Formation of \([\text{L}]{\text{Ni}}(\mu_2-\text{S})_x\{\text{Fe(CO)}_3\}_x\) adducts \((x = 1 \text{ or } 2)\): analogues of the active site of \([\text{NiFe}]\) hydrogenase†

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The binuclear \([\text{Ni}(\text{L})\{\text{Fe(CO)}_3\}_2]\), 1, and trinuclear \([\text{Ni}(\text{L})\{\text{Fe(CO)}_3\}_3]\), 2, complexes adopt unusual structural motifs whereby \(\text{Fe(CO)}_3\) units bind to \([\text{Ni}(\text{L})]\) via \(\mu_2\)-S bridging modes, \(\text{C}^\equiv\text{N}\) imine \(\pi\)-bonds and potential \(\text{Ni–Fe}\) bonding interactions.

The crystal structure of the as-isolated inactive form of \([\text{NiFe}]\) hydrogenase from \(\text{Desulfovibrio gigas}\) reveals an unusual binuclear \([\text{NiFe}]\) assembly (\(\text{Ni–Fe} = 2.9\ \text{Å}\)) at the active site. The \(\text{Ni}\) centre possesses an \(S_4\) co-ordination sphere comprising four cysteine thiolate donors in a non-planar geometry in which Cys530 and Cys533 bridge \(\text{Ni}\) and \(\text{Fe}\) sites. The co-ordination about the \(\text{Fe}\) centre is completed by three heteronuclear molecules which have been identified as one \(\text{CO}\) and two \(\text{CN}\) ligands by FTIR spectroscopy. Considerable attention has focussed on the synthesis and detailed characterisation of synthonic analogues of the active site of the \([\text{NiFe}]\) hydrogenases. In this respect, the development of new methodologies for the control of the formation of thiolate bridged metal aggregates is of particular importance. Recent efforts in this laboratory, and elsewhere, towards the synthesis of structural analogues have centred on the addition of \(\text{Fe}^0\) carbonyl fragments to thiolate bound \(\text{Ni}^{II}\) complexes. These reactions usually result in the formation of trinuclear \([\text{L}]{\text{Ni}}(\mu_2-\text{S}):\{\text{Fe(CO)}_3\}_2]\) moieties. We report herein (i) a facile method for the general preparation of \(\text{Ni(salen)-type}\) (tsalen = \(N,N'\)-ethylenbis(thiosalicyldieneiminato)) complexes (\([\text{Ni}(\text{L})]\), Scheme 1) which have hitherto required multi-step syntheses and (ii) the structural characterisation of the unusual adducts \([\text{L}]{\text{Ni}}(\mu_2-\text{S}):\{\text{Fe(CO)}_3\}_x\) \((x = 1, 2)\) formed upon co-ordination of discrete \(\text{Fe(CO)}_3\) units to \([\text{Ni}(\text{L})]\).

**Scheme 1**

![Scheme 1](image)

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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(4) 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 (ε > 50 000 M^{-1} cm^{-1}) that are assigned to intra-ligand π → π* 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 although complexes incorporating bridging sulfido S^- species have been reported. Recent reports of the reaction of Fe^0 carbonyl compounds with thiolate bound Ni complexes by us and Bouwman et al resulted in the (μ₂-S)₂ co-ordination of Fe(CO)_3 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 dissociation of the Fe₂(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\(^\dagger\) which model the active site of [NiFe] hydrogenase. Complexes 1 and 2 both possess a binuclear Ni(μ₂-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,\(^\dagger\) also within bonding distances. This is supported further by theoretical\(^\dagger\) and mechanistic\(^\dagger\) 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).\(^\dagger\)

Recent crystal structure determinations of [NiFe] hydrogenases from *D. vulgaris Miyazaki F*\(^\dagger\) and *D. gigas*\(^\dagger\) also exhibit shorter Ni–Fe separations (2.55 and 2.53 Å, respectively). We thank the EPSRC for funding and for the provision of a diffractometer and the EPSRC National Service for Mass Spectrometry at the University of Wales, Swansea for mass spectra. We also thank CONACYT and DGAPA-UNAM for support to A. M.-B. M. S. gratefully acknowledges receipt of a Royal Society Wolfson Merit Award and of a Royal Society Leverhulme Trust Senior Research Fellowship.

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

Notes and references

\(^\dagger\) [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(CO)_3 (0.24 g, 6.70 mmol). After 72 h the mixture was filtered and solvent removed in vacuo from the filtrate. Column chromatography (silica gel, CHCl₃ : 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, 1736 vs, 1614 sh, 1589 sh, 1538 w, 1435 w, 1412 w, 1402 w, 1301 w, 1250 m, 1122 w, 1090 w, 1026 w, 945 m, 873 w, 832 w, 752 m, 726 m, 680 w, 643 s, 569 s. MS (FAB, m/z): 538 (M^+, 510 (M – CO)^+, 482 (M – 2CO)^+, 398 (M – Fe(CO)_3)^+). Elemental analysis: found (calculated) for C₂₀H₂₅NiS₂O₃FeC: 48.89 (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, 1538 w, 1526 w, 1483 w, 1465 w, 1384 m, 1326 m, 1197 s, 1182 w, 1100 w, 1026 w, MS (FAB, m/z): 678 (M^+, 622 (M – 2CO)^+, 538 (M – Fe(CO)_3)^+), 482 (M – Fe(CO)_3)^+), 398 (M – Fe(CO)_3)^+). Elemental analysis: found (calculated) for C₂₃H₂₅NiS₂O₃NiFeC: 44.19 (44.23); H 2.84 (2.97); N 4.04 (4.13).

\(\$_{2}$ Crystallographic data for [Ni(L)] C₈H₁₄NiS₂Ni, M = 399.20, triclinic, a = 8.5701(2), b = 9.057(2), c = 11.7673(3) Å, \(\alpha = 76.164(3), \beta = 87.506(3), \gamma = 89.673(3), U = 866.06(6) \AA^3, T = 150(2)K, space group P1, Z = 2, µ(Mo-Kα) = 1.333 mm\(^{-1}\), 7692 data collected, 3995 independent reflections (R(int) = 0.033). Final R₁ [I > 2σ(I)] = 0.0401, wR₁ [all data] = 0.0649. CCDC 278858.

\(\$_{3}$ Crystallographic data for 1: C₂₃H₂₅NiS₂O₃NiFeC = 677.28, monoclinic, a = 12.245(2), b = 15.779(2), c = 16.870(2) Å, \(\alpha = 106.888(2), U = 318.97(3) \AA^3, T = 150(2)K, space group P2₁/n, Z = 4, µ(Mo-Kα) = 1.239 mm\(^{-1}\), 15495 data collected, 6978 independent reflections (R(int) = 0.030). Final R₁ [I > 2σ(I)] = 0.0467, wR₁ [all data] = 0.0603. CCDC 278858.

\(\$_{4}$ Crystallographic data for 2: C₂₂H₂₄NiS₂O₃NiFeC = 678.96, monoclinic, a = 18.1561(16), b = 9.5235(9), c = 15.6850(14) Å, \(\beta = 91.571(2), U = 2711.14(4) \AA^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) = 0.036). Final R₁ [I > 2σ(I)] = 0.0315, wR₁ [all data] = 0.0745. CCDC 278857. For crystallographic data in CIF or other electronic format see DOI:10.1039/b509796c.
