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Controlled synthesis and reversible oxidation of a thiolate-bridged macrocyclic dinickel(II) complex

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The synthesis of *S*-(2,6-Diformyl-4-methylphenyl) dimethylthiocarbamate, a valuable thiolate-containing ligand precursor, is reported in detail for the first time. This precursor has considerable potential in biosite modelling studies. A macrocycle L and a related acyclic ligand L′ have been prepared, as complexes, from the precursor and 1,3-diaminopropane. The macrocycle was successfully templated by both zinc(II) and nickel(II) ions yielding $[Zn_2L(H_2O)_2][O_3SCF_3]_2{\cdot}H_2O$ **1** and the diamagnetic complex $[Ni_2L][ClO_4]_2$ **2**, respectively. A single-crystal X-ray analysis of **1** showed the zinc ions to have trigonal-bipyramidal environments and the macrocycle to have a stepped conformation. In contrast, the structure determination of **2** revealed square-planar N_2S_2 co-ordination for Ni^{II} and a bowed macrocycle conformation which results in much shorter metal–metal and sulfur–sulfur separations than the stepped conformation adopted in the case of Zn^{II} [average Zn ··· Zn 3.351(1), S ··· S 3.363(3) for **1** *vs.* Ni ··· Ni 3.146(2), S ··· S 2.839(5) Å for **2**]. Two one-electron oxidations, the first reversible and the second quasi-reversible, were observed for the dinickel(II) complex, whereas one irreversible two-electron oxidation was observed for the dizinc(II) complex. An acetal forms in the presence of ethanol and leads to the isolation of the acyclic trinickel(II) complex $[Ni_2L'_2Ni][ClO_4]_2$ **3**.

Research into the synthesis, structure and properties of first-row transition-metal complexes of thiolate-containing ligands is expected to shed light on the structure and mechanism of action of thiolate-containing metalloproteins such as Fe–S clusters, nickel–iron hydrogenase and the Cu_A site of cytochrome c oxidase.[1–4] This paper focuses on the development of a route to polynuclear nickel Schiff-base complexes with thiolate 'head units', consideration of the structure and reactivity of which may aid our understanding of the nickel–iron hydrogenases.[3,4] In addition, the properties of these complexes are expected to provide an interesting contrast to those of complexes of the widely used phenol and pyridine 'head units' which provide much harder donors.[5,6] The resulting thiolate-bridged dinickel complexes are first-generation models for the dinuclear nickel–iron hydrogenase active site: until 1995[3] this site was thought to be a mononickel centre so previous model complexes were largely mononuclear[7] despite the general tendency of thiolate complexes to aggregate *via* thiolate bridges.[4] Another common problem is the formation of disulfides.[4] In this work these difficulties have been minimised by incorporating the thiolate donors into Schiff-base macrocycles, thus allowing the formation of thiolate-bridged complexes of controlled nuclearity and avoiding the uncontrolled production of disulfides.[8–10] The use of macrocyclic complexes to model a wide variety of metalloprotein active sites or to mimic their chemistry is well established[11] and may well allow access to the next generation of hydrogenase model complexes: the synthetically challenging mixed metal, nickel–iron, thiolate-bridged complexes.

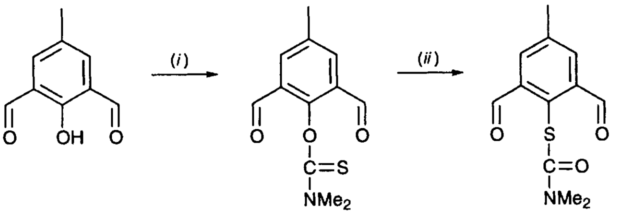
We have recently communicated the successful preparation and structure determination of a trinickel thiolate complex **3**.[8] This paper details the synthesis of the essential thiolate precursor **II** (Scheme 1), and the novel, structurally characterised, thiolate-containing zinc(II) and nickel(II) complexes $[Zn_2L(H_2O)_2][O_3SCF_3]_2{\cdot}H_2O$ **1** $[Ni_2L][ClO_4]_2$ **2** and $[Ni_2L'_2Ni][ClO_4]_2{\cdot}H_2O$ **3**, derived from **II**.

Results and Discussion

Synthesis of *S*-(2,6-diformyl-4-methylphenyl) dimethylthiocarbamate II

This synthesis (Scheme 1) was developed from the general method of Newman and Karnes.[12] The first step is a simplification of that outlined previously yet results in the clean formation of **I** in high yield. Thermolysis of **I** leads to the formation of **II**: the temperature used is critical to the success of this step and a wide range, 120–260 °C, was investigated. Thin-layer chromatography was found to be a quick, easy and sensitive method of determining the presence of **I** in samples of **II** and was therefore used to monitor the success of this reaction. To observe the formation of any **II** the sample must be heated at or above the point that a red melt forms, however one can go too far, with very high temperatures resulting in total destruction of the compound as one might expect. Initially we successfully employed a thermolysis temperature of 160 °C, but have recently moved to a higher temperature, 178 °C.[13] This temperature is easily and reproducibly achieved by employing a refluxing benzaldehyde bath, and has resulted in an improvement in yield. Pure **II** is readily obtained, in high yield, by washing the crude thermolysed material with diethyl ether. If desired, additional **II** can be retrieved from the diethyl ether washes by column chromatography.

