Formation of [(L)Ni(μ_2-S)$_x${Fe(CO)$_3$}$_x$] adducts (x = 1 or 2): analogues of the active site of [NiFe] hydrogenase†

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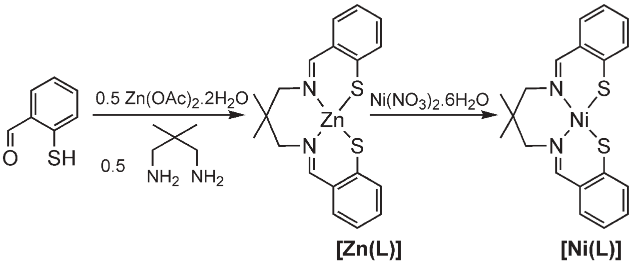
The binuclear [Ni(L)Fe(CO)$_3$], 1, and trinuclear [Ni(L){Fe(CO)$_3$}$_2$], 2, complexes adopt unusual structural motifs whereby Fe(CO)$_3$ units bind to [Ni(L)] *via* μ_2-S bridging modes, C=N imine π-bonds and potential Ni–Fe bonding interactions.

The crystal structure of the as-isolated inactive form of [NiFe] hydrogenase from *Desulfovibrio gigas* reveals an unusual binuclear [NiFe] assembly (Ni–Fe = 2.9 Å) at the active site.[1] The Ni centre possesses an S_4 co-ordination sphere comprising four cysteine thiolate donors in a nonplanar geometry in which Cys530 and Cys533 bridge Ni and Fe sites. The co-ordination about the Fe centre is completed by three heteronuclear molecules which have been identified as one CO and two CN ligands by FTIR spectroscopy.[2] Considerable attention has focussed on the synthesis and detailed characterisation of synthetic analogues of the active site of the [NiFe] hydrogenases.[3–5] In this respect, the development of new methodologies for the control of the formation of thiolate bridged metal aggregates is of particular importance.[6,7] Recent efforts in this laboratory,[8] and elsewhere,[9] towards the synthesis of structural analogues have centred on the addition of Fe^0 carbonyl fragments to thiolate bound Ni^{II} complexes. These reactions usually result in the formation of trinuclear [(L)Ni(μ_2-S)$_2${Fe(CO)$_3$}$_2$] moieties.[8,9] We report herein (i) a facile method for the general preparation of Ni(tsalen)-type (tsalen = *N*,*N*′-ethylenebis(thiosalicylideneiminato)) complexes ([Ni(L)], Scheme 1) which have hitherto required multi-step syntheses[10] and (ii) the structural characterisation of the unusual adducts [(L)Ni(μ_2-S)$_x${Fe(CO)$_3$}$_x$] (x = 1, 2) formed upon co-ordination of discrete Fe(CO)$_3$ units to [Ni(L)].



Scheme 1

ortho-Lithiation of benzenethiol[11] with 2.2 equivalents of ^{n}BuLi followed by quenching with 1-formylpiperidine afforded thiosalicylaldehyde in 79% yield. The crude product was converted to [Zn(L)] *in situ* upon the addition of 0.5 equivalents of 2,2′-dimethyl-1,3-propanediamine *via* a Zn^{II}-templated Schiff-base condensation reaction. Transmetallation to afford the dark brown complex [Ni(L)] was achieved *via* the addition of Ni(NO$_3$)$_2$·6H$_2$O to [Zn(L)] in CH_2Cl_2 solution (Scheme 1). ^{1}H-NMR and ^{13}C-NMR spectroscopy, ES$^+$ mass spectrometry and elemental analytical data confirm the formulation of diamagnetic, air-stable [Zn(L)] and [Ni(L)].‡ X-Ray crystallographic studies on single crystals of [Ni(L)] reveal the formation of a tetraco-ordinate N_2S_2 bound mononuclear complex in which a distorted square planar geometry is adopted about the Ni(II) centre, with a dihedral angle between the N–Ni–N and S–Ni–S planes of 9.0°.

