# First of a new family of tetraamine bis(μ-thiolate)-containing macrocycles: structure and stepwise oxidations and reductions of the dinickel(II) complex

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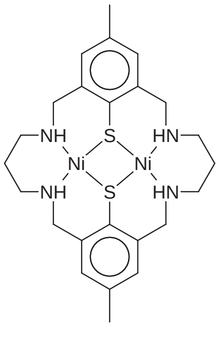
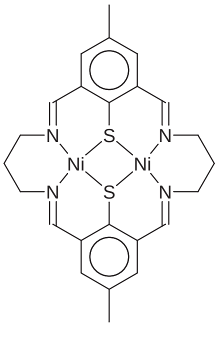
**Reduction of a dinickel(II) dithiolate Schiff-base macrocyclic complex with sodium borohydride results in a 'bowl'-shaped dinickel(II) dithiolate amine macrocyclic complex which exhibits four separate one-electron redox processes.**

The active site of the [Ni,Fe]-hydrogenases, metalloenzymes which catalyse $H_2 = 2H^+ + 2e^-$, has only recently been established to be dimetallic.[1] There has been considerable debate as to the oxidation state(s) of the nickel centre during the catalytic cycle.[2] As the overall reaction is a redox process it seems likely that either one or both of the doubly cysteinate-bridged metal ions, nickel and iron, change oxidation state during the catalytic cycle, although a third possibility, of the thiolate residues being non-innocent, has yet to be ruled out. Early studies of mononickel thiolate model compounds established many important chemical and electrochemical points,[2] and indicated that interactions with species such as carbon monoxide and hydrogen occur in the Ni(I) oxidation state.[2,3] In order to better mimic the dimetallic active site, studies are now probing the impact of the presence of a second metal ion, doubly bridged to the nickel ion by thiolate residues, on the properties of the complexes.[4–8] We have prepared a family of dinickel thiolate model complexes in which the two incorporated nickel(II) ions are bridged by thiolate(s): the polydentate ligands employed supply $N_2S_2$ or $N_2X_1S_1$ (X = O or N) coordination to each nickel ion.[5–7] Here we present the substantial effects on structure and electrochemistry of varying the nature of the nitrogen donors from imine to amine in a dinucleating macrocycle which provides $N_2S_2$ coordination environments to each of the pair of bound nickel(II) ions.

The red, diamagnetic, tetraimine macrocyclic complex **2** was prepared as reported (**CAUTION**: Perchlorate salts are potentially explosive and should therefore be handled with appropriate care).[6] The first of this new generation of tetraamine macrocyclic complexes, complex **1**, was prepared from **2** by sodium borohydride reduction in MeOH in air followed by an acid workup.[9] Red single crystals of **1** were obtained in 60–80% yield by recrystallisation of the crude product from MeCN by vapour diffusion of diethyl ether and an X-ray structure determination carried out.†‡ The nickel(II) ions in **1** have an $N_2S_2$ square planar environment (Fig. 1) as observed in the tetraimine complex **2**.[6] However, in complex **1** the overall shape of the complex is very different to that of **2**. Specifically, in addition to the folding of the two phenyl planes, which is observed in both complexes (angles between phenyl planes: 98.8 and 105.9° in **2** *vs.* 111.5° in **1**), the ligand in complex **1** exhibits a second folding at right angles to the first, which leads to a 'bowl'-shaped complex overall (Fig. 1) rather than the 'bowed' shape observed for **2**.[6] This additional fold is possible in **1** because of the change from conjugated trigonal imine groups in **2** to flexible tetrahedral amine groups in **1**, and this is readily seen by comparison of the distances of the nitrogen atoms from the plane of the respective phenyl rings (**2**, N 0.25–0.52 Å out-of-plane; **1**, N 1.10 and 1.11 Å oop). This leads



