

# Conversion of some substituted phenols to the corresponding masked thiophenols, synthesis of a dinickel(II) dithiolate macrocyclic complex and isolation of some metal- and ligand-based oxidation products

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A modified preparation of the masked thiolate head unit *S*-(2,6-diformyl-4-methylphenyl) dimethylthiocarbamate **6** is detailed and two new masked thiolate head units, *S*-(2,6-diformyl-4-*tert*-butylphenyl) dimethylthiocarbamate **7** and *S*-(2-formylphenyl) dimethylthiocarbamate **8**, are prepared by this method. The synthesis, crystal structure, NMR spectra and electrochemical properties of the first macrocyclic complex to be derived from **7**, [Ni<sub>2</sub>L1](ClO<sub>4</sub>)<sub>2</sub>, are discussed. Oxidation of [Ni<sub>2</sub>L2](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> (L<sup>2-</sup> is derived from **6** and 1,3-diaminopropane) with cerium(IV) ammonium nitrate led to the precipitation of the black complex [Ni<sub>2</sub>L2][Ce(NO<sub>3</sub>)<sub>6</sub>], which is believed to contain a single nickel(III) centre. This complex decomposes in DMF over time (≈24 hours) to form the red dinickel(II) complex [Ni<sub>2</sub>L2](NO<sub>3</sub>)<sub>2</sub>·2DMF which has been structurally characterised. Oxidation of [Ni<sub>2</sub>L3](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> (L<sup>3-</sup> is derived from **6** and 1,4-diaminobutane) with I<sub>2</sub> results in ligand oxidation forming the metal free macrocycle (L<sup>3'</sup>)<sup>2+</sup> which contains two five membered isothiazole rings. This is confirmed by the X-ray crystal structure determinations of (L<sup>3'</sup>)(I<sub>3</sub>)<sub>2</sub> and (L<sup>3'</sup>)(I<sub>2</sub>)<sub>2</sub>.

## Introduction

Interest in the coordination and redox chemistry of nickel thiolate complexes is high due to the discovery of bimetallic thiolate-bridged active sites in metalloproteins such as the [Ni-Fe] hydrogenases.<sup>1-7</sup> Hydrogenase enzymes catalyse the reversible two-electron oxidation of molecular hydrogen, H<sub>2</sub> ⇌ 2H<sup>+</sup> + 2e<sup>-</sup>. Single crystal X-ray diffraction studies of a [Ni-Fe] hydrogenase<sup>1,2</sup> have shown the enzyme to contain a hetero-bimetallic center, where the nickel ion at the active site is bound by four cysteine residues, two of which bridge to an iron atom. Nickel is thought to be a redox centre in this enzyme<sup>3</sup> and therefore considerable attention has focused on the redox chemistry of nickel thiolate complexes.<sup>8-17</sup>

We,<sup>17-24</sup> and others<sup>25-39</sup> have used the masked thiolate head unit *S*-(2,6-diformyl-4-methylphenyl) dimethylthiocarbamate **6** (Fig. 1) in the production of a wide range of thiophenolate complexes since the first report, by Robson and co-workers, of such a complex.<sup>25</sup> In this paper we report a modified synthesis of **6** and the extension of this method to the preparation of two new masked thiolate head units, **7** and **8** (Fig. 1). A new dinickel(II) dithiolate macrocyclic complex, [Ni<sub>2</sub>L1](ClO<sub>4</sub>)<sub>2</sub> (Fig. 2), the first to be prepared from **7**, has been prepared and characterised. Finally, the results of some chemical oxidations of some dinickel(II) dithiolate macrocyclic complexes (Fig. 2) are presented and discussed.

## Experimental

### Materials

Almost all of the 2,6-diformyl-4-methylphenol used was made

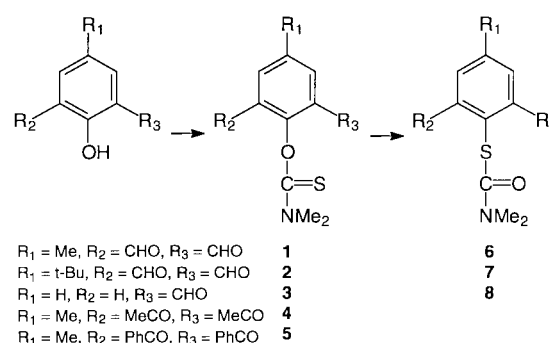
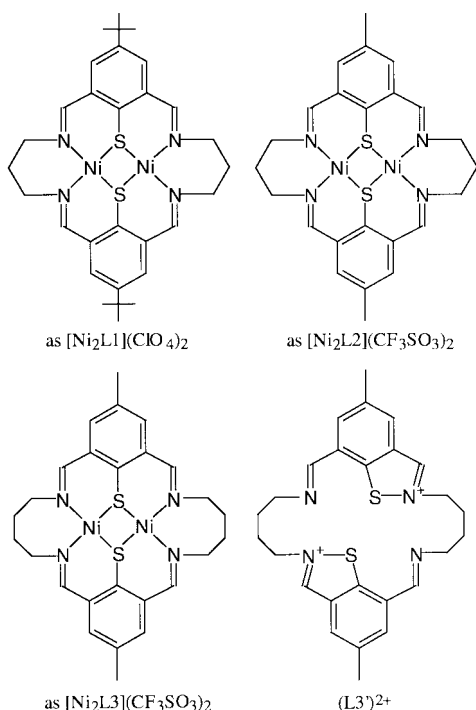


Fig. 1 Synthesis of the *O*-dimethylthiocarbamates **1-5** and the *S*-dimethylthiocarbamates **6-8**.