Despite the use of compound **II** in the preparation of a wide range of *acyclic* ligands and complexes by Robson and co-workers,[6,14] the synthesis and properties of **I** and **II** had not



I **II**

Scheme 1 Synthesis of compound **II**. (*i*) NaH then $ClC(S)NMe_2$; (*ii*) 178 °C

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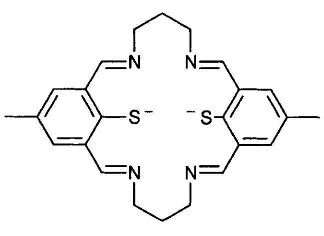
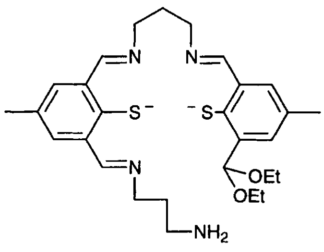


L^{2-}



L'^{2-}

been reported. Therefore, the respective IR spectra are shown (Fig. 1) and the ^{1}H NMR data reported (Experimental section). There are dramatic changes in both spectra on switching the positions of the O and S atoms. For example, significant shifts occur in the 1600–1700 cm^{-1} regions of the IR spectra due to the change from C=S to C=O. In the ^{1}H NMR spectra the most striking changes are observed in the NMe$_2$ region where the two almost superimposed methyl singlets at δ 3.49 and 3.51 for **I** separate into clear singlets at δ 3.04 and 3.24 for **II**. The aldehyde proton signal also shifts from δ 10.09 for **I** to δ 10.54 for **II**.

Hydrolysis of compound II

In order to prepare thiolate-bridged complexes from compound **II** it is necessary to remove the dimethylcarbamoyl moiety from the sulfur atom. Robson and co-workers[6,14] prepared *acyclic* pro-ligands from **II** and reported that the dimethylcarbamoyl fragment could subsequently be cleaved, *in situ*, by mildly basic dimethylformamide (dmf) solutions of metal acetate salts. However, in our hands this method of hydrolysis was not successful in attempts to prepare *macrocycles*. This is probably due to the lack of a good primary ligation site(s) in the case of the macrocycles. In comparison, the *preformed acyclic* pro-ligands may hold the metal ion(s) so that it co-ordinates and polarises the carbamoyl carbonyl group, thus promoting the hydrolysis reaction. To overcome this difficulty we have successfully adopted a nucleophilic base hydrolysis of the carbamoyl protecting group prior to the introduction of the other macrocycle components. This was done in a number of solvents by adding ground NaOH to a refluxing solution of **II**. Isopropyl alcohol was found to be the solvent of choice for this step; ethanol, the solvent we had initially employed, was found to promote acetal formation (see later). An immediate change from pale yellow to bright orange accompanied the addition of NaOH to the solution of **II**. Progress was monitored by thin-layer chromatography and a 5 h reflux was found to be optimal. The development of this effective *in situ* hydrolysis step was critical to our successful synthesis of macrocyclic complexes.

Complex formation

Once compound **II** is hydrolysed the desired complexes are formed by simply adding the appropriate metal salts and the diamine of choice to the refluxing solution.[8–10] Both macrocyclic complexes, $[Zn_2L(H_2O)_2][O_3SCF_3]_2\cdot H_2O$ **1**, a yellow solid, and $[Ni_2L][ClO_4]_2$ **2**, a red solid, were obtained *via* this route in Pr^{i}OH, as was the brown acyclic complex $[Ni_2L'_2Ni][ClO_4]_2\cdot H_2O$ **3** except that it was carried out in EtOH.

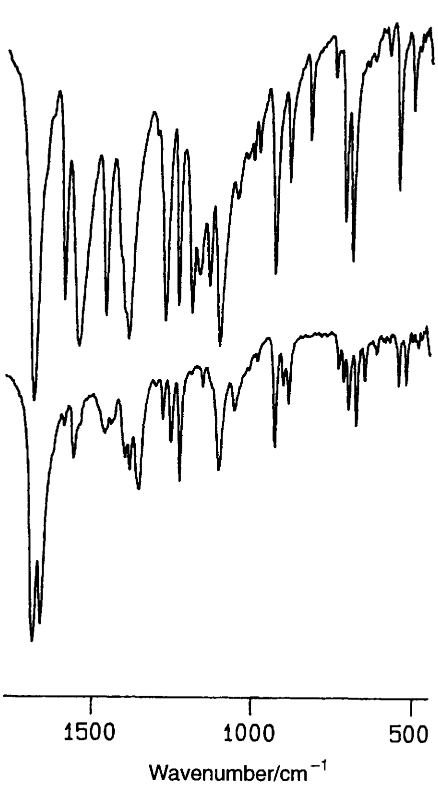


Fig. 1 Comparison of the IR spectra of compounds **I** (upper) and **II** (lower) as KBr discs

The dizinc(II) complex **1** was initially prepared so that it could act as a benchmark for comparisons with the nickel(II) complexes. However, it also opens up access, *via* transmetallation reactions, to other transition-metal complexes. Initially some difficulties were experienced in preparing this complex because the use of stoichiometric quantities of reagents led to the coprecipitation of hydroxide complexes with **1**. To overcome this problem the reaction was performed using an excess of the acidic zinc(II) trifluoromethanesulfonate (triflate)-hexahydrate.

Confirmation that cyclisation had occurred in both cases, **1** and **2**, was obtained by IR spectroscopy; amine and carbonyl absorptions were absent and bands consistent with imine formation were present. The solids could be recrystallised from acetonitrile by vapour diffusion of diethyl ether to yield large single crystals suitable for X-ray structural analysis. In the case of **2** cocrystallisation with $NaClO_4$ occurred but an analytically pure product was obtained by washing the crystals with a large volume of water followed by water-methanol (1 : 1). Importantly, $[Ni_2L]^{2+}$ can also be obtained, as a triflate salt, from **1** by transmetallation with nickel triflate in acetonitrile and subsequent crystallisation from the reaction mixture by diethyl ether diffusion.

