

First example of thiolate-bridged square-pyramidal and octahedral nickel(ii) ions: $[\text{Ni}_2(\text{L}_{\text{SO}})(\text{NCS})_2(\text{dmf})]$

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A structure determination reveals that $[\text{Ni}_2(\text{L}_{\text{SO}})(\text{NCS})_2(\text{dmf})]$ **2 is one of the best structural models to date for the active site of $[\text{Ni},\text{Fe}]$ hydrogenases: it also contains the first example of a high-spin thiolate-bound square-pyramidal nickel(ii) ion.**

There is currently intense interest in dinickel thiolate-bridged complexes as first-generation models for the active site in $[\text{Ni},\text{Fe}]$ hydrogenases,¹ yet only a handful of such complexes have been isolated and fully characterised.² The coordination environment of the dinuclear hydrogenase active site is thought to consist of a combination of five-coordinate nickel and six-coordinate iron ions bridged by two thiolate donors (one axial, one equatorial bridge) and one unknown, possibly oxygen-derived, equatorial bridge.¹ Unfortunately the vast majority of nickel mixed-donor thiolate complexes are poor structural models as they exhibit square-planar nickel ion geometries due to the strong ligand field imposed by the thiolate donors.^{1–4} There are therefore relatively few examples of geometries other than square planar:^{2,5–8} the coordination number five is especially rare, and, to our knowledge, the known examples of this coordination number are all low spin.^{2,8} In Schiff-base macrocyclic complexes in which two bridging thiolates are provided this tendency is also observed, with the nickel(ii) ions adopting square-planar N_2S_2 stereochemistry.^{3,4} Clearly the synthesis of complexes which have coordination environments similar to those observed in the metalloprotein is highly desirable. Hence our research efforts are currently directed towards preparing mixed-donor dinickel thiolate-bridged complexes, in which a range of stereochemistries are observed at nickel(ii), as first-generation structural models for hydrogenase.^{4–7}

Recently we isolated a unique complex, $[\text{Ni}_2(\text{L}_{\text{SO}})(\text{MeCN})_2][\text{ClO}_4]_2$ **1**, in which, despite the macrocycle $\text{L}_{\text{SO}}^{2-}$ providing potentially identical metal-binding environments, two differing geometries were observed for the nickel(ii) ions, specifically N_4SO octahedral and N_2SO square planar (Scheme 1).⁶ Given that this occurred in the presence of only rather weak ligand field ancillary ligands (acetonitrile solvent molecules and perchlorate ions) it seemed likely that greater coordination

numbers could be imposed on the nickel(ii) ions. This paper concerns the intriguing result of adding thiocyanate ions to $[\text{Ni}_2(\text{L}_{\text{SO}})(\text{MeCN})_2][\text{ClO}_4]_2$ **1**.

The addition of 2.2 equiv. sodium thiocyanate to an acetonitrile solution of complex **1** causes precipitation of a solid which on recrystallisation from dmf by vapour diffusion of diethyl ether yields $[\text{Ni}_2(\text{L}_{\text{SO}})(\text{NCS})_2(\text{dmf})]$ **2** in which there has been a dramatic alteration in the nickel ion stereochemistries (Scheme 1). The X-ray structure determination reveals that each nickel ion in **2** is bound by an identical set of macrocycle donors (one amine nitrogen, one imine nitrogen, one bridging thiophenolate sulfur and one bridging phenolate oxygen), yet adopts differing stereochemistry (Fig. 1).[‡] Ni(1) is octahedral binding one thiocyanate ion and a dmf solvent molecule to the remaining 'axial' sites, whilst Ni(2) is square-pyramidal binding one thiocyanate ion only. Comparison of the Ni–X bond lengths with related complexes^{3–8} clearly indicates that Ni(2) is high spin [as is Ni(1)], as does the observation that Ni(2) is 0.26