according to the method of Gagné *et al.*<sup>40</sup> Alternatively the product of the first step of this synthesis, sodium 2,6-bis-(hydroxymethyl)-4-methylphenolate, could be converted into 2,6-bis-(hydroxymethyl)-4-methylphenol (see below) which can then be oxidised in one step to 2,6-diformyl-4-methylphenol by the method of Taniguchi.<sup>41</sup> Similarly, 2,6-diformyl-4-*tert*-butylphenol was prepared from 2,6-bis-(hydroxymethyl)-4-*tert*-butylphenol (see below).<sup>41</sup> 2,6-Diacetyl-4-methylphenol and 2,6-dibenzoyl-4-methylphenol were prepared according to the literature.<sup>42,43</sup> [Ni<sub>2</sub>L2](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> and [Ni<sub>2</sub>L3](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> were prepared as previously described.<sup>17</sup> 1,3-Diaminopropane was distilled from KOH before use. Activated MnO<sub>2</sub> (Aldrich, <5 micron, 85% + grade) was dried at 80 °C for 48 h before use. DABCO [Aldrich, 1,4-diazabicyclo[2.2.2]octane] and BF<sub>3</sub>·OEt<sub>2</sub> (Aldrich, redistilled 99% grade) were used as received. If neces-



**Fig. 2** The dinickel(II) macrocyclic complexes  $[\text{Ni}_2\text{L1}]^{2+}$ ,  $[\text{Ni}_2\text{L2}]^{2+}$  and  $[\text{Ni}_2\text{L3}]^{2+}$ , and the organic oxidation product, the macrocycle  $(\text{L3}')^{2+}$ .

sary  $\text{BF}_3\cdot\text{OEt}_2$  can be redistilled from  $\text{CaH}_2$  after adding a small amount of dry diethyl ether ( $\approx 2\%$  by weight). Spectrophotometric grade 1,2-dichloroethane was used as received from Aldrich. Isopropanol (IPA) was stored over  $\text{CaO}$ , then decanted off and distilled. Toluene was distilled from sodium. HPLC grade MeCN and DMF were distilled from  $\text{CaH}_2$  (DMF *in vacuo*) immediately before use. All other reagents were used as received. Merck silica gel 60  $\text{F}_{254}$  pre-coated TLC plates were used. Measurements were carried out as previously described.<sup>17</sup> **CAUTION:** Perchlorate salts are potentially explosive and should therefore be prepared in small quantities only and handled with appropriate care.

## Syntheses

**Sodium 2,6-bis(hydroxymethyl)-4-tert-butylphenolate.** 4-tert-Butylphenol (25.0 g, 0.17 mol) was added to a stirred solution of NaOH (9.00 g, 0.22 mol) in boiling water (200 mL) and the golden brown solution stirred for 10 min. Fresh 37% formaldehyde (40.0 g, 0.50 mol) was added to the still warm solution and the solution went an orange-brown colour. This was stirred for 20 min and then left to stand overnight. The white crystalline product was collected and dried *in vacuo* (21.0 g, 52%).  $^1\text{H}$  NMR (200 MHz, solvent  $\text{D}_2\text{O}$ , reference  $\text{Me}_3\text{Si}(\text{CH}_2)_3\text{SO}_3\text{Na}$ )  $\delta$  7.14 (2H, s), 4.60 (4H, s), 1.19 (9H, s).

**2,6-Bis(hydroxymethyl)-4-methylphenol.** Sodium 2,6-bis(hydroxymethyl)-4-methylphenolate (10.0 g, 0.05 mol)<sup>40</sup> was dissolved in hot water (35 mL) and left to cool. Glacial acetic acid (about 5 mL, to  $\text{pH} \approx 4$ ) was added dropwise to the solution at room temperature and the resulting white precipitate filtered off, washed with water (200 mL) and dried *in vacuo* (7.20 g, 88%).  $^1\text{H}$  NMR (200 MHz, solvent  $\text{CDCl}_3$ , reference  $\text{SiMe}_4$ )  $\delta$  6.97 (2H, s), 4.55 (4H, s), 2.13 (3H, s).

**2,6-Bis(hydroxymethyl)-4-tert-butylphenol.** Sodium 2,6-bis(hydroxymethyl)-4-tert-butylphenolate (10.0 g, 0.04 mol) was dissolved in hot water (140 mL) and left to cool. Glacial acetic acid (about 5 mL, to  $\text{pH} \approx 4$ ) was added dropwise to the room temperature solution causing a brown oil to form. This was separated from the colourless solution, washed with  $\text{H}_2\text{O}$

( $2 \times 25$  mL) and dried *in vacuo* (6.50 g, 66%).  $^1\text{H}$  NMR (200 MHz, solvent  $\text{CDCl}_3$ , reference  $\text{SiMe}_4$ )  $\delta$  7.11 (2H, s), 4.84 (4H, s), 1.28 (9H, s).  $R_f(\text{CH}_2\text{Cl}_2) = 0.7$ .

**O-(2,6-Diformyl-4-methylphenyl) dimethylthiocarbamate 1.** 2,6-Diformyl-4-methylphenol (3.00 g, 18.3 mmol) was suspended in dry DMF (30 mL) under a nitrogen atmosphere. To this stirred suspension was added solid DABCO (4.00 g, 35.7 mmol) giving a light brown solution. This solution was left stirring and brought to  $35^\circ\text{C}$ . After 15 min solid dimethylthiocarbamoyl chloride (3.35 g, 26.9 mmol) was added. After 15 h stirring under a nitrogen atmosphere at  $35^\circ\text{C}$  a yellow precipitate had developed. Water (100 mL) was added, the mixture cooled to  $0^\circ\text{C}$  and the cream precipitate of **1** collected, washed with water (500 mL) and dried *in vacuo* (4.10 g, 90%) (Found: C, 57.1; H, 5.5; N, 5.5; S, 12.8. Calc. for  $\text{C}_{12}\text{H}_{13}\text{NSO}_3$ : C, 57.4; H, 5.2; N, 5.6; S, 12.8%).  $^1\text{H}$  NMR (200 MHz, solvent  $\text{CDCl}_3$ , reference  $\text{SiMe}_4$ )  $\delta$  10.1 (2H, s), 7.93 (2H, s), 3.47 (3H, s), 3.45 (3H, s), 2.47 (3H, s).  $\nu_{\text{max}}/\text{cm}^{-1}$  (KBr disk) 1685.  $R_f(\text{CH}_2\text{Cl}_2) = 0.2$ .

