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Formation of nickel-thiolate aggregates *via* reaction with CH_2Cl_2

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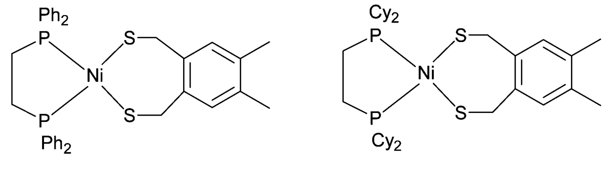
Reaction of the mononuclear nickel-thiolate complex [Ni(L^1)(dppe)] with CH_2Cl_2 affords the novel pentanuclear complex [$Ni_5Cl_2(L^1)_4(dppe)_2$], while [Ni(L^1)(dcpe)] reacts with CH_2Cl_2 to give the binuclear species [$Ni_2Cl_2(L^2)(dcpe)_2$] in which two L^1 units are linked by a methylene group derived from CH_2Cl_2.

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 Darensbourg *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-workers[7] 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 CH_2Cl_2, 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 NiS_2P_2 co-ordination spheres, and have investigated the reactivity of these complexes as a function of variation of phosphine and/or thiolate ligands. When [$NiCl_2$(PP)] (PP = dppe, dcpe) is reacted with 2,4,6-tri-isopropylthiophenol (HL^3) or 2-mercaptomethyl-benzenethiol (H_2L^4) 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 [$Ni(L^3)_2$(PP)] and [Ni(L^4)(PP)] are obtained in good yields and have been fully characterised.† These diamagnetic complexes are stable in CH_2Cl_2 solution and their formulations have been confirmed by X-ray crystallographic studies of single crystals grown from CH_2Cl_2 solution. Reaction of 4,5-dimethyl-1,2-benzenedimethanethiol (H_2L^1) with [$NiCl_2$(dppe)] *via* a procedure similar to that described above,[9] affords the mononuclear complex [Ni(L^1)(dppe)] (Scheme 1) which is stable in the solid state under N_2 or Ar. The formulation of the product as [Ni(L^1)(dppe)] was confirmed by FAB mass spectrometry, NMR spectroscopy and elemental analysis.† The $^{31}P\{^1H\}$ NMR spectrum of [Ni(L^1)(dppe)] in $CDCl_3$ 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 [$Ni(L^3)_2$(PP)] and [Ni(L^4)(PP)], [Ni(L^1)(dppe)] is reactive in CH_2Cl_2 solution, and the $^{31}P\{^1H\}$ NMR spectrum of the crystalline product obtained by diffusion of Et_2O vapour into a solution of [Ni(L^1)(dppe)] in CH_2Cl_2 over a period of 3 days showed in $CDCl_3$ 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, [$Ni_5Cl_2(L^1)_4(dppe)_2$] **1** (Fig. 1, upper) [FAB MS: *m/z* 1910 $(M-Cl)^+$, 1875 $(M-2Cl)^+$]. The complex **1** comprises three central square-planar NiS_4 units and two terminal square-planar P_2NiS_2 units arranged in a zig-zag pattern (Fig. 1, lower). Ni(1) occupies a crystallographic inversion centre and the Ni_5 complex therefore has imposed C_i symmetry. Each terminal Ni(II) centre is further bound by a chloride ion derived from CH_2Cl_2 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 pentanickel(II) complex [$NEt_4]_2[Ni_5(edt)_4(dmit)_2$] (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 [$NEt_4]_2[Ni_5(edt)_4(dmit)_2$] is 102.83°.[10] Thus, **1** represents, to the best of our knowledge, the first example of a linear pentanuclear nickel cluster bridged by thiolates.

