

Formation of nickel-thiolate aggregates *via* reaction with CH₂Cl₂

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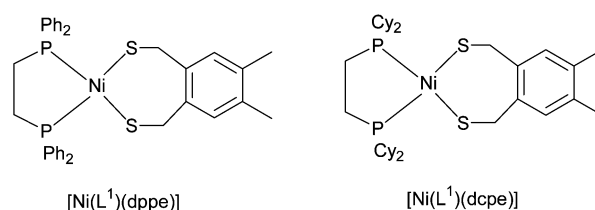
Reaction of the mononuclear nickel-thiolate complex [Ni(L¹)(dppe)] with CH₂Cl₂ affords the novel pentanuclear complex [Ni₅Cl₂(L¹)₄(dppe)₂], while [Ni(L¹)(dcpe)] reacts with CH₂Cl₂ to give the binuclear species [Ni₂Cl₂(L²)(dcpe)₂] in which two L¹ units are linked by a methylene group derived from CH₂Cl₂.

The study of nickel thiolates is frequently complicated by their air sensitivity and a tendency to form polymetallic complexes with bridging μ -SR groups.¹ Steric factors and/or thiolates containing electron-withdrawing groups have been employed to avoid and control such unwanted reactivity,² while another successful strategy for obtaining discrete complexes involves the use of chelating dithiolate ligands with chelating phosphines such as dppe or dcpe [dppe = 1,2-bis(diphenylphosphino)ethane, dcpe = 1,2-bis(dicyclohexylphosphino)ethane].³ Ligand-based reactivity of transition metal thiolates *via* alkylation, metalation, oxygenation, and adduct formation is well documented,⁴ while methylation of the nickel-bound thiolates by electrophiles such as MeI has been observed by Darenbourg *et al.*⁵ Alkylation of ruthenium-bound thiolates has been reported by Sellmann *et al.*⁶ and Grapperhaus *et al.*,⁴ and Jones and co-workers⁷ have recently reported the alkylation of nickel-bound sulfides by 1,2-dichloroethane. We report herein the first example of reaction of nickel thiolate complexes with CH₂Cl₂, and examine the influence of the electronic environment of the nickel-thiolate moiety upon this reactivity.

As part of our wider project on the modelling of the active site of [NiFe] hydrogenase,⁸ we have synthesized a series of nickel thiolate–phosphine complexes with NiS₂P₂ co-ordination spheres, and have investigated the reactivity of these complexes as a function of variation of phosphine and/or thiolate ligands. When [NiCl₂(PP)] (PP = dppe, dcpe) is reacted with 2,4,6-trisopropylthiophenol (HL³) or 2-mercaptomethyl-benzenethiol (H₂L⁴) in the presence of NaOMe in MeOH, *via* a modification of the procedure reported by Bowmaker *et al.*,⁹ the corresponding mononuclear nickel thiolate complexes [Ni(L³)₂(PP)] and [Ni(L⁴)(PP)] are obtained in good yields and have been fully characterised.† These diamagnetic complexes are stable in CH₂Cl₂ solution and their formulations have been confirmed by X-ray crystallographic studies of single crystals grown from CH₂Cl₂ solution. Reaction of 4,5-dimethyl-1,2-benzenedimethanethiol (H₂L¹) with [NiCl₂(dppe)] *via* a procedure similar to that described above,⁹ affords the mononuclear complex [Ni(L¹)(dppe)] (Scheme 1) which is stable in the solid state under N₂ or Ar. The formulation of the product as [Ni(L¹)(dppe)] was confirmed by FAB mass spectrometry, NMR spectroscopy and elemental analysis.† The ³¹P{¹H} NMR spectrum of [Ni(L¹)(dppe)] in CDCl₃ solution shows a single resonance at 55.30 ppm confirming that the two P centres in the complex are, as expected, in identical environments about a *cis* square-planar Ni(II) centre. However, unlike [Ni(L³)₂(PP)] and [Ni(L⁴)(PP)], [Ni(L¹)(dppe)] is reactive in CH₂Cl₂ solution,