**O-(2,6-Diformyl-4-tert-butylphenyl) dimethylthiocarbamate 2.** As for **1** except that 2,6-diformyl-4-tert-butylphenol (0.10 g, 0.49 mmol) was suspended in 5 mL dry DMF. Amounts of other reagents/solvents used: DABCO (0.11 g, 1.00 mmol), dimethylthiocarbamoyl chloride (0.09 g, 0.75 mmol), water (10 mL). The cream precipitate of **2** was collected by filtration, washed with water (10 mL) and dried *in vacuo* (0.50 g, 35%) (Found: C, 61.4; H, 6.6; N, 4.8; S, 10.8. Calc. for  $\text{C}_{15}\text{H}_{19}\text{NSO}_3$ : C, 61.4; H, 6.5; N, 4.8; S, 10.9%).  $^1\text{H}$  NMR (200 MHz, solvent  $\text{CDCl}_3$ , reference  $\text{SiMe}_4$ )  $\delta$  10.2 (2H, s), 8.2 (2H, s), 3.52 (3H, s), 3.52 (3H, s), 1.4 (9H, s).  $\nu_{\text{max}}/\text{cm}^{-1}$  (KBr disk) 1687.  $R_f(\text{CH}_2\text{Cl}_2) = 0.3$ .

**O-(2-Formylphenyl) dimethylthiocarbamate 3.** As for **1** except that salicylaldehyde (0.48 g, 4.0 mmol) was suspended in dry DMF (10 mL). Amounts of other reagents/solvents used: DABCO (0.90 g, 8.0 mmol), dimethylthiocarbamoyl chloride (0.75 g, 6.0 mmol), water (25 mL). The cream precipitate of **3** was collected by filtration, washed with water (250 mL) and dried *in vacuo* (0.74 g, 90%) (Found: C, 57.0; H, 5.5; N, 6.8; S, 15.6. Calc. for  $\text{C}_{10}\text{H}_{11}\text{SNO}_2$ : C, 57.4; H, 5.3; N, 6.7; S, 15.3%).  $^1\text{H}$  NMR (200 MHz, solvent  $\text{CDCl}_3$ , reference  $\text{SiMe}_4$ )  $\delta$  10.09 (1H, s), 7.93 (1H, d), 7.61 (1H, t), 7.44 (1H, t), 7.16 (1H, d), 3.47 (3H, s), 3.42 (3H, s).  $R_f(\text{CH}_2\text{Cl}_2) = 0.5$ .

**O-(2,6-Diacetyl-4-methylphenyl) dimethylthiocarbamate 4.** As for **1** except that 2,6-diacetyl-4-methylphenol (0.10 g, 0.52 mmol) was suspended in dry DMF (5 mL). Amounts of other reagents/solvents used: DABCO (0.11 g, 1.0 mmol), dimethylthiocarbamoyl chloride (0.95 g, 0.75 mmol), water (20 mL). After a few minutes a small amount of orange precipitate was removed by filtration and washed with water (50 mL). This material was insoluble in all common solvents and has not been identified. The combined filtrates yielded tan needles of **4** which were collected, washed with ice-chilled water and dried *in vacuo* (0.05 g, 25%) (Found: C, 60.0; H, 6.4; N, 4.7; S, 11.0. Calc. for  $\text{C}_{14}\text{H}_{17}\text{SNO}_3$ : C, 60.2; H, 6.3; N, 5.0; S, 11.5%).  $^1\text{H}$  NMR (200 MHz, solvent  $\text{CDCl}_3$ , reference  $\text{SiMe}_4$ )  $\delta$  7.67 (2H, s), 3.45 (3H, s), 3.43 (3H, s), 2.68 (3H, s), 2.43 (6H, s).

**O-(2,6-Dibenzoyl-4-methylphenyl) dimethylthiocarbamate 5.** As for **1** except that 2,6-dibenzoyl-4-methylphenol (0.32 g, 1.0 mmol) was suspended in dry DMF (5 mL). Amounts of other reagents/solvents used: DABCO (0.26 g, 2.0 mmol), dimethylthiocarbamoyl chloride (0.19 g, 1.5 mmol), water (25 mL). The cream precipitate of **5** was collected by filtration, washed with water (50 mL) and dried *in vacuo* (0.38 g, 80%) (Found: C, 71.0; H, 5.6; N, 3.2; S, 7.6. Calc. for  $\text{C}_{24}\text{H}_{21}\text{SNO}_3$ : C, 71.4; H, 5.3; N, 3.5; S, 8.0%).  $^1\text{H}$  NMR (200 MHz, solvent  $\text{CDCl}_3$ , reference

SiMe<sub>4</sub>)  $\delta$  7.83 (2H, s), 7.48 (10H, m), 3.0 (3H, s), 2.83 (3H, s), 2.41 (3H, s).

**S-(2,6-Diformyl-4-methylphenyl) dimethylthiocarbamate 6.** BF<sub>3</sub>·OEt<sub>2</sub> (1.32 mL, 11.0 mmol) was slowly injected *via* a syringe into a stirred solution of **1** (2.50 g, 10.0 mmol) in dry toluene (160 mL) held at 60 °C. This caused the formation of a white precipitate and a small amount of brown oil. The temperature was raised to 85 °C and the solution stirred for 15 h by which time the precipitate had disappeared. The yellow solution was cooled to room temperature, decanted from the oil and washed with water (5 × 200 mL). The resulting colourless toluene solution was evaporated to dryness and the resulting cream powder, **6**, dried *in vacuo* (1.80 g, 72%) (Found: C, 57.4; H, 5.2; N, 5.7; S, 12.8. Calc. for C<sub>12</sub>H<sub>13</sub>NSO<sub>3</sub>: C, 57.4; H, 5.2; N, 5.6; S, 12.8%). <sup>1</sup>H NMR (200 MHz, solvent CDCl<sub>3</sub>, reference SiMe<sub>4</sub>)  $\delta$  10.5 (2H, s), 7.95 (2H, s), 3.24 (3H, s), 3.04 (3H, s), 2.50 (3H, s). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub> reference SiMe<sub>4</sub>)  $\delta$  190.4, 163.9, 141.2, 138.3, 134.2, 131.9, 37.5, 37.3, 21.2.  $\nu_{\max}/\text{cm}^{-1}$  (KBr disk) 1687, 1663. FAB mass spectrum:  $m/z$  251.  $R_f$  (CH<sub>2</sub>Cl<sub>2</sub>) = 0.1.