Reaction of H_2L^1 with [$NiCl_2$(dcpe)] affords [Ni(L^1)(dcpe)] (Scheme 1) as confirmed by FAB mass spectrometry, NMR spectroscopy and elemental analysis.† The $^{31}P\{^1H\}$ NMR spectrum of [Ni(L^1)(dcpe)] in $CDCl_3$ solution shows a single resonance at 73.56 ppm confirming a *cis* square-planar configuration at Ni(II). [Ni(L^1)(dcpe)], however, reacts with CH_2Cl_2/*n*-hexane stored at -10°C for 7 days to afford crystals of the unexpected binuclear complex [$Ni_2Cl_2(L^2)$(dcpe)] **2** (L^2 = [bis-(4,5-dimethyl-1,2-benzenedimethanethiolato)methane]) (Fig. 2). The structure of **2** reveals that the *cis* thiolates in [Ni(L^1)(dcpe)] have been alkylated by CH_2Cl_2 to yield the corresponding methylene-bridged dithoether/thiolate ligand $[L^2]^{2-}$ bound to Ni(II). C(61) lies on a crystallographic two-fold axis, and the dinickel complex has imposed C_2 symmetry. Thus, a thiolate centre in each of two [Ni(L^1)(dcpe)] moieties is alkylated by reaction with one equivalent of CH_2Cl_2 with the



[Ni(L^1)(dppe)] [Ni(L^1)(dcpe)]

Scheme 1

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† Electronic supplementary information (ESI) available: syntheses and characterisation of [Ni(L^1)(dppe)], [Ni(L^1)(dcpe)], [$Ni(L^3)_2$(PP)] and [Ni(L^4)(PP)], and crystallographic data for **1**·$4CH_2Cl_2$ and **2**·$4CH_2Cl_2$. See http://www.rsc.org/suppdata/cc/b3/b309523a/

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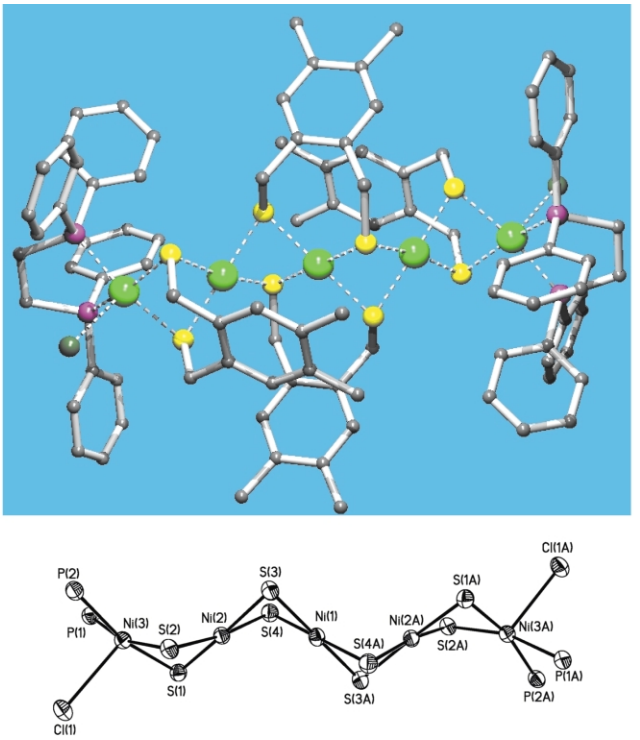

Fig. 1 (upper) Molecular structure of **1**; (lower) diagram showing the zig-zag structural pattern of **1**. Selected bond lengths (Å) and angles (°): Ni(1)–S(3) 2.1813(9), Ni(1)–S(4) 2.1922(9), Ni(2)–S(1) 2.1874(10), Ni(2)–S(2) 2.2031(10), Ni(2)–S(3) 2.1840(10), Ni(2)–S(4) 2.2000(10), Ni(3)–P(1) 2.1616(10), 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)$\cdots$Ni(2) 2.7738(5), Ni(2)$\cdots$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).

