

## Synthesis and Structure of a Unique Nickel-thiolate Dimer, $[(RS)Ni(\mu_2-SR)_3Ni(SR)]^{1-}$ . An Example of Face-sharing Bitetrahedra

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The reaction of  $Ni(OAc)_2$  with  $Li[S-2,4,5-Pr^i_3C_6H_2]$  and  $[Ph_4P]Br$  in a 1 : 5 : 1 ratio produces  $[PPh_4][Ni_2(S-2,4,5-Pr^i_3-C_6H_2)_5]^-$  **1**; the anion of **1** was shown by X-ray crystallography to possess the rare face-sharing bitetrahedral geometry—the face-sharing  $[Ni(\mu_2-SR)_3Ni]$  unit is described by acute Ni–S–Ni angles of  $69^\circ$  and a short Ni–Ni interaction of 2.607 Å.

The chemistry of nickel with thiolate ligands has assumed a new importance owing to studies that have indicated nickel–sulfur centres in such enzymes as hydrogenase and carbon monoxide dehydrogenase.<sup>1</sup> In addition, biological  $Ni^{II}$  cysteine centres have also been produced by the incorporation of nickel in such proteins as rubredoxin, alcohol dehydrogenase and metallothionein.<sup>2</sup> In our attempts to use sterically encumbered thiolate ligands to replicate biological  $Ni^{II}$ –cysteine coordination modes, we have synthesized an unusual dimeric nickel-thiolate compound that possesses the rare face-sharing bitetrahedral coordination geometry.

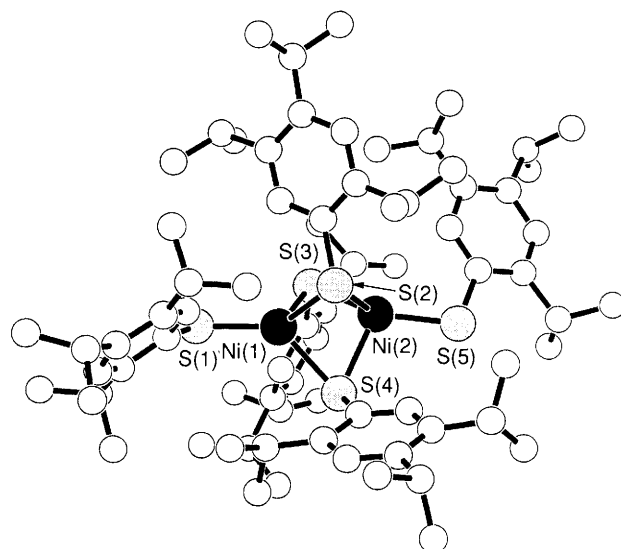
The reaction of  $Ni(OAc)_2$  with 5 equiv. of lithium 2,4,5-triisopropylbenzenethiolate,  $Li[S-2,4,5-Pr^i_3-C_6H_2]$ , in MeCN followed by the addition of  $[Ph_4P]Br$  produces brown crystals of  $[PPh_4][Ni_2(S-2,4,5-Pr^i_3-C_6H_2)_5]^-$ . An X-ray crystal structure determination† revealed the structure to consist of a dimer with two approximately tetrahedral  $[Ni(SR)_4]$  units joined by three bridging thiolate ligands that define a common threefold face (Fig. 1). As such, the structure is an unusual example of a compound possessing the face-sharing bitetrahedral geometry. Although metal tetrahedra sharing vertices and edges are widespread in structural inorganic chemistry, examples of face-sharing bitetrahedra are rare.<sup>3</sup> Examples of two other discrete dimers have been structurally characterized,  $[BrLi(hmpa)_3LiBr]$  (*hmpa* = hexamethylphosphoramide) and  $[(PPh_3)Cu_3Cu(PPh_3)]^{1-}$ ,<sup>4,5</sup> as well as a series of oligomeric and polymeric  $[Cu_xI_y]$  compounds that contain the face-sharing tetrahedral subunits.<sup>6</sup>

Some comments on the structure of the  $[Ni_2(S-2,4,5-Pr^i_3-C_6H_2)_5]^{1-}$  anion **1** are presented. The average Ni–S distance about each nickel in **1** is 2.275 Å which compares with the 2.28 Å distance found in several  $[Ni(SPh)_4]^{2-}$  structures.<sup>7,8</sup> However, the Ni–S<sub>terminal</sub> distances (2.19 Å) are shorter than the mean, and the Ni–S<sub>bridging</sub> distances are longer (2.30 Å) than the mean. The distortions in the  $[(RS)Ni(\mu_2-SR)_3Ni(SR)]$  unit from an idealized  $C_3$  axis of symmetry is reflected in the metrical parameters of the S(1)–Ni(1)–Ni(2) and S(5)–Ni(2)–Ni(1) angles [of  $157.4(2)^\circ$  and  $163.6(2)^\circ$ , respectively] and the S<sub>i</sub>–Ni–S<sub>j</sub> angles [which vary from  $102.6$  to  $138.2^\circ$ ]. The nature of these distortions can be understood by a consideration of steric interactions of the phenyl rings of the terminal thiolate ligands with the  $[Ni(\mu_2-SR)_3Ni]$  core. This type of interaction is well-documented as the source of the distortions in  $[M(SPh)_4]^{2-}$  complexes.<sup>7,9</sup>