**S-(2,6-Diformyl-4-tert-butylphenyl) dimethylthiocarbamate 7.** As for **6** except that reagents/solvents used were: BF<sub>3</sub>·OEt<sub>2</sub> (0.13 mL, 1.1 mmol), **2** (0.10 g, 0.35 mmol), dry toluene (20 mL), water wash (5 × 30 mL). The resulting cream powder, **7**, was dried *in vacuo* (0.30 g, 30%) (Found: C, 60.8; H, 6.6; N, 4.8; S, 10.5. Calc. for C<sub>15</sub>H<sub>19</sub>NSO<sub>3</sub>: C, 61.4; H, 6.5; N, 4.8; S, 10.9%). <sup>1</sup>H NMR (200 MHz, solvent CDCl<sub>3</sub>, reference SiMe<sub>4</sub>)  $\delta$  10.5 (2H, s), 8.2 (2H, s), 3.2 (3H, s), 3.0 (3H, s), 1.3 (9H, s). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, reference SiMe<sub>4</sub>)  $\delta$  190.6, 164.2, 154.1, 138.1, 132.6, 130.7, 37.5, 30.9.  $\nu_{\max}/\text{cm}^{-1}$  (KBr disk) 1680. FAB mass spectrum:  $m/z$  293.  $R_f$  (CH<sub>2</sub>Cl<sub>2</sub>) = 0.1.

**S-(2-Formylphenyl) dimethylthiocarbamate 8.** BF<sub>3</sub>·OEt<sub>2</sub> (0.22 mL, 2.2 mmol) was slowly injected *via* a syringe into a stirred solution of **3** (0.42 g, 2.0 mmol) in 1,2-dichloroethane (50 mL) held at 60 °C. This caused the formation of a brown oil. The temperature was raised to 85 °C and the solution stirred for 24 h. The yellow solution was cooled to room temperature, decanted from the oil and washed with water (5 × 200 mL). The yellow 1,2-dichloroethane solution was evaporated to dryness giving a light brown oil, **8**, which was dried *in vacuo* (0.38 g, 90%) (Found: C, 57.3; H, 5.8; N, 6.3; S, 14.9. Calc. for C<sub>10</sub>H<sub>11</sub>SNO<sub>2</sub>: C, 57.4; H, 5.3; N, 6.7; S, 15.3%). <sup>1</sup>H NMR (200 MHz, solvent CDCl<sub>3</sub>, reference SiMe<sub>4</sub>)  $\delta$  10.3 (2H, s), 7.95 (2H, s), 3.2 (3H, s), 3.0 (3H, s). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, reference SiMe<sub>4</sub>)  $\delta$  192, 138.0, 133.9, 130.3, 128.9, 37.4. FAB mass spectrum:  $m/z$  209.  $R_f$  (CH<sub>2</sub>Cl<sub>2</sub>) = 0.2.

**[Ni<sub>2</sub>L1](ClO<sub>4</sub>)<sub>2</sub>.** S-(2,6-Diformyl-4-tert-butylphenyl) dimethylthiocarbamate **7** (293 mg, 1.00 mmol) dissolved in IPA (80 mL) was brought to reflux under a nitrogen atmosphere. Ground NaOH (40.0 mg, 1.00 mmol) was added and the resulting orange solution refluxed for 5 h. Nickel(II) perchlorate hexahydrate (365 mg, 1.00 mmol) in IPA (20 mL) was then added. To the dark red-brown mixture was added 1,3-diaminopropane (74.0 mg, 1.00 mmol) in IPA (20 mL). The mixture was refluxed for 5 h and then filtered whilst hot. The resulting red-brown solid was recrystallised from MeCN by vapour diffusion of diethyl ether to yield [Ni<sub>2</sub>L1](ClO<sub>4</sub>)<sub>2</sub> as red single crystals (116 mg, 28%) (Found: C, 42.8; H, 4.7; N, 6.9; S, 7.7. Calc. for C<sub>30</sub>H<sub>38</sub>N<sub>4</sub>S<sub>2</sub>Ni<sub>2</sub>Cl<sub>2</sub>O<sub>8</sub>: C, 43.2; H, 4.6; N, 6.7; S, 7.7%).  $\nu_{\max}/\text{cm}^{-1}$  (KBr disk) 1626, 1093, 624. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>NO<sub>2</sub>, referenced to solvent)  $\delta$  7.96 (2H, s), 7.79 (2H, s), 4.35 (2H, t), 3.80 (2H, d), 2.42 (1H, d), 1.85 (1H, q) 1.35 (9H, s). <sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>NO<sub>2</sub>, referenced to solvent)  $\delta$  168.2, 154.4, 137.0, 135.9, 123.2, 63.1, 36.1, 30.8, 29.3.  $\lambda_{\max}/\text{nm}$  (MeCN) ( $\epsilon/\text{L}^{-1} \text{mol}^{-1} \text{cm}^{-1}$ ) 510 (1250).  $A_m(\text{MeCN}) = 235 \text{ mol}^{-1} \text{cm}^2 \Omega^{-1}$  (*cf.* 220–300 mol<sup>-1</sup> cm<sup>2</sup> Ω<sup>-1</sup>

for a 2:1 electrolyte in MeCN).<sup>44</sup> FAB mass spectrum:  $m/z$  734 [Ni<sub>2</sub>L1](ClO<sub>4</sub>)<sup>+</sup>, 634 [Ni<sub>2</sub>L1]<sup>+</sup>.

**[Ni<sub>2</sub>L2][Ce(NO<sub>3</sub>)<sub>6</sub>].** [Ni<sub>2</sub>L2](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> (100 mg, 0.134 mmol) was dissolved in dry MeCN (7 mL), under a nitrogen atmosphere (the nitrogen was bubbled into the solution which caused a stirring effect), giving a red solution which was cooled in an ice bath. To this solution was added, in a dropwise fashion, an orange solution of cerium(IV) ammonium nitrate (CAN) (74.0 mg, 0.134 mmol) in dry MeCN (5 mL). A black precipitate of [Ni<sub>2</sub>L2][Ce(NO<sub>3</sub>)<sub>6</sub>] formed immediately. This was filtered off, washed with IPA (2 mL) and dried under vacuum (108 mg, 85%) (Found: C, 27.3; H, 2.7; N, 13.4; S, 6.4. Calc. for C<sub>24</sub>H<sub>26</sub>N<sub>10</sub>S<sub>2</sub>O<sub>18</sub>Ni<sub>2</sub>Ce: C, 27.0; H, 2.5; N, 13.1; S, 6.0%).  $\nu_{\max}/\text{cm}^{-1}$  (KBr disk) 1625, 1447, 1319, 1031.  $\mu = 3.5 \mu_{\text{B}}$  per complex at 292 K.  $\lambda_{\max}/\text{nm}$  (DMF) ( $\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ) 870 (1320), 485 (2950). FAB mass spectrum:  $m/z$  550 [Ni<sub>2</sub>L2]<sup>+</sup>.

