

Nickel(II) in an almost regular tetrahedral thiolate environment: a first generation synthetic analogue of the active site of nickel CO-dehydrogenase

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Reaction of the iron(II)-carbonyl chelate ligand $[\text{Fe}(\text{NS}_3)(\text{CO})]^-$ [$\text{NS}_3 = \text{N}(\text{CH}_2\text{CH}_2\text{S})_3^{3-}$] with the dmsolvate of nickel(II) chloride gives the structurally characterised trinuclear linear complex $[\text{Ni}\{\text{Fe}(\text{NS}_3)(\text{CO})-\text{S},\text{S}'\}_2]$, which has an almost regular tetrahedral arrangement of sulfur about nickel and structural features similar to those proposed for the active site of nickel CO-dehydrogenase.

Nickel(II) in a thiolate environment virtually always has a square planar geometry, as the d^8 configuration prefers such a geometry in the presence of strong field donor ligands. The only examples of complexes where a pseudo-tetrahedral geometry is observed are: $[\text{Ni}(\text{SR})_4]^{2-}$ (R = aryl),^{1,2} $[\text{Ni}_2(\text{S}'\text{Bu})_6]^{2-}$ and the central nickel atom in $[\text{Ni}_3(\text{L5S})_4]^{2+}$ [$\text{L5SH} = (2\text{-sulfanyphenyl})\text{bis}(\text{pyrazolyl})\text{methane}$].³ All show distortions from a regular NiS_4 tetrahedron with one or two of the S–Ni–S angles less than 93° .

As part of our continuing studies to new routes to synthetic analogues of the active sites of nickel-iron enzymes,⁴ in particular that of nickel CO-dehydrogenase, we have prepared a nickel-thiolate complex with more regular tetrahedral geometry about nickel(II). It has been proposed recently,^{5,6} in the absence of an X-ray crystal structure, that the active site of nickel CO-dehydrogenase from *Rhodospirillum rubrum* consists of a binuclear $[\text{FeNi}]$ centre linked, probably, through cysteinyl-sulfur to an $[\text{Fe}_4\text{S}_4]$ cluster. The iron(II) and nickel(II) atoms within the $[\text{FeNi}]$ centre are said to be bridged through two cysteinyl-sulfurs and, in addition, that there is a nitrogen (from histidine) and a molecule of carbon monoxide bound to the iron(II) atom; other ligands are yet to be defined. Ni-XANES results are consistent with five-coordinate or tetrahedral coordination about the nickel atom.⁷

The reaction of the dmsolvate of nickel(II) chloride with two equivalents of $[\text{NET}_4][\text{Fe}(\text{NS}_3)(\text{CO})]^{8-}$ gives the linear complex $[\text{Ni}\{\text{Fe}(\text{NS}_3)(\text{CO})-\text{S},\text{S}'\}_2]$ **1**,[†] the structure of which is shown in Fig. 1.[‡] This complex is made up of two trigonal bipyramidal $\text{Fe}(\text{NS}_3)(\text{CO})$ units, each of which bridges to a central nickel atom, which lies on a two-fold symmetry axis and is slightly distorted from regular tetrahedral geometry. The tetrahedral geometry about nickel is supported further by a pre-edge XANES§ peak at ≈ 8331 eV; tetrahedral complexes have strong $1s \rightarrow 3d$ transitions because p–d mixing is allowed in this geometry. There is no $1s \rightarrow 3p$ peak at ≈ 8336 eV, thus ruling out a planar four-coordinate geometry. Complex **1** is isostructural with the analogous complexes $[\text{Fe}\{\text{Fe}(\text{NS}_3)(\text{CO})-\text{S},\text{S}'\}_2]$ **2**^{8,9} and $[\text{Co}\{\text{Fe}(\text{NS}_3)(\text{CO})-\text{S},\text{S}'\}_2]$ **3**;⁹ the Fe and Ni complexes show alternative sites for the carbonyl O-atom, but no disorder was found in the Co complex. Only in the dimensions about the central metals of these complexes do we note any significant variation: in each complex, one M–S