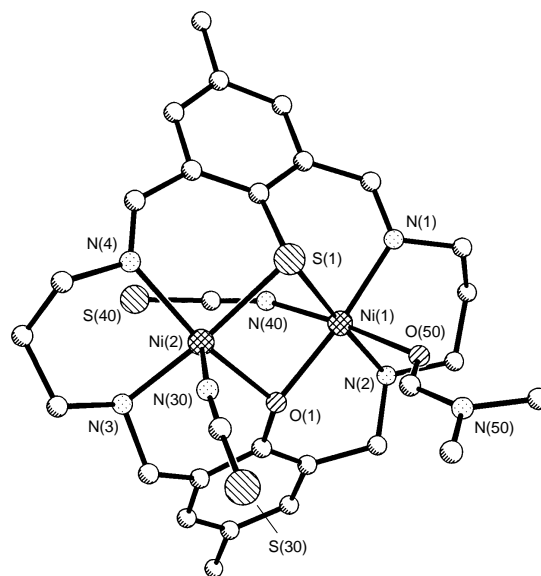
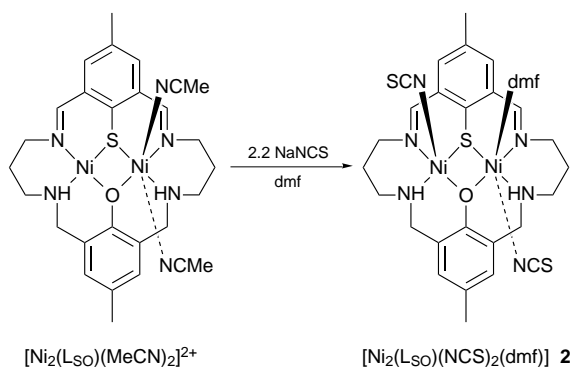


Fig. 1 Perspective view of $[\text{Ni}_2(\text{L}_{\text{SO}})(\text{NCS})_2(\text{dmf})]$ **2**. Selected bond distances (Å) and angles (°): Ni(1)–N(40) 2.066(7), Ni(1)–N(2) 2.073(7), Ni(1)–N(1) 2.074(7), Ni(1)–O(50) 2.102(6), Ni(1)–O(1) 2.121(6), Ni(1)–S(1) 2.373(3), Ni(2)–N(30) 2.005(8), Ni(2)–N(3) 2.061(6), Ni(2)–N(4) 2.085(7), Ni(2)–O(1) 2.113(6), Ni(2)–S(1) 2.341(3), Ni(1)–Ni(2) 3.172(2), S(1)–O(1) 3.036(6); N(40)–Ni(1)–N(2) 91.7(3), N(40)–Ni(1)–O(50) 86.4(3), N(1)–Ni(1)–O(50) 89.4(3), N(40)–Ni(1)–O(1) 84.9(2), N(2)–Ni(1)–O(1) 95.9(3), N(1)–Ni(1)–O(1) 171.2(3), O(50)–Ni(1)–O(1) 91.2(2), N(40)–Ni(1)–S(1) 92.6(2), N(2)–Ni(1)–S(1) 175.7(2), N(1)–Ni(1)–S(1) 86.4(2), O(50)–Ni(1)–S(1) 89.3(2), O(1)–Ni(1)–S(1) 84.8(2), N(30)–Ni(2)–N(3) 94.3(3), N(30)–Ni(2)–N(4) 99.7(3), N(3)–Ni(2)–N(4) 91.1(3), N(30)–Ni(2)–O(1) 95.8(3), N(3)–Ni(2)–O(1) 93.2(2), N(4)–Ni(2)–O(1) 163.5(2), N(30)–Ni(2)–S(1) 98.4(2), N(3)–Ni(2)–S(1) 167.3(2), N(4)–Ni(2)–S(1) 86.6(2), O(1)–Ni(2)–S(1) 85.8(2), Ni(2)–S(1)–Ni(1) 84.59(9), Ni(2)–O(1)–Ni(1) 97.0(2).