The  $[Ni(\mu_2-SR)_3Ni]$  unit is described by a short Ni–Ni distance of 2.607(3) Å and acute Ni(1)–S<sub>b</sub>–Ni(2) angles of  $68.2$ – $69.4^\circ$ . The S<sub>b</sub>–Ni–S<sub>b</sub> angles fall in the range of  $87$  to  $95^\circ$ , indicative of the orthogonal orientation of the Ni–S<sub>b</sub> bonds. Short Ni–Ni distances have also been found in  $[Ni(\mu_2-SR)_2Ni]$  fragments;<sup>10</sup> for example Ni–Ni distances of 2.66–2.69 Å occur in  $[Ni(\mu_2-SR)_2]_4$  compounds.<sup>11</sup> A short Ni–Ni distance does not necessitate a metal–metal bond.<sup>12</sup>

The marked tendency of thiolate complexes of transition metal ions (and of nickel in particular) to form oligomeric complexes is well documented.<sup>13</sup> In this realm, several examples of confacial bioctahedra are known.<sup>13</sup> For nickel, a more common mode of linkage is the sharing of edges between square planar metal arrays.<sup>10,11</sup> With aromatic thiolate ligands, nickel is known to form monomeric tetrahedral complexes,  $[Ni(SPh)_4]^{2-}$  and a square planar, dimeric complex,  $[Ni_2(S-p-C_6H_4Cl)_6]^{2-}$ .<sup>7,8,14</sup> The characterization of **1** as a face-sharing bitetrahedral complex provides a new geometric coordination mode in metal–thiolate chemistry.

There is nothing in the structure of the  $[Ni(\mu_2-SR)_3Ni]$  unit of **1** that would suggest that this new type of nickel–thiolate structure was imposed by the steric properties of the thiolate ligands. Rather, it would appear that the use of this bulky aromatic thiolate has prevented the generation of the polymeric materials that were previously obtained with benzene thiolate. The synthesis of this novel nickel–thiolate dimer



**Fig. 1** Structural diagram of  $[Ni(S-2,4,5-Pr^i_3-C_6H_2)_5]^{1-}$ . Selected bond distance (Å) and angles ( $^\circ$ ). Ni(1)–S(1) 2.190(4); Ni–S(2) 2.267(4); Ni(1)–S(3) 2.307(4); Ni(1)–S(4) 2.324(4); Ni(1)–Ni(2) 2.607(3); Ni(2)–S(5) 2.194(4); Ni(2)–S(2) 2.311(4); Ni(2)–S(3) 2.282(4); Ni(2)–S(4) 2.324(4); S(1)–Ni(1)–S(2) 135.9(2); S(1)–Ni(1)–S(3) 102.6(2); S(1)–Ni(1)–S(4) 131.4(2); S(5)–Ni(2)–S(2) 122.9(2); S(5)–Ni(2)–S(3) 138.2(2); S(5)–Ni(2)–S(4) 109.3(2); S(2)–Ni(1)–S(3) 91.8(2); S(2)–Ni(1)–S(4) 87.9(2); S(3)–Ni(1)–S(4) 93.9(2); S(2)–Ni(2)–S(3) 91.3(2); S(2)–Ni(2)–S(4) 86.8(2); S(3)–Ni(2)–S(4) 94.5(2); Ni(1)–S(2)–Ni(2) 69.4(2); Ni(1)–S(3)–Ni(2) 69.2(2); Ni(1)–S(4)–Ni(2) 68.2(1); Ni(1)–S(1)–C(11) 103.9(3); Ni(2)–S(5)–C(51) 104.7(4).

† Crystal data for **1**:  $Ni_2S_5P_1C_{99}H_{135}$ , monoclinic, space group  $P2_1/c$ ,  $a = 14.701(8)$ ,  $b = 47.08(3)$ ,  $c = 13.997(4)$  Å,  $\beta = 99.49(4)^\circ$ ,  $V = 9555$  Å<sup>3</sup>,  $Z = 4$ . Data were collected at ambient temperature with an Enraf-Nonius CAD4 diffractometer using Mo–K $\alpha$  radiation. 3019 unique reflections (with  $I > \sigma(I)$ ), which were collected using  $\omega$  scans with  $0 < 2\theta < 40$ , were used in the structure solution to give a final  $R$  value of 0.054 ( $R_w = 0.059$ ). In the final least-squares refinement the phenyl rings were treated as rigid groups and all remaining non-hydrogen atoms were refined anisotropically for a total of 541 variables. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

provides an indication that thiolate ligands substituted in only one of the *ortho* positions may also be useful in moderating the chemistry of metal–thiolate compounds.<sup>15</sup>

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