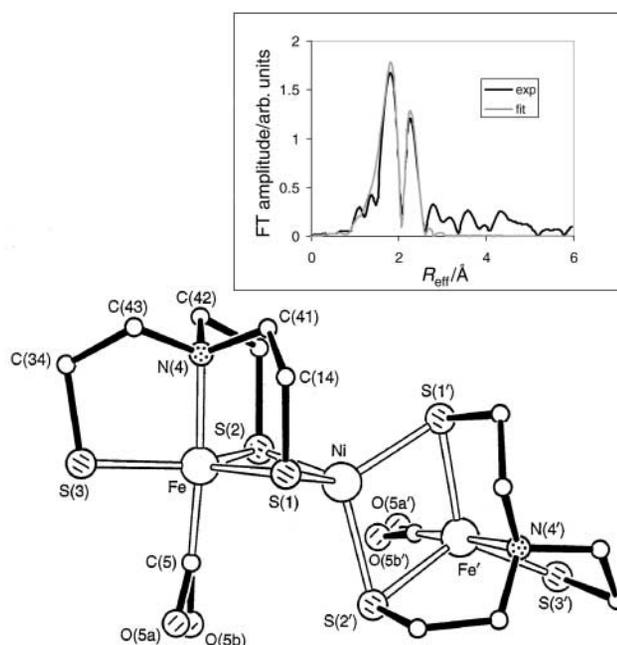


Fig. 1 A molecule of $[\text{Ni}\{\text{Fe}(\text{NS}_3)(\text{CO})-\text{S},\text{S}'\}_2]$ **1** showing the principal atoms and, insert, its Ni K-edge EXAFS Fourier transform and best fit. Selected distances (Å) and angles ($^\circ$): Ni–S(1) 2.229(2), Ni–S(2) 2.287(2), Fe–S(1) 2.266(2), Fe–S(2) 2.249(2), Fe–S(3) 2.207(2), Fe–N(4) 2.046(6), Fe–C(5) 1.780(10); S(1)–Ni–S(1') 124.20(14), S(1)–Ni–S(2) 107.19(8), S(1)–Ni–S(2') 103.00(8), S(2)–Ni–S(2') 112.42(14), Ni–S(1)–Fe 71.83(7), Fe–S(2)–Ni 71.10(7), N(4)–Fe–C(5) 175.4(3), mean N(4)–Fe–S 88.0(3), Fe...Ni...Fe' 155.35(9).

distance is longer than the other; the longer distance at *ca.* 2.29 Å is constant but the shorter distance decreases from 2.2775(2) in the Fe complex (**2**) to 2.242(2) for Co (**3**) and 2.229(2) Å for Ni (**1**). The crystallographic cell lengths show corresponding slight decreases.

In complex **1**, the shorter Ni–S distance is marginally shorter than in most reported approximately tetrahedral NiS_4 complexes. In NiS_4 complexes with four terminal Ni–S bonds, there are two S–Ni–S angles of *ca.* 90° involving opposite pairs of thiolate ligands,^{1,2} in thiolate bis-bridged dinuclear complexes, there is one angle of *ca.* 84° (subtended by the bridging S atoms) and an opposite large angle of *ca.* 130° (between the terminal S atoms),² and in the only trinuclear, bis-bridged, Ni_3 complex, tetrahedral Ni has two opposing angles of *ca.* 90° (both in Ni_2S_2 rings).³ Complex **1** has a more regular tetrahedral shape with S–Ni–S angles in the range 103.00(8) to 124.20(14) $^\circ$. We also note that the Ni...Ni distances in the bridged complexes are all *ca.* 3.4 Å whereas the Ni...Fe

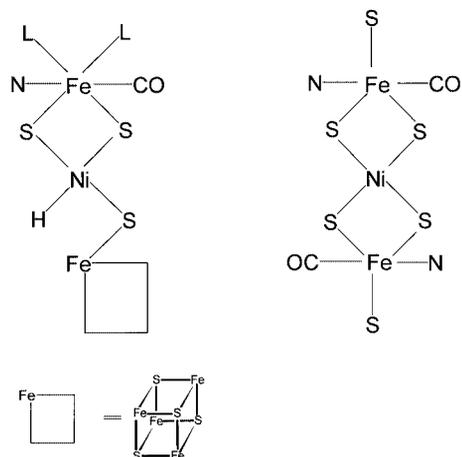


Fig. 2 A schematic comparison of the proposed active site of nickel CO-dehydrogenase of *R. rubrum* (left) and the core of complex **1** (right).

distance in complex **1** is 2.6372(11) Å. Ni-EXAFS data for complex **1** ($4 \times \text{S}$ at 2.23 Å; $2 \times \text{Fe}$ at 2.61 Å) are in good agreement with the crystallographically determined dimensions about the central nickel atom.