Attempts to prepare $[Ni_2L][ClO_4]_2$ **2** in ethanol resulted in the formation of a trinickel complex $[Ni_2L'_2Ni][ClO_4]_2\cdot H_2O$ **3**, of a related acyclic ligand L′, in addition to the expected cyclic complex **2**. When more concentrated solutions were employed we were able to improve the yield of **3** to an acceptable 50%. The IR spectrum contained no bands corresponding to a carbonyl functionality, however, a series of weak bands in the region 3302–3254 cm^{-1} and an additional band at 2963 cm^{-1} were consistent with the formation of the acetal complex **3**, and this was subsequently confirmed by X-ray crystallography.[8]

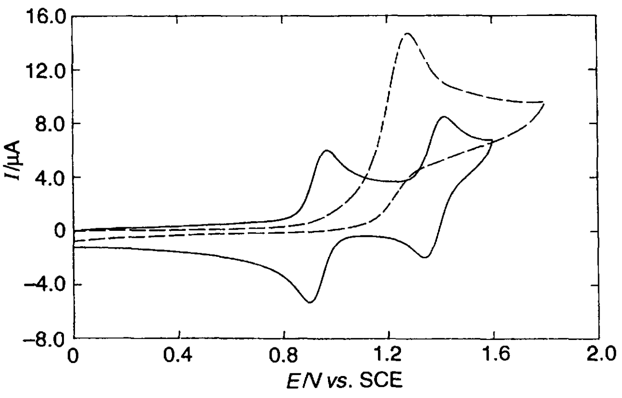


Fig. 2 Cyclic voltammetry of complexes **1** (– – –) and **2** (——) in MeCN (0.1 mol dm^{-3} NEt_4ClO_4, platinum electrode, 100 mV s^{-1})

Physicochemical studies

As expected all three complexes are 2 : 1 conductors in acetonitrile (Λ_m = 220–300 Ω^{-1} cm^2 mol^{-1} for a 2 : 1 electrolyte in MeCN). Preliminary results from cyclic voltammetry studies in acetonitrile indicate that the dinickel(II) complex **2** undergoes two one-electron oxidations, the first reversible and the second quasi-reversible (Fig. 2: $E_{\frac{1}{2}}$ = 0.93 V, peak separation 67 mV; $E_{\frac{1}{2}}$ = 1.38 V, peak separation 80 mV). Further spectroscopic studies (ESR, resonance Raman, UV/VIS) are underway to confirm that these processes are metal (not ligand) centred.[10] The dizinc(II) complex **1** shows a completely different behaviour undergoing an irreversible two-electron oxidation at a similar potential (Fig. 2), suggesting that a substantial structural change occurs on oxidation. One possibility is that the change might be the result of disulfide formation, and this is currently being explored.[10] The nickel–iron hydrogenase active cycle involves oxidation-state changes and one of the unresolved questions concerns the identity of the redox-active moiety (Ni, Fe or RS^-).[3,4] The full results of our redox studies, and comparisons with related complexes,[6] will be the subject of a future paper.[10]

Crystallography

The structures of the dizinc(II) complex **1**, dinickel(II) complex **2** and trinickel(II) complex **3** are shown in Figs. 3–6. Selected bond lengths and angles are given in Tables 1 and 2 for **1** and **2** respectively; those for **3** have been previously communicated.[8]

Complex 1. The asymmetric unit consists of two independent dizinc(II) macrocyclic complexes, molecule **1a** and **1b**: no major differences are observed between the two (Fig. 3, Table 1). In each case the zinc atoms have N_2S_2O trigonal-bipyramidal co-ordination to two imine nitrogen atoms, two bridging thiolate sulfur atoms and a water molecule.

The macrocycles in molecules **1a** and **1b** are not flat but rather adopt a stepped conformation such that the planes of the two phenyl rings intersect at similar angles in each case [147.7(2) and 141.4(2)° respectively]. The step conformation is consistent with both the expected tetrahedral distortion of the bridging thiolate donors (in contrast to the approximate trigonal-planar geometry of bridging phenolate donors)[5,6,8–10,14,15] and the trigonal-bipyramidal geometry at the zinc atoms. In each case the trigonal plane consists of one thiolate donor, one imine donor and the bound water molecule (Figs. 3 and 4; the trigonal plane is indicated by hollow bonds). The zinc atoms lie within 0.04 Å of this plane in all four cases, and the trigonal planes within a dinuclear molecule intersect at *ca.* 82° in both cases. Thus, despite the slight differences in the macrocycle step conformations of **1a** and **1b**, very similar co-ordination is observed for all four zinc atoms, as well as very similar S · · · S and Zn · · · Zn separations (Table 1).

π–π Interactions are observed both between the molecules within the asymmetric unit [Fig. 3: the aromatic ring attached to S(2) is 3.31–3.45 Å from that attached to S(4)] and between adjacent symmetry-related molecules [the aromatic ring attached to S(1) is 3.28–3.99 Å from a symmetry-generated aromatic ring attached to S(3)], and result in chains of π-stacked molecules. In addition, one of the two co-ordinated water molecules is hydrogen bonded (Fig. 4) to a water molecule of crystallisation [O(1) · · · O(5) 2.637(7) and O(4) · · · O(6) 2.574(7) Å for **1a** and **1b** respectively] and to a triflate anion [O(1) · · · O(60) 2.736(7) and O(4) · · · O(80) 2.682(8) Å respectively]. In each case this triflate anion bridges to the second co-ordinated water molecule by hydrogen bonding [O(2) · · · O(61) 2.669(7) and O(3) · · · O(81) 2.770(7) Å respectively]. Hydrogen bonding to the second co-ordinated

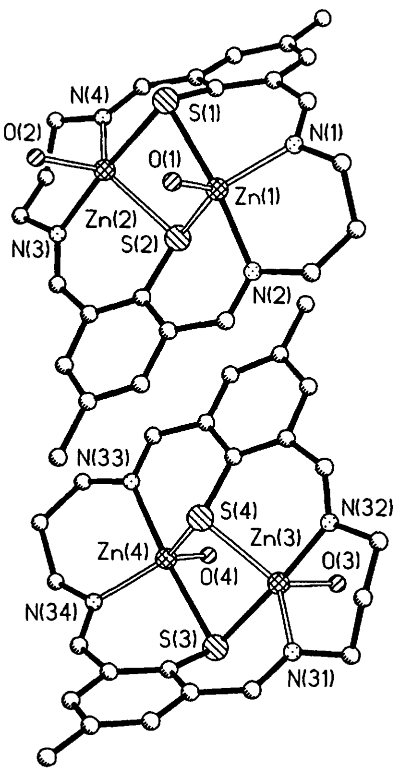


Fig. 3 Perspective view of the two independent cations of complex **1**, $[Zn_2L(H_2O)_2]^{2+}$