as $[Ni_2L1][ClO_4]_2$ **1**



as $[Ni_2L2][ClO_4]_2$ **2**

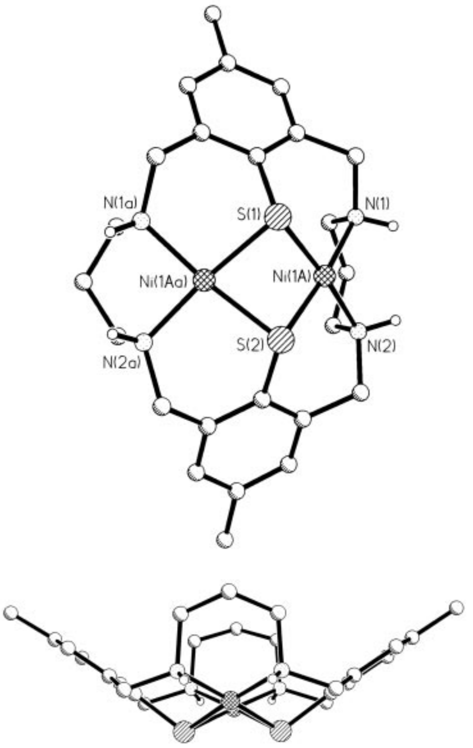


**Fig. 1** Perspective diagrams of the cation of **1**, $[Ni_2L1]^{2+}$. No hydrogen atoms, except those on the amine nitrogen atoms, are shown. Selected bond lengths (Å) and angles (°): Ni(1A)–N(2) 1.951(4), Ni(1A)–N(1) 1.951(4), Ni(1A)–S(1) 2.1685(18), Ni(1A)–S(2) 2.177(2), N(2)–Ni(1A)–N(1) 88.72(18), N(2)–Ni(1A)–S(1) 174.37(14), N(1)–Ni(1A)–S(1) 96.45(14), N(2)–Ni(1A)–S(2) 96.62(14), N(1)–Ni(1A)–S(2) 174.22(14), S(1)–Ni(1A)–S(2) 78.13(8), C(15)–S(1)–Ni(1A) 107.3(2), C(15)–S(1)–Ni(1Aa) 107.3(2), Ni(1A)–S(1)–Ni(1Aa) 88.19(9), C(25)–S(2)–Ni(1Aa) 106.8(2), C(25)–S(2)–Ni(1A) 106.8(2), Ni(1Aa)–S(2)–Ni(1A) 87.76(12), where symmetry transformation a is $x, -y - 1/2, z$.

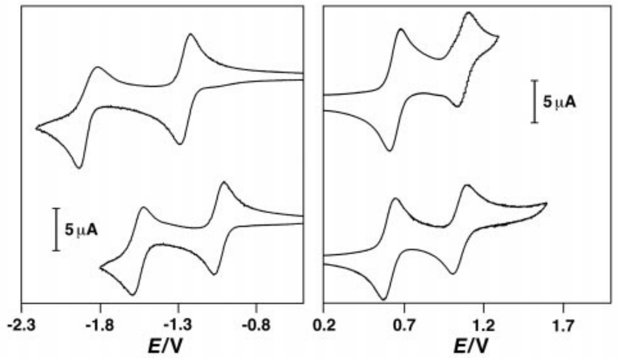


**Fig. 2** Cyclic voltammograms of **1** (top) and **2** (bottom). Conditions: 1 mM complex in MeCN, 200 mV $s^{-1}$, 0.1 M $NBu_4ClO_4$ electrolyte, referenced to Ag/0.01 M $AgNO_3$ (the $Fc/Fc^+$ couple occurred at +0.13 V). Reduction potentials (V) for the dinickel complexes **1** (L*n* = L1) and **2** (L*n* = L2) respectively: $E_{1/2}$ $[Ni_2Ln]^{3+/4+}$ +1.10$^{QR}$, +1.07$^{QR}$; $E_{1/2}$ $[Ni_2Ln]^{2+/3+}$ +0.69$^{R}$, +0.63$^{R}$; $E_{1/2}$ $[Ni_2Ln]^{+/2+}$ −1.18$^{R}$, −1.01$^{R}$; $E_{1/2}$ $[Ni_2Ln]^{0/+}$ −1.86$^{QR}$, −1.46$^{R}$. $K_d$ (**1**, ox) = $1.2 \times 10^{-7}$, $K_d$ (**1**, red) = $1.1 \times 10^{-11}$, $K_d$ (**2**, ox) = $3.6 \times 10^{-8}$, $K_d$ (**2**, red) = $2.5 \times 10^{-8}$; $^{R}$ reversible, $^{QR}$ quasi-reversible.[14]

to the $N_2S_2$ mean planes of the two encircled nickel atoms intersecting at an angle much closer to 90° in **1** (124°) than is observed in **2** (146.3 and 146.4°), which in turn results in shorter Ni···Ni separations in**1** (3.14 and 3.15 Å in **2** *vs.* 3.02 Å in **1**): a shortening of the S···S separations (2.84 and 2.85 Å in**2** *vs.* 2.74 Å in **1**) is also observed in **1**, along with changes in the angles at sulfur (Fig. 1 caption).[6] The 'bowl' created by this new macrocyclic ligand distinguishes the two axial sites on the nickel atoms, producing an 'inside' and 'outside' surface which may lead to interesting features when reactivity studies are carried out. All of the amine hydrogen atoms point in the same direction (*cis*) with respect to the macrocyclic 'bowl'.