Scheme 1 Formation of $[\text{Ni}_2(\text{L}_{\text{SO}})(\text{NCS})_2(\text{dmf})]$ **2**

Å out of the N₂SO donor plane towards the bound thiocyanate ion.⁹ The assignment of Ni(2) as high spin is also consistent with a preliminary magnetic measurement of 4.5 μ_B for **2** at room temperature.⁷ This contrasts dramatically with the situation found in **1**: in both **1** and **2** one nickel(ii) ion is octahedral, however the second nickel(ii) ion is low-spin square planar in **1** whereas it is high-spin square pyramidal in **2**. To our knowledge this is the first example of a thiolate-bound high-spin square-pyramidal nickel(ii) ion. Overall complex **2** is currently one of the best first-generation structural models available for the hydrogenase active site.

It is interesting that reaction of [Ni₂(L_{SO})(MeCN)₂][ClO₄]₂ with an excess of thiocyanate ions also yields **2**: further thiocyanate ions are not bound at the vacant axial site on the high-spin Ni(2) ion or as a replacement for the dmf molecule on Ni(1). This is presumably due to each nickel ion already satisfying the electroneutrality principle due to the coordination of anionic thiophenolate, phenolate and thiocyanate donors. This interpretation is consistent with the observation that one thiocyanate ion binds to each nickel ion in **2** in contrast with the situation in **1** where both neutral ancillary ligands bind to just one of the two nickel ions. Once two thiocyanate ions are bound the complex is neutral so lack of solubility may also play an important role in the formation and isolation of **2**.

The macrocycle is very bent: the two phenyl ring planes intersect at 100.5° and the two macrocycle N₂SO donor planes intersect at 143°. This is due in part to the differing geometries of the thiophenolate sulfur and phenolate oxygen atoms;^{10,11} the former is tetrahedrally distorted [Ni–S(1)–X 84.6–103.3°] whilst the latter is closer to trigonal planar [Ni–O(1)–X 97.0–124.1°]. However, the Ni(1)–O(1)–Ni(2) angle of 97.0° is the smallest observed to date for a phenolate-bridged dinickel macrocyclic complex, and is far from trigonal.¹¹ The small Ni–X–Ni angles in **2** should have interesting consequences magnetically and this is under investigation.⁷

In summary, the ligand L_{SO}²⁻ is of intermediate field strength, and the macrocyclic cavity quite flexible, so that it is able to accommodate a combination of either high-spin–high-spin or high-spin–low-spin nickel(ii) ions as is demonstrated herein. This is a unique situation and augurs well for the ability of the L_{SO}²⁻ macrocycle to yield further exciting first-generation models for the active site of the [Ni,Fe] hydrogenases. Hence further binding studies are under way, as are redox and XAS investigations.⁷

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Footnotes

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‡ *Crystal data* for **2**·Et₂O: C₃₃H₄₇N₇Ni₂O₃S₃, yellow oblong plate, 0.7 × 0.3 × 0.1 mm, triclinic, *P* $\bar{1}$, *a* = 11.391(4), *b* = 12.617(4), *c* = 14.082(4) Å, α = 75.450(10), β = 78.29(2), γ = 85.78(2)°, *U* = 1918(1) Å³, *Z* = 2, μ = 1.19 mm⁻¹, *D*_c = 1.391 g cm⁻³. Data were collected at 168 K on a Siemens P4 four-circle diffractometer using graphite-monochromated Mo-Kα radiation. 5088 Reflections were collected, 4 < 2θ < 45°, and the 4992 independent reflections were used in the structural analysis after a semi-empirical absorption correction had been applied. The structure was solved by direct methods (SHELXS-86)¹² and refined against all *F*² data (SHELXL-93)¹³ to *R*₁ = 0.062 [for 2662 *F* > 4σ(*F*); *wR*₂ = 0.145 and goodness of fit = 0.85 for all 4992 *F*²; 428 parameters; all non-hydrogen atoms except the disordered diethyl ether molecule of crystallisation anisotropic; max., min. residual electron density +0.62, -0.52 e Å⁻³]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/366.

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