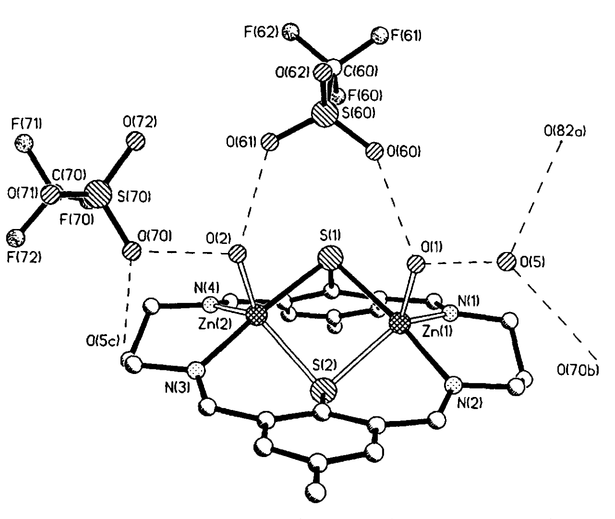


Fig. 4 Perspective view of molecule **1a** showing the hydrogen-bonding network

Table 1 Selected bond lengths (Å) and angles (°) for complex **1**

Zn(1)–O(1)	1.993(5)	Zn(1)–N(1)	2.036(6)
Zn(1)–N(2)	2.119(6)	Zn(1)–S(2)	2.379(2)
Zn(1)–S(1)	2.497(2)	Zn(2)–O(2)	2.012(5)
Zn(2)–N(4)	2.046(6)	Zn(2)–N(3)	2.120(6)
Zn(2)–S(2)	2.376(2)	Zn(2)–S(1)	2.469(2)
Zn(3)–N(31)	2.035(6)	Zn(3)–O(3)	2.048(5)
Zn(3)–N(32)	2.120(6)	Zn(3)–S(4)	2.362(2)
Zn(3)–S(3)	2.500(2)	Zn(4)–O(4)	1.992(5)
Zn(4)–N(34)	2.037(6)	Zn(4)–N(33)	2.129(6)
Zn(4)–S(4)	2.373(2)	Zn(4)–S(3)	2.477(2)
Zn(1) • • • Zn(2)	3.373(1)	S(1) • • • S(2)	3.363(3)
Zn(3) • • • Zn(4)	3.328(1)	S(3) • • • S(4)	3.363(3)
O(1)–Zn(1)–N(1)	112.0(2)	O(1)–Zn(1)–N(2)	90.0(2)
N(1)–Zn(1)–N(2)	95.8(2)	O(1)–Zn(1)–S(2)	122.1(2)
N(1)–Zn(1)–S(2)	125.8(2)	N(2)–Zn(1)–S(2)	87.3(2)
O(1)–Zn(1)–S(1)	89.9(2)	N(1)–Zn(1)–S(1)	90.3(2)
N(2)–Zn(1)–S(1)	173.4(2)	S(2)–Zn(1)–S(1)	87.16(7)
O(2)–Zn(2)–N(4)	111.9(2)	O(2)–Zn(2)–N(3)	87.3(2)
N(4)–Zn(2)–N(3)	95.7(2)	O(2)–Zn(2)–S(2)	126.4(2)
N(4)–Zn(2)–S(2)	121.7(2)	N(3)–Zn(2)–S(2)	86.9(2)
O(2)–Zn(2)–S(1)	92.7(2)	N(4)–Zn(2)–S(1)	90.3(2)
N(3)–Zn(2)–S(1)	173.6(2)	S(2)–Zn(2)–S(1)	87.90(7)
C(1)–S(1)–Zn(2)	98.9(2)	C(1)–S(1)–Zn(1)	96.4(2)
Zn(2)–S(1)–Zn(1)	85.55(7)	C(13)–S(2)–Zn(2)	102.5(2)
C(13)–S(2)–Zn(1)	102.3(2)	Zn(2)–S(2)–Zn(1)	90.36(7)
N(31)–Zn(3)–O(3)	111.8(2)	N(31)–Zn(3)–N(32)	93.5(2)
O(3)–Zn(3)–N(32)	90.5(2)	N(31)–Zn(3)–S(4)	123.2(2)
O(3)–Zn(3)–S(4)	125.0(2)	N(32)–Zn(3)–S(4)	88.4(2)
N(31)–Zn(3)–S(3)	88.8(2)	O(3)–Zn(3)–S(3)	91.80(14)
N(32)–Zn(3)–S(3)	175.8(2)	S(4)–Zn(3)–S(3)	87.46(7)
O(4)–Zn(4)–N(34)	114.7(2)	O(4)–Zn(4)–N(33)	89.1(2)
N(34)–Zn(4)–N(33)	95.4(2)	O(4)–Zn(4)–S(4)	122.3(2)
N(34)–Zn(4)–S(4)	122.9(2)	N(33)–Zn(4)–S(4)	88.5(2)
O(4)–Zn(4)–S(3)	90.2(2)	N(34)–Zn(4)–S(3)	89.3(2)
N(33)–Zn(4)–S(3)	175.1(2)	S(4)–Zn(4)–S(3)	87.76(7)
C(31)–S(3)–Zn(4)	96.2(2)	C(31)–S(3)–Zn(3)	96.4(2)
Zn(4)–S(3)–Zn(3)	83.93(7)	C(43)–S(4)–Zn(3)	100.8(2)
C(43)–S(4)–Zn(4)	101.5(2)	Zn(3)–S(4)–Zn(4)	89.31(7)

water molecule is completed by interaction with the second triflate anion [O(2) • • • O(70) 2.783(7) and O(3) • • • O(90) 2.703(8) Å respectively]. Hydrogen bonding also occurs between O(5) and O(6) and neighbouring symmetry-generated triflate anions [O(5) • • • O(70b) 2.792(8), O(5) • • • O(82a) 2.844(7), O(6) • • • O(62d) 2.790(7), O(6) • • • O(92e) 2.738(8) Å].

