Trinickel(II) Complex of an Acyclic Thiophenolate Ligand: the X-Ray Crystal Structure of $[Ni_2L_2Ni](ClO_4)_2(H_2O)$ Reveals Alternating Square-planar and Octahedral Nickel Ions

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Nickel(II) ions catalyse the formation of the first acetal to be derived from 2-sulfanyl-5-methylisophthaldehyde; the structure of $[Ni_2L_2Ni](ClO_4)_2(H_2O)$ **1** reveals thiolate-bridged nickel(II) ions with successive N_2S_2 square planar, N_4S_2 octahedral and N_2S_2 square planar nickel environments.

Nickel is recognised as a metal of considerable biological importance, forming the active site of a variety of metalloproteins including hydrogenases, CO dehydrogenase, methyl-*S*-coenzyme-M reductase and urease.[1] To model those sites which contain sulfur and nitrogen–oxygen donor atoms and to prepare nickel complexes which are expected to be of interest in their own right, we have derived a series of Schiff-base ligands from 2-sulfanyl-5-methylisophthaldehyde.[2] Previous work by Robson *et al.*, with 2-sulfanyl-5-methylisophthaldehyde yielded a range of acyclic ligands which were exploited largely for coordination of palladium.[3] Recently interest has turned to the incorporation of this dicarbonyl component into cyclic ligands.[2,4] We have prepared a range of macrocycles from 2-sulfanyl-5-methylisophthaldehyde as part of our programme to introduce new dicarbonyl head units into Schiff base macrocyclic chemistry.[2,5] Here we present a novel trinickel(II) complex of the acyclic ligand L^{2-} which forms during the cyclisation reaction outlined in Fig. 1.

The complex $[Ni_2L_2Ni](ClO_4)_2(H_2O)$ **1**† was prepared, using Schlenk techniques, from deprotonated 2-sulfanyl-5-methylisophthaldehyde **2**,[2,3] nickel(II) perchlorate and 1,3-diaminopropane, in ethanol (Fig. 1). The IR spectrum of **1** was consistent with imine and acetal formation, and no peaks corresponding to unreacted carbonyl were present. Gold-brown crystals of **1** suitable for X-ray crystal structure analysis‡ were obtained, in 15% yield based on **2**, by fractional recrystallisation of the crude product from acetonitrile by diethyl ether diffusion.§

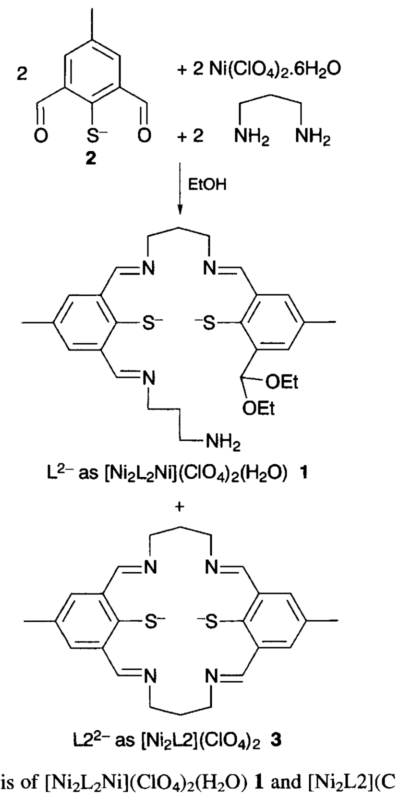

Fig. 1 Synthesis of $[Ni_2L_2Ni](ClO_4)_2(H_2O)$ **1** and $[Ni_2L2](ClO_4)_2$ **3**§

The structure determination of **1** reveals that the complex is indeed trinuclear, with two square planar N_2S_2 nickel atoms, Ni(1) and Ni(2), and a central octahedral N_4S_2 nickel atom, Ni(3), bridging the two mononuclear acyclic units (Fig. 2; to help distinguish the two ligands from each other, one is shown with hollow bonds whilst the other is shown with solid bonds). The square planar nickel atoms, Ni(1) and Ni(2), are only 0.040(2) and 0.010(2) Å out of the respective N_2S_2 planes. Bonds between the donor atoms and the square planar nickel atoms are shorter than those to the octahedral nickel atom by 0.19–0.38 Å. This is consistent with the observed difference in geometry.[8] Each of the two acyclic ligands is somewhat buckled; the two aromatic rings are inclined at 147.9(2)° (hollow bonds) and 153.7(3)° (solid bonds) to each other. This is due in part to the distorted geometries the thiolate sulfur donors adopt (∠Ni–S–X 97.6–143.2°). The two largest of these angles, 137.5 and 143.2°, correspond to Ni–S–Ni(3) bridging by S(2) and S(4) respectively; the remaining angles at S fall in the range 97.6–112.1°. The imine nitrogen atoms range from 0.095(9) to a substantial 0.626(8) Å out of the plane of the