The solid state infrared carbonyl stretch of **1** at 1933 cm^{-1} is similar to that observed for complexes **2** (1937 cm^{-1}) and **3** (1938 cm^{-1}). The Mössbauer parameters at 77 K (relative to natural Fe at 298 K) for the series of complexes **1–3** show very similar isomer shifts (IS) and a gradual increase in quadrupole splitting (QS) with atomic number of the central metal atom (**1**, IS = 0.19, QS = 1.40; **2**, IS = 0.21, QS = 1.18; **3**, IS = 0.21, QS = 1.29 mm s^{-1}), consistent with iron(II). An EPR spectrum of a frozen dimethylformamide solution of **1** shows $S = 1$ ($g_{\parallel} = 4.0$), which is further confirmation that the nickel atom has tetrahedral coordination.

The core of **1** has similarities to that proposed for the active site of nickel CO-dehydrogenase of *R. rubrum*, Fig. 2, and can thus be considered as a first-generation structural analogue of the active site of this important metalloenzyme. The common features are: CO and N coordinated to iron(II); iron bridged through two thiolate-sulfurs to nickel; nickel bridged through a further thiolate-sulfur to another iron atom (part of the $[\text{Fe}_4\text{S}_4]_{\text{C}}$ cluster in the enzyme active site); tetrahedral geometry about the nickel.

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Notes and references

† Under an atmosphere of dinitrogen, $[\text{NiCl}_2]$ (0.14 g, 1.08 mmol) was refluxed in anhydrous dmsO (18 cm^3) for 1 h. The solution became blue upon refluxing and cooled to a green colour. On to the surface of the cooled solution was layered $[\text{NEt}_4][\text{Fe}(\text{NS}_3)(\text{CO})]$ (0.88 g, 2.15 mmol) dissolved in anhydrous dmsO (32 cm^3). The reaction mixture was left undisturbed for 24 h during which time black crystals formed, these were collected by filtration, washed repeatedly with diethyl ether and dried (0.27 g, 41%). Found: C, 27.5; H, 4.2; N, 4.6; Fe, 17.6; Ni, 9.8. $\text{C}_{14}\text{H}_{24}\text{Fe}_2\text{N}_2\text{NiO}_2\text{S}_6$ requires: C, 27.3; H, 3.9; N, 4.6; Fe, 18.2, Ni, 9.5%.
‡ Crystal data: $\text{C}_{14}\text{H}_{24}\text{Fe}_2\text{N}_2\text{NiO}_2\text{S}_6$, $M = 615.1$, tetragonal, space group $I4_1cd$ (no. 110), $a = b = 13.5088(4)$, $c = 24.371(2)$ Å, $V = 4447.5(4)$ Å³, $Z = 8$, $D_c = 1.84 \text{ g cm}^{-3}$, $F(000) = 2512$, $T = 293(2)$ K, $\mu(\text{Mo-K}\alpha) = 2.70 \text{ mm}^{-1}$, $\lambda(\text{Mo-K}\alpha) = 0.71069$ Å. 1691 Unique reflections were measured to $\theta_{\text{max}} = 30^\circ$ (1350 with $I > 2\sigma_I$). Structure determined by analogy with isostructural Fe complex, **2**, refined with all data, on F^2 , in SHELXL¹⁰ to $wR_2 = 0.137$, $R_1 = 0.067$; for the 'observed' data, $R_1 = 0.057$. CCDC reference number 156275. See <http://www.rsc.org/suppdata/dt/b1/b102607k/> for crystallographic data in CIF or other electronic format.
§ The EXAFS spectra were recorded on SSRL beamline 7-3 with a Si(220) monochromator.

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