Complex 2. There are two dinickel(II) macrocyclic complexes, molecules **2a** and **2b**, in the asymmetric unit (Fig. 5, Table 2) Differences between the two molecules are minor. In both cases the nickel atoms have a N_2S_2 square planar environment and lie close to the N_2S_2 plane. Atoms Ni(1) and Ni(3) interact weakly with the oxygen atoms of perchlorate ions and are out of the N_2S_2 plane by 0.07 Å towards these atoms. In contrast Ni(2) and Ni(4) do not interact with the nearby perchlorate ions *via* the closest oxygen atoms, O(21) and O(41) respectively, as they are 0.04 and 0.03 Å respectively out of the N_2S_2 plane in the opposite direction to them (Table 2). In comparison, weak axial interactions observed for both nickel ions in the related complexes $[Ni_2L][PF_6]_2$·2dmf [Ni • • • O(1s) 2.644(15) Å] and $[Ni_2L^2][ClO_4]_2$[Ni • • • O(1) 2.89(1) Å].[15]

The macrocycles are distinctly bowed; the planes of the phenyl rings intersect each other at 74.1(2)° in molecule **2a** and 81.2(2)° in **2b**. Despite this difference in macrocycle conformation the co-ordination of the nickel atoms is very similar in **2a** and **2b**. In addition, the N_2S_2 square planes intersect at very similar angles [146.4(2) in **2a** and 146.3(2)° in **2b**] and the Ni • • • Ni and S • • • S separations are very similar (Table 2).

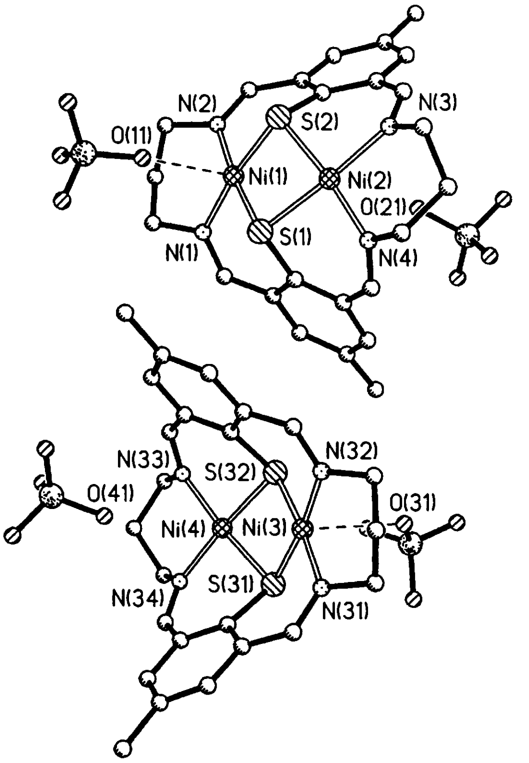


Fig. 5 Perspective view of the two independent molecules of complex **2**, $[Ni_2L][ClO_4]_2$

Table 2 Selected bond lengths (Å) and angles (°) for complex **2**

Ni(1)–N(1)	1.906(4)	Ni(1)–N(2)	1.907(4)
Ni(1)–S(2)	2.159(2)	Ni(1)–S(1)	2.162(2)
Ni(2)–N(4)	1.891(4)	Ni(2)–N(3)	1.918(4)
Ni(2)–S(2)	2.150(2)	Ni(2)–S(1)	2.168(2)
Ni(3)–N(32)	1.908(4)	Ni(3)–N(31)	1.916(4)
Ni(3)–S(31)	2.154(2)	Ni(3)–S(32)	2.168(2)
Ni(4)–N(34)	1.910(4)	Ni(4)–N(33)	1.912(4)
Ni(4)–S(31)	2.154(2)	Ni(4)–S(32)	2.162(2)
Ni(1) • • • O(11)	2.760(5)	Ni(2) • • • O(21)	3.169(5)
Ni(1) • • • Ni(2)	3.141(2)	S(1) • • • S(2)	2.846(5)
Ni(3) • • • O(31)	2.715(4)	Ni(4) • • • O(41)	3.344(5)
Ni(3) • • • Ni(4)	3.150(2)	S(31) • • • S(32)	2.831(5)
N(1)–Ni(1)–N(2)	93.9(2)	N(1)–Ni(1)–S(2)	172.15(14)
N(2)–Ni(1)–S(2)	91.53(13)	N(1)–Ni(1)–S(1)	91.86(13)
N(2)–Ni(1)–S(1)	173.43(14)	S(2)–Ni(1)–S(1)	82.40(5)
N(1)–Ni(1)–O(11)	95.3(2)	N(2)–Ni(1)–O(11)	96.7(2)
S(2)–Ni(1)–O(11)	89.66(11)	S(1)–Ni(1)–O(11)	85.78(12)
N(4)–Ni(2)–N(3)	94.5(2)	N(4)–Ni(2)–S(2)	173.54(14)
N(3)–Ni(2)–S(2)	91.89(13)	N(4)–Ni(2)–S(1)	91.08(14)
N(3)–Ni(2)–S(1)	173.26(14)	S(2)–Ni(2)–S(1)	82.47(5)
C(1)–S(1)–Ni(1)	101.3(2)	C(1)–S(1)–Ni(2)	99.6(2)
Ni(1)–S(1)–Ni(2)	92.98(5)	C(13)–S(2)–Ni(2)	101.8(2)
C(13)–S(2)–Ni(1)	101.4(2)	Ni(2)–S(2)–Ni(1)	93.60(5)
N(32)–Ni(3)–N(31)	94.1(2)	N(32)–Ni(3)–S(31)	172.30(13)
N(31)–Ni(3)–S(31)	91.50(13)	N(32)–Ni(3)–S(32)	92.28(13)
N(31)–Ni(3)–S(32)	172.70(13)	S(31)–Ni(3)–S(32)	81.84(5)
N(32)–Ni(3)–O(31)	87.1(2)	N(31)–Ni(3)–O(31)	91.0(2)
S(31)–Ni(3)–O(31)	98.15(10)	S(32)–Ni(3)–O(31)	92.92(10)
N(34)–Ni(4)–N(33)	94.5(2)	N(34)–Ni(4)–S(31)	91.60(13)
N(33)–Ni(4)–S(31)	173.82(13)	N(34)–Ni(4)–S(32)	173.30(13)
N(33)–Ni(4)–S(32)	91.90(13)	S(31)–Ni(4)–S(32)	82.00(5)
C(31)–S(31)–Ni(4)	101.8(2)	C(31)–S(31)–Ni(3)	102.2(2)
Ni(4)–S(31)–Ni(3)	93.96(5)	C(43)–S(32)–Ni(4)	100.6(2)
C(43)–S(32)–Ni(3)	101.8(2)	Ni(4)–S(32)–Ni(3)	93.32(5)