**(L3')·10I.** [Ni<sub>2</sub>L3](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> (100 mg, 0.11 mmol) was dissolved in MeCN (7 mL) giving a red solution. To this solution was added an excess of iodine (80.0 mg, 0.32 mmol) in MeCN (5 mL). The solution immediately turned brown. Over approximately one day, small brown single crystals and several small red single crystals developed. These were filtered off, washed with MeCN (3 mL) and dried *in vacuo* (24.0 mg, 13%) (Found: C, 17.8; H, 1.5; N, 3.0; S, 4.1; I, 73.7. Calc. for C<sub>26</sub>H<sub>30</sub>N<sub>4</sub>S<sub>2</sub>I<sub>10</sub>: C, 18.0; H, 1.8; N, 3.2; S, 3.7; I, 73.3%).  $\nu_{\max}/\text{cm}^{-1}$  (KBr disk) 1617.

#### X-Ray crystallography

Data were collected on a Bruker SMART diffractometer, using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71013 \text{ \AA}$ ). The data were corrected for Lorentz and polarisation effects and semi-empirical absorption corrections were applied. The structures were solved by direct methods (SHELXS-97)<sup>45,46</sup> and refined against all  $F^2$  data (SHELXL-97).<sup>47</sup> Hydrogen atoms were inserted at calculated positions 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).

**Crystal data for [Ni<sub>2</sub>L1](ClO<sub>4</sub>)<sub>2</sub>·0.5H<sub>2</sub>O·0.5Et<sub>2</sub>O.** Space group *Pbcn*,  $a = 20.517(2) \text{ \AA}$ ,  $b = 27.241(3) \text{ \AA}$ ,  $c = 15.7733(17) \text{ \AA}$ ,  $V = 8815.6(17) \text{ \AA}^3$ ,  $R1 = 0.1374$  for 4607  $F > 4\sigma(F)$ ;  $wR2 = 0.4096$  and  $\text{GOF} = 1.173$  for all 7768  $F^2$ . The data allowed only the gross structure to be determined.

**Crystal data for [Ni<sub>2</sub>L3](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>·Et<sub>2</sub>O.** C<sub>32</sub>H<sub>40</sub>F<sub>6</sub>N<sub>4</sub>O<sub>7</sub>S<sub>4</sub>Ni<sub>2</sub>,  $M = 952.34$ , monoclinic, space group *C2/c*,  $a = 25.0993(16) \text{ \AA}$ ,  $b = 10.9758(7) \text{ \AA}$ ,  $c = 17.1135(11) \text{ \AA}$ ,  $V = 3972.9(4) \text{ \AA}^3$ ,  $Z = 4$ ,  $\mu = 1.236 \text{ mm}^{-1}$ . A total of 13534 reflections were collected at 158 K and the 3887 independent reflections were used in the structural analysis after correcting for absorption.  $R1 = 0.036$  for 3275  $F > 4\sigma(F)$ ;  $wR2 = 0.096$  and  $\text{GOF} = 1.034$  for all 3887  $F^2$ ; 249 parameters, all non-hydrogen atoms except the disordered diethyl ether molecules anisotropic [C(60) and C(70) diethyl ether molecules each 0.5 occupancy].

**Crystal data for [Ni<sub>2</sub>L2](NO<sub>3</sub>)<sub>2</sub>·2DMF.** C<sub>30</sub>H<sub>40</sub>N<sub>8</sub>Ni<sub>2</sub>O<sub>8</sub>S<sub>2</sub>,  $M = 822.24$ , monoclinic, space group *C2/c*,  $a = 21.884(6) \text{ \AA}$ ,  $b = 9.948(3) \text{ \AA}$ ,  $c = 18.441(5) \text{ \AA}$ ,  $\beta = 117.713(3)^\circ$ ,  $V = 3554.0(16) \text{ \AA}^3$ ,  $Z = 4$ ,  $\mu = 1.237 \text{ mm}^{-1}$ . A total of 12389 reflections were collected at 173 K and the 3593 independent reflections were used in the structural analysis after correcting for absorption.  $R1 = 0.0255$  for 2636  $F > 4\sigma(F)$ ;  $wR2 = 0.0602$  and  $\text{GOF} = 0.931$  for all 2636  $F^2$ ; 229 parameters, all non-hydrogen atoms anisotropic.

**Crystal data for (L3')(I<sub>3</sub>)<sub>2</sub>.** C<sub>26</sub>H<sub>30</sub>N<sub>4</sub>I<sub>6</sub>S<sub>2</sub>,  $M = 1224.06$ , triclinic, space group *P1*,  $a = 8.9104(19) \text{ \AA}$ ,  $b = 9.1521(19) \text{ \AA}$ ,

$c = 12.172(3)$  Å,  $a = 70.605(3)^\circ$ ,  $\beta = 85.336(3)^\circ$ ,  $\gamma = 68.074(3)^\circ$ ,  $V = 867.6(3)$  Å<sup>3</sup>,  $Z = 1$ ,  $\mu = 5.514$  mm<sup>-1</sup>. A total of 11120 reflections were collected at 168 K and the 3511 independent reflections were used in the structural analysis after correcting for absorption.  $R1 = 0.0284$  for 2969  $F > 4\sigma(F)$ ;  $wR2 = 0.0715$  and  $GOF = 1.093$  for all 3511  $F^2$ ; 173 parameters, all non-hydrogen atoms anisotropic.