The cyclic voltammograms obtained for complexes **1** and **2** are shown in Fig. 2. In both cases a series consisting of four separate one-electron steps is readily identified: the dinickel(II) complexes can be oxidised in two steps or reduced in two steps. From EPR studies and comparisons with related $N_2X_1S_1$ (X = O or N) square planar dinickel thiolate complexes and dizinc complexes these processes are believed to be largely metal-centred (*i.e.* $Ni^{I}_2 \leftrightarrow Ni^{I}Ni^{II} \leftrightarrow Ni^{II}_2 \leftrightarrow Ni^{II}Ni^{III} \leftrightarrow Ni^{III}_2$).[6,7] The mixed valent forms of the complexes prepared by electrochemical oxidation or reduction exhibit axial EPR spectra consistent with metal-based Ni(III) or Ni(I) species respectively. In the former, *g* values are of the order of $g_{\parallel}$ 2.02 and $g_{\perp}$ 2.20 and in the latter, $g_{\parallel}$ 2.01 and $g_{\perp}$ 2.08. These values are consistent with those derived for the oxidised and reduced forms of the metal with equatorial tetraaza-donors. Precise data will be reported elsewhere.[7] Interestingly the potentials at which the two sequential oxidation processes of $[Ni^{II}_2Ln]^{2+}$ ($n$ = 1 or 2) occur do not vary much with the change from imine to amine nitrogen donors. In contrast the potentials of the two sequential reduction processes of $[Ni^{II}_2Ln]^{2+}$ ($n$ = 1 or 2) differ significantly: there is a substantial shift to more negative potentials on changing from imine to amine nitrogen donors, as expected given that this equates to a reduction of π-acceptor ability.[10] A second feature is that the two waves have a greater $\Delta E$, corresponding to the mixed valent species $[Ni_2L1]^+$ being more stable with respect to disproportionation. It is curious that the dramatic differences in the reductive processes of **1** when compared with **2** are not reflected in the oxidative processes and we are further investigating this point.[7]

The successful synthesis of this tetraamine complex, **1**, represents a major step towards the production of stable dimetallic species suitable for redox and binding studies as the macrocycle is hydrolytically stable in contrast to the parent Schiff base. The nature and reactivity of the redox products are of considerable interest both in their own right and due to their relevance to the redox process catalysed by [Ni,Fe]-hydrogenases.[11] Further work is under way to explore these exciting aspects of our dinickel thiolates.[7]

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## Notes and References

† Satisfactory C,H,N,S analyses were obtained for **1** and **2**. NMR (300 MHz, $CD_3CN$, ref. ext. TMS): **1** $\delta_H$ (298 K) 7.18 (4H, s), 3.64 (8H, d), 3.47 (4H, d), 2.92 (4H, dd), 2.47 (4H, d), 2.27 (6H, s); **2** $\delta_H$ (343 K) 9.48 (4H, s, br), 7.54 (4H, s), *ca.* 4.50 (4H, br), *ca.* 4.31 (4H, br), 2.46 (6H, s), 2.24 (2H, d, br), 1.64 (2H, br).

‡ *Crystal data* for **1**: $C_{28}H_{40}Cl_2N_6Ni_2O_{10}S_2$, dark red square block, crystal dimensions $0.40 \times 0.35 \times 0.13$ mm, orthorhombic, *Pnma*, $a$ = 16.825(3), $b$ = 11.190(2), $c$ = 19.160(4) Å, $U$ = 3607.3(12) Å$^3$, $\mu$ = 1.37 mm$^{-1}$. Data were collected at 149 K on a Bruker SMART diffractometer using graphite-monochromated Mo-K$\alpha$, $\lambda$ = 0.71073 Å. A total of 26349 reflections were collected in the range $3 < 2\theta < 53°$ and the 3900 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 after resolution of severe disorder problems (electronic supplementary information: see http://www.rsc.org/suppdata/cc/1998/2131) the refinement on $F^2$ against all data (SHELXL-97)[13] converged satisfactorily to $R1$ = 0.068 [for 3036$F > 4\sigma(F)$; $wR2$ = 0.191 and goodness of fit = 1.14 for all 3900 $F^2$; 390 parameters; 230 restraints; +0.70/−0.57 eÅ$^{-3}$]. CCDC 182/993.

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