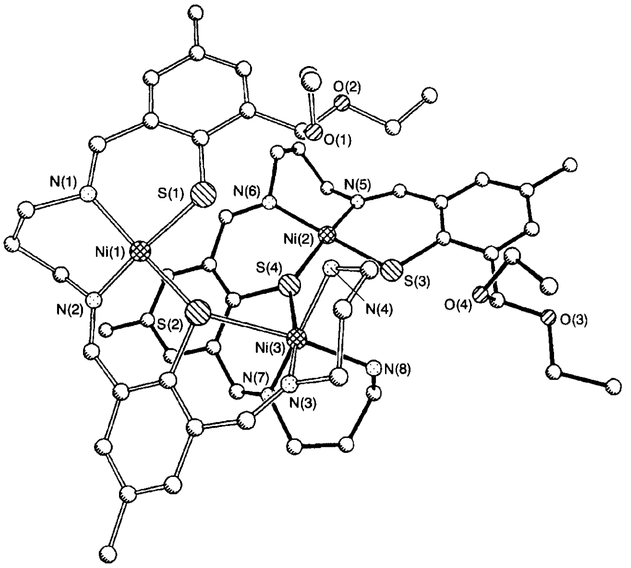

Fig. 2 Perspective view of the $[Ni_2L_2Ni]^{2+}$ cation. Selected interatomic distances (Å) and angles (°): Ni(1)–N(1) 1.893(4), Ni(1)–N(2) 1.900(4), Ni(1)–S(1) 2.160(2), Ni(1)–S(2) 2.147(2), Ni(2)–N(5) 1.881(4), Ni(2)–N(6) 1.909(4), Ni(2)–S(3) 2.142(2), Ni(2)–S(4) 2.167(2), Ni(3)–N(3) 2.071(4), Ni(3)–N(4) 2.085(4), Ni(3)–N(7) 2.058(4), Ni(3)–N(8) 2.111(4), Ni(3)–S(2) 2.526(2), Ni(3)–S(4) 2.436(2), Ni(1)···Ni(3) 4.357(2), Ni(2)···Ni(3) 4.369(2), N(1)–Ni(1)–N(2) 91.5(2), N(1)–Ni(1)–S(2) 166.85(13), S(2)–Ni(1)–N(2) 96.04(12), N(1)–Ni(1)–S(1) 91.73(12), N(2)–Ni(1)–S(1) 172.96(13), S(1)–Ni(1)–S(2) 81.97(5), N(5)–Ni(2)–N(6) 91.4(2), N(5)–Ni(2)–S(3) 95.10(13), N(6)–Ni(2)–S(3) 169.96(13), N(5)–Ni(2)–S(4) 172.85(13), N(6)–Ni(2)–S(4) 91.03(12), S(3)–Ni(2)–S(4) 83.39(5), N(3)–Ni(3)–N(7) 98.7(2), N(4)–Ni(3)–N(7) 169.9(2), N(3)–Ni(3)–N(4) 91.3(2), N(7)–Ni(3)–N(8) 86.4(2), N(3)–Ni(3)–N(8) 94.4(2), N(4)–Ni(3)–N(8) 91.4(2), N(7)–Ni(3)–S(4) 83.67(12), N(3)–Ni(3)–S(4) 169.15(11), N(4)–Ni(3)–S(4) 86.77(12), N(8)–Ni(3)–S(4) 96.35(11), N(7)–Ni(3)–S(2) 92.08(11), N(3)–Ni(3)–S(2) 78.17(11), N(4)–Ni(3)–S(2) 91.37(12), N(8)–Ni(3)–S(2) 172.10(11), S(4)–Ni(3)–S(2) 91.18(5).

respective phenyl rings, thus adding a further twist to the acyclic ligands and facilitating binding to the central Ni(3) atom.

To our knowledge this is the first example of acetal formation by 2-sulfanyl-5-methylisophthaldehyde. Acetal formation is not uncommon in the chemistry of the related 2,6-diformylphenol moiety however.[9]

A search of the Cambridge Structural Database[10] revealed that no other examples of discrete trinickel clusters with both square and octahedral nickel centres of ligands containing at least one sulfur donor have been structurally characterised.[11] Further characterisation, including X-ray absorption studies,[12] of this unique complex and related complexes is underway.[2]

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Footnotes

† Satisfactory C, H, N elemental analyses were obtained for **1** and **3**. Chemically irreversible oxidation of **1** in MeCN–NEt$_4$(ClO$_4$) with a Pt electrode occurs with a peak in the cyclic voltammogram at about 1.1 V *vs.* SCE. The wave height corresponds to a 2 or 3 electron oxidation.

‡ *Crystal data* for $C_{56}H_{78}N_8O_{13}S_4Cl_2Ni_3$, gold-brown rectangular plate, 0.2 × 0.4 × 0.9 mm, triclinic, space group $P\bar{1}$, $a = 12.497(5)$, $b = 13.858(4)$, $c = 20.737(5)$ Å, $\alpha = 91.51(3)$, $\beta = 105.32(2)$, $\gamma = 109.10(3)°$, $U = 3248(2)$ Å^3, $Z = 2$, $\mu = 1.14$ mm^{-1}. Data were collected at 130 K on a Siemens P4 four circle diffractometer using graphite monochromated Mo-Kα radiation, 8644 reflections were collected in the range $4 < 2\theta < 45°$ and the 8503 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)[6] and refined against all F^2 data (SHELXL-93)[7] to $R_1 = 0.0401$ [for 5752 $F > 4\sigma(F)$; w$R_2 = 0.0923$ and goodness of fit = 0.865 for all 8503 F^2; 793 parameters; all non-H atoms anisotropic; one perchlorate disordered]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ The less soluble [Ni$_2$L2](ClO$_4$)$_2$ **3** was also isolated, in 23% crude yield based on **2**, from this reaction. However, pure samples of red crystals of **3** are more readily isolated, in 43% yield, by carrying out the reaction in propan-2-ol.[2]

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