**Crystal data for (L3')(I<sub>2</sub>)<sub>2</sub>(I<sub>2</sub>)<sub>5</sub>.** C<sub>26</sub>H<sub>30</sub>N<sub>4</sub>I<sub>12</sub>S<sub>2</sub>,  $M = 1985.46$ , monoclinic, space group  $C2/c$ ,  $a = 11.854(7)$  Å,  $b = 15.450(7)$  Å,  $c = 25.559(14)$  Å,  $\beta = 91.291(10)^\circ$ ,  $V = 4680(4)$  Å<sup>3</sup>,  $Z = 4$ ,  $\mu = 8.053$  mm<sup>-1</sup>. A total of 29085 reflections were collected at 183 K and the 4775 independent reflections were used in the structural analysis after correcting for absorption.  $R1 = 0.0645$  for 3008  $F > 4\sigma(F)$ ;  $wR2 = 0.1854$  and  $GOF = 1.040$  for all 4775  $F^2$ ; 195 parameters, all non-hydrogen atoms anisotropic except C(10).

CCDC reference number 186/2113.

See <http://www.rsc.org/suppdata/dt/b0/b004214p/> for crystallographic files in .cif format.

## Results and discussion

### Organic synthesis

The synthesis of **6** (Fig. 1) was modified in order to avoid the need for time-consuming, large-scale column chromatography.<sup>20</sup> In an attempt to improve the solubility of the dinickel(II) thiolate complexes obtained from **6**, especially in non-polar solvents, the new head unit *S*-(2,6-diformyl-4-*tert*-butylphenyl) dimethylthiocarbamate **7**, in which the *para* group on the aromatic head unit was changed from methyl (**6**) to *tert*-butyl (**7**), was prepared by this method. The synthesis of *S*-(2-formylphenyl) dimethylthiocarbamate **8** was also achieved by this route but attempts to further extend this method to include the preparation of the related ketones from **4** and **5** (Fig. 1) was not successful.

Almost all of the 2,6-diformyl-4-methylphenol used was made according to the method of Gagné *et al.*<sup>40</sup> However, we have recently switched to utilising an alternative oxidation pathway which involves a simple one step oxidation of 2,6-bis(hydroxymethyl)-4-methylphenol (*vide infra*), using MnO<sub>2</sub> as the oxidant, in thoroughly dried chloroform, at room temperature.<sup>41</sup> Taniguchi also reported the preparation of 2,6-diformyl-4-*tert*-butylphenol<sup>41</sup> so in order to utilise this synthesis we prepared the necessary starting material, bis(hydroxymethyl)-4-methylphenol, from sodium bis(hydroxymethyl)-4-methylphenolate. The sodium salt was prepared using a slight modification (higher temperatures and larger solvent volumes were necessary in the first step due to the low solubility of 4-*tert*-butylphenol compared to 4-methylphenol in water) of the first step of the Gagné synthesis (*vide infra*).<sup>40</sup> Two phenol diketones, 2,6-diacetyl-4-methylphenol and 2,6-dibenzoyl-4-methylphenol, were prepared according to the literature.<sup>42,43</sup>

The conversion of these phenol aldehydes and ketones into the corresponding masked thiophenol aldehydes and ketones was attempted *via* a two step procedure where a Newman–Kwart rearrangement of the appropriate *O*-phenyldimethylthiocarbamate derivative should give access to the, thermodynamically more stable, *S*-phenyl dimethylthiocarbamate derivative (Fig. 1).<sup>20,48</sup>

The first step involves removing the phenol proton with base and ‘clipping’ on the dimethylthiocarbamate group (Fig. 1). A minor modification to the literature method<sup>20,48</sup> has been made with the hindered base DABCO being used instead of sodium hydride.<sup>49</sup> In comparison with the previously reported synthesis of **1**<sup>20</sup> this reaction is more reliable, although the yields are no higher than the best yields obtained using the previous method. Compounds **2** and **3** were prepared on a smaller scale but in the same manner as **1**: compound **2** in a lower yield (35%), presum-

ably due to it having higher solubility in DMF, and compound **3** in excellent yield (90%). Two phenol diketones were also reacted in this manner to form *O*-(2,6-diacetyl-4-methylphenyl) dimethylthiocarbamate **4** (25% yield) and *O*-(2,6-dibenzoyl-4-methylphenyl) dimethylthiocarbamate **5** (80% yield) (Fig. 1). In summary, all of the parent phenol compounds were successfully converted into the corresponding *O*-phenyl dimethylthiocarbamate derivatives.

Electron-withdrawing groups on the phenyl ring are known to facilitate the Newman–Kwart rearrangement, which is believed to occur by nucleophilic attack of the thiocarbamoyl sulfur at the  $\alpha$ -carbon of the aromatic ring (C1), so the presence of aldehyde and ketone functional groups in the compounds of interest is advantageous.<sup>48</sup> Consistent with this, the thermal rearrangement of neat **1** to **6** occurs at 178 °C which is at the lower end of the temperature range expected.<sup>20</sup> However, the rearrangement of neat **1** to **6** yields a mixture of both compounds under these conditions, necessitating column chromatography on a large time and solvent consuming scale. Hence improvements to the rearrangement reaction were sought for the conversion of **1** to **6** before extending the synthesis to include the other *O*-phenyl dimethylthiocarbamates of interest.

The thermal rearrangement of *O*-(2-formyl-3-methacryloxymethyl-5-nitrophenyl) dimethylthiocarbamate has been reported to occur in refluxing toluene (bp = 111 °C).<sup>50</sup> This temperature was found to be insufficient to rearrange significant quantities of **1** to **6** even after a reaction time of several days. However, the addition of the Lewis acid boron trifluoride diethyl etherate to **1** in refluxing dry benzene (bp = 80 °C) did result in rearrangement to **6**. Dry toluene, held at 85 °C, can be used in place of dry benzene and was the solvent of choice. The work up of this reaction is simple and quick: the reaction solution is allowed to cool, is decanted from a small amount of oily residue, washed with water and then evaporated to dryness to give **6** in good yield (72%). It was found that adding the boron trifluoride diethyl etherate to the solution of **1** in dry toluene at around 60 °C rather than at 85 °C resulted in a smaller amount of oil formation and hence gave better yields. This method gives cleaner material and is much less labour intensive than the literature method due to avoiding the need for column chromatography.<sup>20</sup> The reaction can also be scaled up by a factor of at least four with only a small ( $\approx 10\%$ ) drop in yield.