π–π Interactions are observed both between the molecules within the asymmetric unit [Fig. 5: the aromatic ring attached to S(1) is 3.35–3.45 Å from that attached to S(32)], and between adjacent symmetry-related molecules, and result in a network of π-stacked molecules.

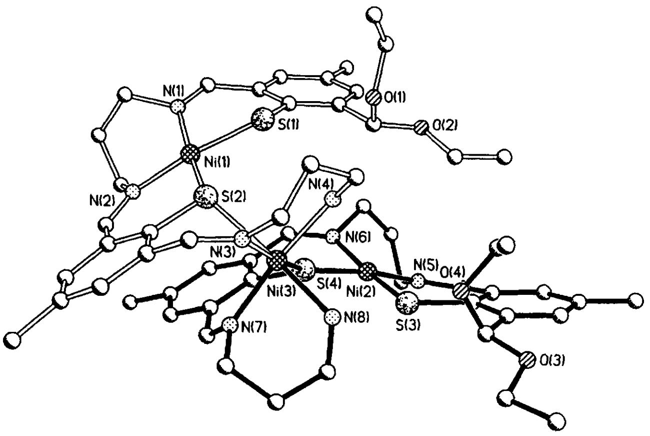


Fig. 6 Perspective view of the cation of complex 3, $[Ni_2L'_2Ni]^{2+}$

Comparison of complexes 2 and 3 (Fig. 6).[8] Bond lengths and angles at the square-planar nickel(II) atom are similar in both complexes **2** [*e.g.* Ni–S 2.150(2)–2.168(2) Å] and **3** [*e.g.* Ni–S 2.142(2)–2.167(2) Å]. As expected,[8–10,16] significantly longer distances are found for bonds to the octahedral nickel(II) centre in **3** [*e.g.* Ni–S 2.436(2), 2.526(2) Å], although they are longer than expected on the basis of our related high-spin complexes (*e.g.* high-spin nickel–thiolate distances observed to date 2.312–2.372 Å).[8–10] This is presumably a result of the bridging role that Ni(3) plays in holding the two mononickel complexes together.

As in complex **2**, π–π interactions are observed in **3**. In addition, in **3** there are hydrogen bonds between the perchlorate anions and both the primary amine, N(8), and the water molecule of crystallisation, O(50).

The isolation and identification of acyclic complex **3** has played an important part in our successful development of the synthesis of the macrocyclic complexes **1** and **2** described here. It is likely that the formation of this acetal had been a significant problem in earlier attempts to form macrocyclic complexes as ethanol (or methanol) is commonly used in these reactions.

Comparison of complexes 1 and 2. These structures show that the macrocycle L is sufficiently flexible to adopt two considerably different conformations in order to provide the incorporated metal ions with a suitable geometry. The stepped conformation observed with the trigonal-bipyramidal zinc(II) complex minimises the S ··· S interactions and is therefore a low-energy conformation. However, in the case of the dinickel(II) complex sufficient stabilisation is gained from the nickel becoming square planar to offset the higher-energy bowed macrocycle conformation (with significantly shorter S ··· S interactions) which is required to provide this geometry.

Conclusion

The synthesis of a valuable thiolate-containing 'head unit' **II** has been detailed, and the successful preparation of Schiff-base macrocyclic complexes described. The critical step in forming these complexes was the development of an effective hydrolysis step to remove the carbamoyl group from **II** thus exposing the thiolate for co-ordination. With this difficulty overcome, and with the problem of acetal formation in ethanol identified, we now expect rapid growth in the number of exciting new macrocycles and complexes derived from **II**.[10]

Experimental

Measurements

Elemental analyses (C, H, N, S, F, Cl) were performed by the Campbell Microanalytical Laboratory, University of Otago. Infrared spectra were recorded on a Bio-Rad FTS-7 spectrometer, NMR spectra on a Varian VXR 300 MHz spectrometer, and molar conductances were measured with a Phillips Magic Eye PR 9500 instrument.

Materials

2,6-Diformyl-4-methylphenol[17] and dimethylthiocarbamoyl chloride[18] were prepared according to the literature procedures. Methanol (Grignard), ethanol (Grignard) and dmf (molecular sieves) were dried before use. Isopropyl alcohol (stored over CaO then decanted off before distillation) and acetonitrile (CaH_2) were distilled immediately before use. All reactions were performed under a nitrogen atmosphere using Schlenk techniques. **CAUTION:** whilst no problems were encountered in the course of this work, perchlorate salts are potentially explosive and should therefore be handled with appropriate care.