The reaction of [Ni(L)] with excess Fe$_2$(CO)$_9$ in toluene affords a deep red/brown solution that contains two new species by TLC, which were identified by X-ray crystallography as **1** and **2**. Complexes **1** and **2** were separated by anaerobic column chromatography (silica gel eluted with toluene : CH_2Cl_2, 1 : 1) and isolated as red/brown crystalline solids that are stable under Ar both in the solid state and in CH_2Cl_2 solution. The appearance of ν_{CO} stretching vibrations at 2045 and 1973 cm^{-1} and at 2050, 2000 and 1977 cm^{-1} in the IR spectra (KBr pellet) of **1** and **2**, respectively, confirmed the binding of Fe–carbonyl unit(s) onto the [Ni(L)] framework.

Single crystals of **1** and **2** were obtained by layering hexane onto toluene solutions of **1** and **2** at 253 K.§ The X-ray crystal structures of **1** and **2** (Fig. 1) reveal unusual binuclear Ni(μ_2-S)Fe(CO)$_3$ and trinuclear Ni(μ_2-S)$_2$[Fe(CO)$_3$]$_2$ cores with one or two Fe(CO)$_3$ units bound to a single [Ni(L)] unit.

The Ni^{II} centres of **1** and **2** are each co-ordinated by two thiolate S-donors and two imine N-donors in a distorted square planar geometry in which the dihedral angles between the planes defined by S–Ni–S and N–Ni–N are 21.2° and 15.0°, respectively. The Fe(CO)$_3$ fragments bind to [Ni(L)] through one bridging thiolate S-donor and one C=N imine π-bond. The Ni–Fe bond distances of 2.8924(6) and 2.8928(4) Å for **1** and **2**, respectively, are comparable to the sum of the empirical atomic radii for Ni and Fe (1.35 and 1.40 Å, respectively)[12] and may indicate a bonding interaction between the metal centres in these complexes.[8,9] A linear Fe–Ni–Fe arrangement is adopted by the three metal centres in **2** in which Fe(1) and Fe(1A) are symmetrically equivalent and lie *trans* to one another. Each Fe^0 centre of **1** and **2** co-ordinates to one S-donor,

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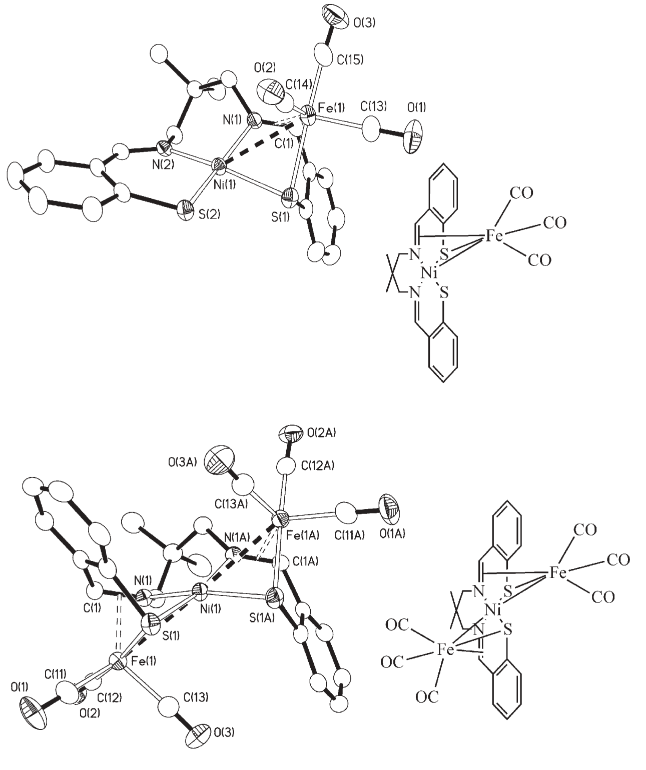

Fig. 1 Molecular structures of **1** (top) and **2** (bottom) with ellipsoids drawn at the 50% probability level and H atoms omitted for clarity.

one C=N imine π-bond and three CO ligands in a distorted geometry. The elongation of the C=N bond with respect to that in [Ni(L)] (C(1)–N(1) = 1.398(3), 1.399(4) and 1.293(3) Å for **1**, **2** and [Ni(L)], respectively) is consistent with the back-donation of π-electron density from the Fe^0 centre to the C=N moiety.