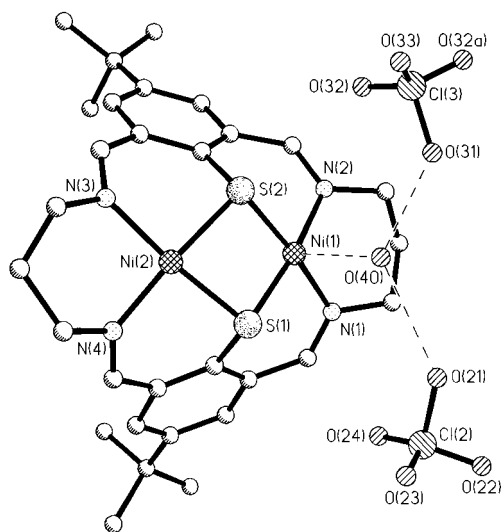
The *tert*-butyl analogue **2** was successfully converted into **7** by this method albeit in a modest yield (30%). The conversion of **3** to **8** proceeded smoothly and in a high yield (90%), but in 1,2-dichloroethane rather than toluene (as an insoluble precipitate formed on the addition of boron trifluoride diethyl etherate to the toluene solution of **3** and resulted in the formation of intractable tars). Other chlorinated solvents were tried but the boiling points were too low to give complete conversion.

The rearrangement of ketones **4** and **5** (Fig. 1) was tried *via* this method but in both cases the reactions were unsuccessful. Compound **4** was unexpectedly hydrolysed back to 2,6-diacetyl-4-methylphenol on the addition of boron trifluoride diethyl etherate, perhaps due to the presence of traces of water. No rearrangement was observed for compound **5**, even in refluxing toluene, indicating that a higher temperature may be needed, but this was not explored further.

Thin layer chromatography was found to be a sensitive and quick method for determining the end point of all of these reactions and was the principle method of checking the purity of these compounds as the microanalysis is unchanged on rearrangement.

### Synthesis of [Ni<sub>2</sub>L1](ClO<sub>4</sub>)<sub>2</sub>

In order to prepare the thiolate complexes from the masked thiolates it is necessary to first remove the dimethylcarbamoyl group from the sulfur atom. The *in situ* nucleophilic base hydrolysis in IPA reported for unmasking **6**<sup>20</sup> was successfully



**Fig. 3** Perspective view of the cation of  $[\text{Ni}_2\text{L1}](\text{ClO}_4)_2 \cdot 0.5\text{H}_2\text{O} \cdot 0.5\text{Et}_2\text{O}$  (hydrogen atoms, full occupancy perchlorate ion and diethyl ether molecule omitted for clarity).

employed for **7**. Nickel(II) template ions were then added followed by 1,3-diaminopropane yielding a red tetraimine complex  $[\text{Ni}_2\text{L1}](\text{ClO}_4)_2$  in an acceptable yield (28%) (Fig. 2).

IR spectroscopy showed imine formation ( $1626\text{ cm}^{-1}$ ) and that no unreacted carbonyl or primary amine functional groups were present. As expected  $[\text{Ni}_2\text{L1}](\text{ClO}_4)_2$  is a 2:1 conductor in MeCN. The UV/Vis spectrum of the red MeCN solution of  $[\text{Ni}_2\text{L1}](\text{ClO}_4)_2$  showed an absorption band at  $510\text{ nm}$  ( $\epsilon = 1250\text{ L mol}^{-1}\text{ cm}^{-1}$ ) which was assigned as a ligand to metal charge transfer (LMCT) transition,  $\text{S}\pi \rightarrow \text{Ni}$ .<sup>17,51</sup> This complex, with a *para tert*-butyl group on each of the aromatic head units, is more soluble in common solvents such as MeCN and DMF than the related complexes,  $[\text{Ni}_2\text{L2}](\text{ClO}_4)_2$  and  $[\text{Ni}_2\text{L3}](\text{ClO}_4)_2$ , which have *para* methyl groups on the aromatic head units.<sup>17</sup>  $[\text{Ni}_2\text{L1}](\text{ClO}_4)_2$  has sparing solubility in  $\text{CHCl}_3$  but this is not sufficient for further characterisation by techniques such as NMR spectroscopy or cyclic voltammetry.

#### Crystal structures of $[\text{Ni}_2\text{L1}](\text{ClO}_4)_2$ and $[\text{Ni}_2\text{L3}](\text{CF}_3\text{SO}_3)_2$

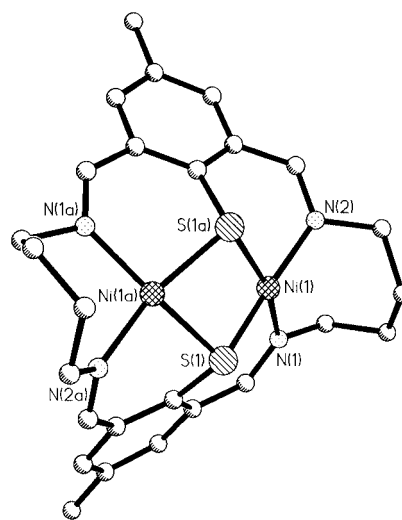
Poor quality red crystals of  $[\text{Ni}_2\text{L1}](\text{ClO}_4)_2 \cdot 0.5\text{H}_2\text{O} \cdot 0.5\text{Et}_2\text{O}$  were grown by the slow diffusion of diethyl ether vapour into a MeCN solution of  $[\text{Ni}_2\text{L1}](\text{ClO}_4)_2$  and the X-ray structure determined (Fig. 3). The structure is not of sufficient quality to be published in full and therefore no detailed discussion can be made but the gross structure has been determined. There is one complete complex in the asymmetric unit. There are two square planar nickel(II) ions within each macrocycle and they are bridged by two thiolate sulfur atoms from the macrocycle. The remaining two coordination sites on each nickel atom are occupied by imine nitrogen atoms, giving each nickel(II) ion a  $\text{N}_2\text{S}_2$  coordination sphere. The complex adopts a bowed shape and there are  $\pi$ - $\pi$  stacking interactions between adjacent macrocycles with the phenyl ring on one macrocycle lying over the imine group of another macrocycle.