and the ³¹P{¹H} NMR spectrum of the crystalline product obtained by diffusion of Et₂O vapour into a solution of [Ni(L¹)(dppe)] in CH₂Cl₂ over a period of 3 days showed in CDCl₃ solution a single resonance at 33.78 ppm, confirming the equivalence of the terminal phosphine ligands. A single crystal X-ray structural determination confirmed† the formation of a highly unusual pentanuclear nickel(II) aggregate, [Ni₅Cl₂(L¹)₄(dppe)₂] **1** (Fig. 1, upper) [FAB MS: *m/z* 1910 (M–Cl)⁺, 1875 (M–2Cl)⁺]. The complex **1** comprises three central square-planar NiS₄ units and two terminal square-planar P₂NiS₂ units arranged in a zig-zag pattern (Fig. 1, lower). Ni(1) occupies a crystallographic inversion centre and the Ni₅ complex therefore has imposed C_i symmetry. Each terminal Ni(II) centre is further bound by a chloride ion derived from CH₂Cl₂ and occupies the apical position of a square pyramid at the Ni(II) centres. The angle between the least-squares mean planes through P(1)–P(2)–Ni(3)–S(1)–S(2) and S(1)–S(2)–Ni(2)–S(3)–S(4) is 65.32(2)°, while that between the S(1)–S(2)–Ni(2)–S(3)–S(4) and S(3)–S(4)–Ni(1)–S(3A)–S(4A) planes is 70.30(3)°. This brings the metals into fairly close proximity with Ni(1)⋯Ni(2) = 2.7738(5) Å, Ni(2)⋯Ni(3) = 2.8552(6) Å. These Ni⋯Ni distances are comparable to the mean value of 2.8345(1) Å in the thiolate-bridged pentanuclear nickel(II) complex [NEt₄]₂[Ni₅(edt)₄(dmit)₂] (edt = ethane-1,2-dithiolate; dmit = 2-thione-1,3-dithiole-4,5-dithiolate) reported by Sheng *et al.*¹⁰ However, whereas the Ni(1)⋯Ni(2)⋯Ni(3) angle of 176.30(2)° in **1** is close to linearity, the corresponding angle in [NEt₄]₂[Ni₅(edt)₄(dmit)₂] is 102.83°. Thus, **1** represents, to the best of our knowledge, the first example of a linear pentanuclear nickel cluster bridged by thiolates.

Reaction of H₂L¹ with [NiCl₂(dcpe)] affords [Ni(L¹)(dcpe)] (Scheme 1) as confirmed by FAB mass spectrometry, NMR spectroscopy and elemental analysis.† The ³¹P{¹H} NMR spectrum of [Ni(L¹)(dcpe)] in CDCl₃ solution shows a single resonance at 73.56 ppm confirming a *cis* square-planar configuration at Ni(II). [Ni(L¹)(dcpe)], however, reacts with CH₂Cl₂/*n*-hexane stored at –10°C for 7 days to afford crystals of the unexpected binuclear complex [Ni₂Cl₂(L²)(dcpe)₂] **2** (L² = [bis-(4,5-dimethyl-1,2-benzenedimethanethiolato)methane]) (Fig. 2). The structure of **2** reveals that the *cis* thiolates in [Ni(L¹)(dcpe)] have been alkylated by CH₂Cl₂ to yield the corresponding methylene-bridged dithioether/thiolate ligand [L²]^{2–} bound to Ni(II). C(61) lies on a crystallographic two-fold axis, and the dinuclear complex has imposed C₂ symmetry. Thus, a thiolate centre in each of two [Ni(L¹)(dcpe)] moieties is alkylated by reaction with one equivalent of CH₂Cl₂ with the



Scheme 1

† Electronic supplementary information (ESI) available: syntheses and characterisation of [Ni(L¹)(dppe)], [Ni(L¹)(dcpe)], [Ni(L³)₂(PP)] and [Ni(L⁴)(PP)], and crystallographic data for **1**·4CH₂Cl₂ and **2**·4CH₂Cl₂. See <http://www.rsc.org/suppdata/cc/b3/b309523a/>