The accommodation of $Fe(CO)_3$ fragments onto [Ni(L)] requires significant structural rearrangements of the co-ordination sphere in [Ni(L)]. The donation of Fe^0 π-electron density to C=N results in the loss of planarity of the conjugated π-system of L^{2-} in the [Ni(L)] fragment and the displacement of the adjacent aromatic ring such that it lies almost perpendicular to the approximately planar NiN_2S_2 unit.

1, **2** and [Ni(L)] show intense transitions at *ca.* 270 and 230 nm ($\varepsilon > 50\,000$ M^{-1} cm^{-1}) that are assigned to intra-ligand $\pi \rightarrow \pi^*$ transitions. **2** and [Ni(L)] show absorption bands at 385 nm (ε = 19 000 M^{-1} cm^{-1}) and 400 nm (ε = 6600 M^{-1} cm^{-1}) respectively, and **1** and **2** possess a band at 458 nm (ε = 6000 M^{-1} cm^{-1}), 457 nm (ε = 5400 M^{-1} cm^{-1}) respectively. These transitions are tentatively assigned to LMCT transitions on the basis of their intensities and energies.

The binding of discrete $Fe(CO)_3$ fragments to a Ni complex *via* thiolate RS^- bridges is rare[13] although complexes incorporating bridging sulfido S^{2-} species have been reported.[14] Recent reports of the reaction of Fe^0 carbonyl compounds with thiolate bound Ni complexes by us[8] and Bouwman *et al.*[9] resulted in the (μ_2-S)$_2$ co-ordination of $Fe_2(CO)_6$ units. Thus, the π-acceptor characteristics of the C=N imine bond and the inherent steric instability associated with the *cis* configuration drive the co-ordination of a *single* $Fe(CO)_3$ in **1** and the disassociation of the $Fe_2(CO)_6$ unit into discrete *trans* configured $Fe(CO)_3$ fragments in **2**. Our synthetic approach to drive the co-ordination of a single $Fe(CO)_3$ fragment to a NiN_2S_2 core to form **1** resembles that used to generate related covalent NiFe complexes and clusters[5,8] which model the active site of [NiFe] hydrogenase. Complexes **1** and **2** both possess a binuclear Ni(μ_2-S)Fe core with Ni···Fe separations approaching bonding distance. X-Ray absorption studies of [NiFe] hydrogenase from *Chromatium vinosum* suggest a Ni···Fe separation in the reduced and active Ni-SI form of the enzyme of 2.5 Å–2.6 Å,[15] also within bonding distances. This is supported further by theoretical[16] and mechanistic[17,18] studies which suggest relatively short Ni–Fe separations (2.5 Å) in the active form of the enzyme, compared to that observed in the structure of its oxidised, inactive form (2.9 Å).[1] Recent crystal structure determinations of [NiFe] hydrogenases from *D. vulgaris Miyazaki F*[19] and *D. gigas*[20] also exhibit shorter Ni–Fe separations (2.55 and 2.53 Å, respectively).