Syntheses

***O*-(2,6-Diformyl-4-methylphenyl) dimethylthiocarbamate I.** To a stirred, ice-bath-cooled suspension of 2,6-diformyl-4-methylphenol (10.00 g, 60.9 mmol) in dmf (50 cm^3) was added 60% sodium hydride in mineral oil (2.68 g, 67 mmol). The ice-bath was removed and once hydrogen evolution had ceased dimethylthiocarbamoyl chloride (9.00 g, 72.9 mmol) in dmf (20 cm^3) was added to the intense yellow, very viscous mixture. After stirring for 15 h at 35 °C, water (100 cm^3) was added to the now orange-brown mixture. The cream precipitate which formed was filtered off. A further crop was obtained by filtration after addition of water (900 cm^3) to the filtrate. The cream solids were combined and washed with water, then taken up in CH_2Cl_2. The water layer was separated off, the CH_2Cl_2 layer dried over $MgSO_4$, and the CH_2Cl_2 removed *in vacuo*. The cream solid, **I**, was dried *in vacuo* (14.50 g, 95%) (Found: C, 57.6; H, 5.2; N, 5.7; S, 12.7. $C_{12}H_{13}NO_3S$ requires C, 57.4; H, 5.2; N, 5.6; S, 12.8%). δ_H(300 MHz, solvent $CDCl_3$, standard $SiMe_4$) 10.09 (2 H, s), 7.95 (2 H, s), 3.51 (3 H, s), 3.49 (3 H, s) and 2.48 (3 H, s). λ_{max}/nm (MeCN) (ε/dm^3 mol^{-1} cm^{-1}) 317 (2610) and 232 (59 120). $\tilde{\nu}_{max}$/cm^{-1} (KBr disc) 1685s.

***S*-(2,6-Diformyl-4-methylphenyl) dimethylthiocarbamate II.** Compound **I** was thermolysed by placing a 2 g portion in a quickfit thimble which was then placed in the side-arm of a multineck quickfit round-bottom flask containing benzaldehyde. The benzaldehyde was brought to reflux (178 °C)[13] and held at reflux for 20 min. This procedure was repeated four times. The combined thermolysed material was broken up and washed with diethyl ether (4 × 40 cm^3), then stirred with diethyl ether (60 cm^3) for 20 min to remove traces of **I**, leaving pure **II** as an off-white solid (5.81 g, 72%) To obtain further pure **II** the diethyl ether was evaporated off the combined washings, the residue loaded onto a 100 g silica column, and the column eluted with dichloromethane–hexane (9:1). The first fraction recovered was 2,6-diformyl-4-methylphenol (R_f 0.29, CH_2Cl_2), the second fraction unrearranged material (**I**, R_f 0.21, CH_2Cl_2) and the third fraction the desired product (**II**, R_f 0.07, CH_2Cl_2). A clean fraction of **II** was collected and the solvent removed *in vacuo* (1.06 g, 13%). In addition, 0.19 g of material to re-thermolyse and/or re-column was retrieved. Overall yield of pure **II**, 6.87 g, (85%) (Found C, 57.1; H, 5.3; N, 5.3; S, 12.7. $C_{12}H_{13}NO_3S$ requires C, 57.4; H, 5.2; N, 5.6; S, 12.8%). δ_H(300 MHz, solvent $CDCl_3$, standard $SiMe_4$) 10.54 (2 H, s), 8.04 (2 H, s), 3.24 (3 H, s), 3.04 (3 H, s) and 2.49 (3 H, s). λ_{max}/nm (MeCN) (ε/dm^3 mol^{-1} cm^{-1}) 310 (1560) and 236 (49 620). $\tilde{\nu}_{max}$/cm^{-1} (KBr disc) 1687s and 1663s.

$[Zn_2L(H_2O)_2][O_3SCF_3]_2 \cdot H_2O$ 1. Compound **II** (0.251 g, 1.00 mmol) was dissolved in Pr^{i}OH (80 cm^3) and brought to reflux. Ground NaOH (0.040 g, 1.00 mmol) was added to the clear pale yellow solution and caused an instantaneous change to bright orange. The orange solution was refluxed for 5 h. To this was added a Pr^{i}OH (20 cm^3) solution of zinc(II) trifluoromethanesulfonate hexahydrate (0.567 g, 1.20 mmol) which caused an immediate change to canary yellow. 1,3-Diaminopropane (0.074 g, 1.00 mmol) in Pr^{i}OH (20 cm^3) was quickly added and resulted in the formation of a small amount of fine, suspended precipitate. The mixture was refluxed for 1 h and filtered whilst hot to remove the trace of suspended powder. The filtrate was evaporated to dryness and the residue recrystallised from acetonitrile by vapour diffusion of diethyl ether to produce **1** as large yellow crystals suitable for X-ray structural analysis (0.183 g, 40%) (Found: C, 34.2; H, 3.6; F, 12.4; N, 6.3; S, 14.0. $C_{26}H_{32}F_6N_4O_9S_4Zn_2$ requires C, 34.0; H, 3.5; F, 12.4; N, 6.1; S, 14.0%). λ_{max}/nm (MeCN) 370 (ε/dm^3 mol^{-1} cm^{-1} 7600). $\tilde{\nu}_{max}$/cm^{-1} (KBr disc) 2927m, 2862w, 1639s, 1276s, 1258s and 639s. Λ_m = 255 Ω^{-1} cm^2 mol^{-1} in MeCN.

$[Ni_2L][ClO_4]_2$ 2. Hydrolysis of compound **II** (0.251 g, 1.00 mmol) was carried out with NaOH as above. After the 5 h reflux nickel(II) perchlorate hexahydrate (0.365 g, 1.00 mmol) in Pr^{i}OH (20 cm^3) was added. To the dark red-brown mixture was added 1,3-diaminopropane (0.074 g, 1.00 mmol) in Pr^{i}OH (20 cm^3). The mixture was refluxed for 4 h and then filtered whilst hot. The resulting red-brown solid was repeatedly recrystallised from acetonitrile by vapour diffusion of diethyl ether to yield **2** as large red crystals suitable for X-ray structural analysis (0.161 g, 43%) (Found: C, 38.4; H, 3.7; Cl, 9.8; N, 7.6; S, 8.4. $C_{24}H_{26}Cl_2N_4Ni_2O_8S_2$ requires C, 38.4; H, 3.5; Cl, 9.4; N, 7.5; S, 8.5%). λ_{max}/nm (MeCN) 510 (ε 1500 dm^3 mol^{-1} cm^{-1}). $\tilde{\nu}_{max}$/cm^{-1} (KBr disc) 2928w, 2856w, 1624m, 1090s (br) and 623s. Λ_m = 265 Ω^{-1} cm^2 mol^{-1} in MeCN.