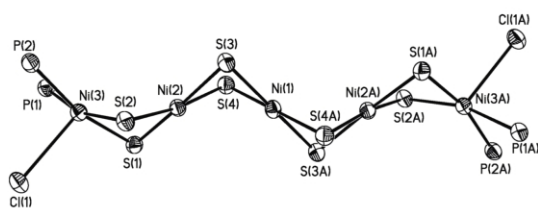
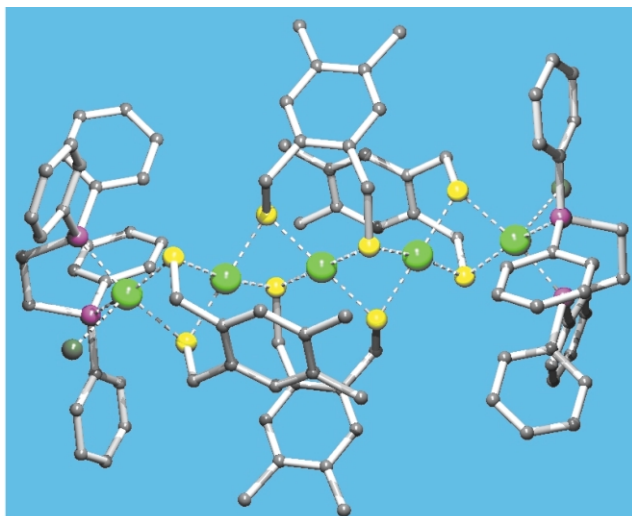


Fig. 1 (upper) Molecular structure of **1**; (lower) diagram showing the zig-zag structural pattern of **1**. Selected bond lengths (Å) and angles (°): Ni(1)–S(3) 2.1813(9), Ni(1)–S(4) 2.1922(9), Ni(2)–S(1) 2.1874(10), Ni(2)–S(2) 2.2031(10), Ni(2)–S(3) 2.1840(10), Ni(2)–S(4) 2.2000(10), Ni(3)–P(1) 2.1616(10), Ni(3)–P(2) 2.1687(10), Ni(3)–S(1) 2.2343(10), Ni(3)–S(2) 2.2300(10), Ni(3)–Cl(1) 2.6217(10), Ni(1)···Ni(2) 2.7738(5), Ni(2)···Ni(3) 2.8552(6), S(3)–Ni(1)–S(4) 75.95(3), S(1)–Ni(2)–S(3) 173.26(4), S(3)–Ni(2)–S(4) 75.73(4), S(1)–Ni(2)–S(4) 98.38(4), S(3)–Ni(2)–S(2) 96.55(4), S(1)–Ni(2)–S(2) 88.98(4), S(2)–Ni(2)–S(4) 170.62(4), Ni(1)–Ni(2)–Ni(3) 176.30(2), P(1)–Ni(3)–P(2) 84.16(4), P(1)–Ni(3)–S(2) 165.17(4), P(2)–Ni(3)–S(2) 91.44(4), P(1)–Ni(3)–S(1) 93.83(4), P(2)–Ni(3)–S(1) 166.42(4), S(1)–Ni(3)–S(2) 87.13(4), P(1)–Ni(3)–Cl(1) 90.17(4), P(2)–Ni(3)–Cl(1) 94.27(4), S(2)–Ni(3)–Cl(1) 104.30(4), S(1)–Ni(3)–Cl(1) 99.17(4).

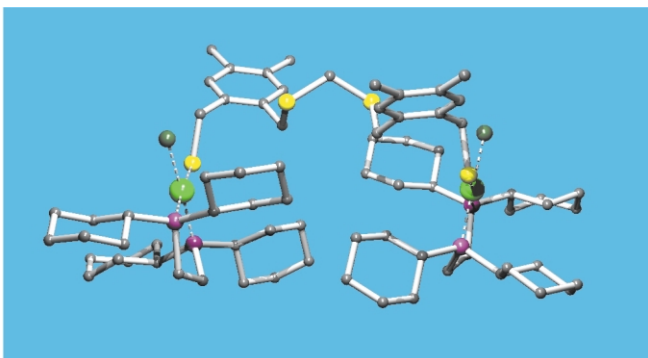


Fig. 2 Molecular structure of **2**. Selected bond lengths (Å) and angles (°): Ni–P(1) 2.1652(8), Ni–P(2) 2.1796(8), Ni–S(1) 2.2042(8), Ni–Cl 2.2170(8), S(2)–C(61) 1.803(3), P(1)–Ni–P(2) 88.65(3), P(1)–Ni–S(1) 88.40(3), P(2)–Ni–S(1) 175.66(3), P(1)–Ni–Cl 174.02(3), P(2)–Ni–Cl 85.45(3), S(1)–Ni–Cl 97.54(3), S(2)–C(61)–S(2A) 117.6(3).

two displaced chloride ions binding each to a Lewis acid Ni centre¹¹ to yield **2**.

It should be noted that when a solution of [Ni(L¹)(dcpe)] in CH₂Cl₂ is stirred at room temperature for 7 days under nitrogen, [NiCl₂(dcpe)] is obtained. This confirms that the Ni–S bonds are labile in solution¹² leading to potential reaction with CH₂Cl₂ and abstraction of chloride by Ni(II). It is interesting to note that Darensbourg *et al.*¹³ have observed that the reaction of square-planar Ni(II)-dithiolate [NiS₂N₂] complexes with alkyl halides typically leads to metal-bound dithioether complexes, either as a square planar dication or a halide bound octahedral complex

without any breaking of Ni–S bonds. Thus, introduction of a single chelate in L¹, rather than a polychelate thiolate as in the the Darensbourg system,¹³ reduces the stability of the [Ni(L¹)] chelate. This increased lability of the NiS₂P₂ complex in our case opens up new pathways for manipulating reactivity at S-centres involving the breaking of labile Ni–S bonds. In [Ni(L¹)(dpe)], the lability of dpe allows the formation of a pentanuclear nickel species. However, when the electron-donating power of the phosphine is increased by changing from dpe to dcpe, the Ni–P bond cleavage is inhibited and CH₂Cl₂ is activated leading to the formation of two [NiClSP₂] centres. Intriguingly, the splitting of CH₂Cl₂ by concerted attack of a Lewis acidic metal centre and basic sulfur reveals a direct analogy with one of the proposed mechanisms for heterolytic cleavage of dihydrogen by [NiFe] hydrogenase.^{8,14}

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Notes and references

‡ Crystallographic data for **1**: 4CH₂Cl₂: C₉₂H₉₆Cl₂Ni₅P₄S₈·4CH₂Cl₂, *M* = 2286.20, triclinic, *a* = 11.0330(7), *b* = 13.1947(8), *c* = 19.0517(12) Å, α = 89.446(2), β = 82.054(2), γ = 66.885(2)°, *U* = 2523.3(5) Å³, *T* = 150(2) K, space group *P* $\bar{1}$, *Z* = 1, μ (Mo–Kα) = 1.454 mm^{−1}, 15902 data collected, 11126 unique (*R*_{int} = 0.019). Final *R*1 [*I* > 2σ(*I*)] = 0.0463, *wR*₂ [all data] = 0.145.

Crystallographic data for **2**: 4CH₂Cl₂: C₇₃H₁₂₂Cl₂Ni₂P₄S₄·4CH₂Cl₂, *M* = 1779.85, monoclinic, *a* = 21.971(3), *b* = 17.011(2), *c* = 23.878(3) Å, β = 92.151(2)°, *U* = 8918(4) Å³, *T* = 150(2) K, space group *C*2/*c*, *Z* = 4, μ (Mo–Kα) = 0.926 mm^{−1}, 22072 data collected, 10528 unique (*R*_{int} = 0.030). Final *R*1 [*I* > 2σ(*I*)] = 0.0416, *wR*₂ [all data] = 0.113.

CCDC reference numbers 217239–217240. See <http://www.rsc.org/suppdata/cc/b3/b309523a/> for crystallographic data in .cif format.

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