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Notes and references

‡ [Zn(L)] and [Ni(L)] were characterised by elemental analysis, NMR and IR spectroscopies and mass spectrometry. See the ESI for details and for experimental details. Syntheses of **1** and **2**: to a stirred suspension of [Ni(L)] (0.27 g, 0.67 mmol) in toluene (20 ml) was added $Fe_2(CO)_9$ (0.24 g, 0.67 mmol). After 72 h the mixture was filtered and solvent removed *in vacuo* from the filtrate. Column chromatography (silica gel, CH_2Cl_2 : toluene, 1 : 1) yielded orange/brown [Ni(L){Fe(CO)$_3$}$_2$], **2** (0.16 g, 0.23 mmol, 34%), and red/brown [Ni(L)Fe(CO)$_3$], **1** (0.11 g, 0.21 mmol, 31%), as the first and second bands, respectively.

1: IR (KBr, cm^{-1}): 2958 w, 2930 w, 2045 vs, 1973 vs, 1614 m, 1589 m, 1538 w, 1462 m, 1385 w, 1368 w, 1250 w, 1219 w, 1081 w, 1026 w, 752 m, 623 m, 614 m. MS (FAB, *m/z*): 538 (M^+), 510 ([M − CO]$^+$), 482 ([M − 2CO]$^+$), 398 ([M − Fe(CO)$_3$]$^+$). Elemental analysis: found (calculated for $C_{22}H_{20}N_2S_2O_3NiFe$) C 48.98 (49.02); H 3.67 (3.74); N 5.07 (5.20).

2: IR (KBr, cm^{-1}): 2962 w, 2936 w, 2050 vs, 2000 vs, 1977 vs, 1636 m, 1591 m, 1575 m, 1524 w, 1484 m, 1457 m, 1384 m, 1261 m, 1129 w, 1080 w, 1026 w. MS (FAB, *m/z*): 678 (M^+), 622 ([M − 2CO]$^+$), 538 ([M − Fe(CO)$_3$]$^+$), 482 ([M − Fe(CO)$_5$]$^+$), 398 ([M − Fe$_2$(CO)$_6$]$^+$). Elemental analysis: found (calculated for $C_{25}H_{20}N_2S_2O_6NiFe_2$) C 44.19 (44.23); H 2.84 (2.97); N 4.04 (4.13).

§ *Crystallographic data for* [Ni(L)]: $C_{19}H_{20}N_2S_2Ni$, M = 399.20, triclinic, a = 8.5701(2), b = 9.057(2), c = 11.767(3) Å, α = 76.164(3), β = 87.506(3), γ = 89.673(3)°, U = 866.0(6) Å^3, T = 150(2) K, space group $P\bar{1}$, Z = 2, μ (Mo-Kα) = 1.333 mm^{-1}, 7692 data collected, 3955 independent reflections (R_{int} = 0.033). Final R_1 [$I > 2\sigma(I)$] = 0.0401, wR_2 [all data] = 0.0649. CCDC 278858.

Crystallographic data for **1**: $C_{22}H_{20}N_2S_2O_3NiFe\cdot1.5C_7H_8$, M = 677.28, monoclinic, a = 12.245(2), b = 15.779(2), c = 16.870(2) Å, β = 106.888(2)°, U = 3118.9(7) Å^3, T = 150(2) K, space group $P2_1/n$, Z = 4, μ (Mo-Kα) = 1.239 mm^{-1}, 15495 data collected, 6978 independent reflections (R_{int} = 0.0300). Final R_1 [$I > 2\sigma(I)$] = 0.0467, wR_2 [all data] = 0.0603. CCDC 278856.

Crystallographic data for **2**: $C_{25}H_{20}N_2S_2O_6NiFe_2$, M = 678.96, monoclinic, a = 18.1561(16), b = 9.5235(9), c = 15.6850(14) Å, β = 91.571(2)°, U = 2711.1(4) Å^3, T = 150(2) K, space group $C2/c$, Z = 4, μ (Mo-Kα) = 1.940 mm^{-1}, 6675 data collected, 3196 independent reflections (R_{int} = 0.022). Final R_1 [$I > 2\sigma(I)$] = 0.0315, wR_2 [all data] = 0.0745. CCDC 278857. For crystallographic data in CIF or other electronic format see DOI:10.1039/b509798c.

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