$[Ni_2L'_2Ni][ClO_4]_2 \cdot H_2O$ 3. Hydrolysis of compound **II** (0.251 g, 1.00 mmol) was carried out with NaOH as above except that the solvent used was ethanol (25 cm^3). After the 5 h reflux an ethanol solution (10 cm^3) of nickel(II) perchlorate hexahydrate (0.365 g, 1.00 mmol) was added followed by 1,3-diaminopropane (0.074 g, 1.00 mmol) in ethanol (10 cm^3). After 2 h the red-brown mixture had become yellow-brown and the brown precipitate which formed was filtered from the hot solution. A second crop was obtained on concentration of the filtrate to *ca.* 10 cm^3. The combined solids were repeatedly fractionally recrystallised from MeCN by vapour diffusion of diethyl ether to give **3** as brown crystals (trace amounts of red crystals of the less soluble **2** were formed first and removed) suitable for X-ray structural analysis (0.185 g, 50%) (Found: C, 46.3; H, 5.6; N, 7.7; S, 8.5. $C_{56}H_{78}Cl_2N_8Ni_3O_{13}S_4$ requires C, 46.5; H, 5.4; N, 7.7; S, 8.9%). λ_{max}/nm (MeCN), (ε/dm^3 mol^{-1} cm^{-1}) 371 (15 700), 617 (300) and 912 (40): $\tilde{\nu}_{max}$/cm^{-1} (KBr disc) 3302w, 3280w, 3254w, 2963m, 2922m, 2874m, 1623m, 1093vs and 623m. Λ_m = 266 Ω^{-1} cm^2 mol^{-1} in MeCN.

X-Ray crystallography

Data were collected on a Siemens P4 four-circle diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.710 13 Å). Crystal stability was monitored by recording three check reflections every 97 and no significant variations were observed. The data were corrected for Lorentz-polarisation effects and empirical absorption corrections were applied based on ψ-scan data. In each case the structure was solved by direct methods (SHELXS 86),[19] which revealed most of the non-hydrogen atoms, and the remaining atoms were located from Fourier-difference maps. Hydrogen atoms were inserted at calculated positions except where noted otherwise, and rode on the atoms to which they are attached (including isotropic thermal parameters which were equal to 1.2 times the equivalent isotropic displacement parameter for the attached non-hydrogen atom).

Complex 1. *Crystal data.* $C_{26}H_{32}F_6N_4O_9S_4Zn_2$, yellow-orange block, crystal dimensions 0.9 × 0.6 × 0.4 mm, monoclinic, space group $P2_1/n$, a = 17.712(3), b = 14.169(4), c = 28.455(7) Å, β = 92.27(2)°, U = 7136(3) Å^3, μ = 1.66 mm^{-1}, Z = 8, D_c = 1.71 g cm^{-3}, $F(000)$ = 3728.

Data were collected at 160 K. The unit cell parameters were determined by least-squares refinement of 13 accurately centred reflections ($8 < 2\theta < 25°$). Using 1.6° ω scans at a fixed 12° min^{-1} scan speed, 9344 reflections were collected in the range $4 < 2\theta < 45°$ of which 9329 were independent and used, after absorption correction (T_{min} = 0.32, T_{max} = 0.41), in the refinement against all F^2 data (SHELXL 93).[20] There were two independent macrocycles in the asymmetric unit. All zinc, sulfur, fluorine and oxygen atoms anisotropic. The hydrogen atoms on water molecules O(1)–O(6) were located from Fourier-difference maps and then fixed. The refinement of 681 parameters converged to $R1 = 0.0474$ [for 5091 $F > 4\sigma(F)$], $wR2 = 0.1135$ and goodness of fit 0.86 (for 9328 F^2). The function minimised in the F^2 refinements was $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^2]^{\frac{1}{2}}$, where $w = [\sigma^2(F_o^2) + (0.0438P)^2]^{-1}$ and $P = (F_o^2 + 2F_c^2)/3$. Peak and hole 0.66 and −0.42 e Å^{-3}.

Complex 2. *Crystal data.* $C_{24}H_{26}Cl_2N_4Ni_2O_8S_2$, red plate, crystal dimensions 0.8 × 0.6 × 0.2 mm, triclinic, space group $P\bar{1}$, a = 8.680(2), b = 14.979(3), c = 22.380(4) Å, α = 72.91(1), β = 83.24(2), γ = 82.92(2)°, U = 2749.9(10) Å^3, μ = 1.77 mm^{-1}, Z = 4, D_c = 1.814 g cm^{-3}, $F(000)$ = 1536.

Data were collected at 130 K. The unit-cell parameters were determined by least-squares refinement of 40 accurately centred reflections ($5 < 2\theta < 25°$). Using 1.16° ω scans at variable scan speed (4–60° min^{-1}) 9348 reflections were collected in the range $4 < 2\theta < 48°$ of which 8539 were independent and used, after absorption correction, in the refinement against all F^2 data (SHELXL 93).[20] There were two independent macrocycles in the asymmetric unit. All non-hydrogen atoms anisotropic. The refinement of 761 parameters converged to $R1 = 0.0442$ [for 6329 $F > 4\sigma(F)$], $wR2 = 0.1004$ and goodness of fit 1.06 (for all 8539 F^2). The function minimised in the F^2 refinements was $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^2]^{\frac{1}{2}}$, where $w = [\sigma^2(F_o^2) + (0.0357P)^2 + 3.9134P]^{-1}$ and $P = (F_o^2 + 2F_c^2)/3$. Peak and hole 1.27 and −0.70 e Å^{-3}.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/91.

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