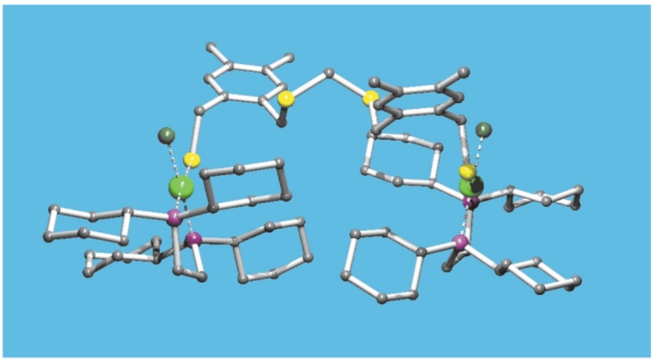

Fig. 2 Molecular structure of **2**. Selected bond lengths (Å) and angles (°): Ni–P(1) 2.1652(8), Ni–P(2) 2.1796(8), Ni–S(1) 2.2042(8), Ni–Cl 2.2170(8), S(2)–C(61) 1.803(3), P(1)–Ni–P(2) 88.65(3), P(1)–Ni–S(1) 88.40(3), P(2)–Ni–S(1) 175.66(3), P(1)–Ni–Cl 174.02(3), P(2)–Ni–Cl 85.45(3), S(1)–Ni–Cl 97.54(3),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

two displaced chloride ions binding each to a Lewis acid Ni centre[11] to yield **2**.

It should be noted that when a solution of [Ni(L^1)(dcpe)] in CH_2Cl_2 is stirred at room temperature for 7 days under nitrogen, [$NiCl_2$(dcpe)] is obtained. This confirms that the Ni–S bonds are labile in solution[12] leading to potential reaction with CH_2Cl_2 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 [NiS_2N_2] 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 L^1, rather than a polychelate thiolate as in the the Darensbourg system,[13] reduces the stability of the [Ni(L^1)] chelate. This increased lability of the NiS_2P_2 complex in our case opens up new pathways for manipulating reactivity at S-centres involving the breaking of labile Ni–S bonds. In [Ni(L^1)(dppe)], the lability of dppe allows the formation of a pentanuclear nickel species. However, when the electron-donating power of the phosphine is increased by changing from dppe to dcpe, the Ni–P bond cleavage is inhibited and CH_2Cl_2 is activated leading to the formation of two [$NiClSP_2$] centres. Intriguingly, the splitting of CH_2Cl_2 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**$\cdot$ $4CH_2Cl_2$: $C_{92}H_{96}Cl_2Ni_5P_4S_8\cdot 4CH_2Cl_2$, $M = 2286.20$, triclinic, $a = 11.0330(7)$, $b = 13.1947(8)$, $c = 19.0517(12)$ Å, $\alpha = 89.446(2)$, $\beta = 82.054(2)$, $\gamma = 66.885(2)°$, $U = 2523.3(5)$ Å^3, $T = 150(2)$ K, space group $P\bar{1}$, $Z = 1$, μ (Mo–Kα) = 1.454 mm^{-1}, 15902 data collected, 11126 unique ($R_{\rm int} = 0.019$). Final $R1$ [$I > 2\sigma(I)$] = 0.0463, wR_2 [all data] = 0.145.

Crystallographic data for **2**$\cdot 4CH_2Cl_2$: $C_{73}H_{122}Cl_2Ni_2P_4S_4\cdot 4CH_2Cl_2$, $M = 1779.85$, monoclinic, $a = 21.971(3)$, $b = 17.011(2)$, $c = 23.878(3)$ Å, $\beta = 92.151(2)°$, $U = 8918(4)$ Å^3, $T = 150(2)$ K, space group $C2/c$, $Z = 4$, μ (Mo–Kα) = 0.926 mm^{-1}, 22072 data collected, 10528 unique ($R_{\rm int} = 0.030$). Final $R1$ [$I > 2\sigma(I)$] = 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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