Red crystals of  $[\text{Ni}_2\text{L3}](\text{CF}_3\text{SO}_3)_2 \cdot \text{Et}_2\text{O}$  were grown from MeCN solution by vapour diffusion of diethyl ether and the structure determined (Fig. 4, Table 1). The asymmetric unit consists of one half of the complex with the other half generated by a two fold rotation. Each of the nickel atoms is in a square planar  $\text{N}_2\text{S}_2$  environment [Ni(1)  $0.037\text{ \AA}$  out of this plane] although there is a degree of tetrahedral twist in the  $\text{N}_2\text{S}_2$  plane ( $16.4^\circ$ ) which is comparable to that observed for the perchlorate salt of  $[\text{Ni}_2\text{L3}]^{2+}$  ( $15.4$ – $18.9^\circ$ ).<sup>17</sup> The complex is folded: the phenyl rings make an angle of  $86.87(7)^\circ$  with each other and the  $\text{N}_2\text{S}_2$  planes intersect at  $40.76(3)^\circ$ . The packing of these macrocycles is different to that observed for the perchlorate

**Table 1** Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for  $[\text{Ni}_2\text{L3}](\text{CF}_3\text{SO}_3)_2 \cdot \text{Et}_2\text{O}$

Ni(1)–N(2)	1.924(2)	S(1)–C(1)	1.766(3)
Ni(1)–N(1)	1.934(2)	Ni(1)⋯Ni(1)#1	3.1567(6)
Ni(1)–S(1)	2.1535(7)	S(1)⋯S(1)#1	2.7890(12)
Ni(1)–S(1)#1	2.1690(7)		
N(2)–Ni(1)–N(1)	96.91(9)	S(1)–Ni(1)–S(1)#1	80.36(3)
N(2)–Ni(1)–S(1)	165.27(7)	C(1)–S(1)–Ni(1)	106.57(8)
N(1)–Ni(1)–S(1)	95.25(7)	C(1)–S(1)–Ni(1)#1	98.33(8)
N(2)–Ni(1)–S(1)#1	89.79(6)	Ni(1)–S(1)–Ni(1)#1	93.82(3)
N(1)–Ni(1)–S(1)#1	165.19(7)		

Symmetry transformations used to generate equivalent atoms: #1  $-x, y, -z + 1/2$ .



**Fig. 4** Perspective view of the cation of  $[\text{Ni}_2\text{L3}](\text{CF}_3\text{SO}_3)_2 \cdot \text{Et}_2\text{O}$  (hydrogen atoms, triflate ions and diethyl ether molecules omitted for clarity).

analogue, where a perchlorate anion acted as a template for the formation of a “star” of four  $\pi$ - $\pi$  stacked macrocycles, but  $\pi$ - $\pi$  stacking is also a feature in the triflate structure.

#### NMR studies

The  $^1\text{H}$  NMR spectra of compounds **1**–**4** all featured two nearly superimposed singlets at  $\delta$  3.4–3.5, while **5** has two singlets at  $\delta$  3.0 and 2.8, due to the  $\text{NMe}_2$  groups. In each case the  $\text{NMe}_2$  signals in the  $^1\text{H}$  NMR spectra of the rearranged compounds **6**–**8** are split into two clearly separated singlets and the aldehyde proton resonances are shifted downfield relative to the starting materials (**1**–**3** respectively).

In the non-coordinating solvent  $\text{CD}_3\text{NO}_2$   $[\text{Ni}_2\text{L1}](\text{ClO}_4)_2$  gave easily assigned diamagnetic  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra. As observed for related dinickel dithiolate complexes<sup>17</sup> the methylene protons give rise to four resonances, at  $\delta$  4.35 and 3.80 (H9, H9') and at  $\delta$  2.42 and 1.85 (H10, H10'), in the  $^1\text{H}$  NMR spectrum. This is consistent with the folded shape (Fig. 3) being retained in solution.

#### Electrochemical studies on $[\text{Ni}_2\text{L1}](\text{ClO}_4)_2$

Cyclic voltammetry studies in MeCN show that  $[\text{Ni}_2\text{L1}](\text{ClO}_4)_2$  undergoes two quasi-reversible, approximately one electron, oxidations at +0.69 and +1.16 V and two quasi-reversible, approximately one electron, reductions at  $-0.96$  and  $-1.45\text{ V}$  vs. 0.01 M  $\text{AgNO}_3/\text{Ag}$ . These processes are very similar to those reported for the closely related complex  $[\text{Ni}_2\text{L2}](\text{ClO}_4)_2$ .<sup>17,20,23</sup>

#### Isolation of metal- and ligand-based redox products from dinickel(II) dithiolate macrocyclic complexes

Due to the biological significance of the nickel(III) oxidation

**Table 2** Observations from a series of attempted chemical oxidations of room temperature acetonitrile solutions of the red complex  $[\text{Ni}_2\text{L2}](\text{CF}_3\text{SO}_3)_2$ 

Oxidant	Initial colour change	Comment
$(\text{NH}_4)_2\text{S}_2\text{O}_8(\text{s})$	No change	Remains a red solution
$\text{HNO}_3(\text{aq})$	Green	Solution quickly goes colourless
$\text{NOBF}_4(\text{s})$	Purple	Solution quickly goes colourless
Acidic $[\text{Co}(\text{H}_2\text{O})_6]^{3+}(\text{s})$	Purple	Solution stable for minutes
$\text{I}_2(\text{in MeCN})$	Dark brown	Brown single crystals form
$\text{CAN}(\text{in MeCN})$	Black	Insoluble black precipitate forms

state<sup>3</sup> and current interest in mixed valent complexes<sup>15,16,52–57</sup> the isolation of mixed valent dinickel(II/III) dithiolate complexes was targeted. The black complex  $[\text{Ni}_2\text{L2}][\text{Ce}(\text{NO}_3)_6]$ , which we believe to be a Ni(II)Ni(III) complex, has been isolated. Given the rich redox chemistry of the series of dinickel(II) dithiolate complexes<sup>17,20,23</sup> the isolation of nickel(I) products and fully oxidised Ni(III)<sub>2</sub> complexes was also attempted, but unsuccessfully.

There are two approaches, electrochemical and chemical oxidation, to making nickel(III) complexes from nickel(II) analogues.<sup>58–60</sup> