).

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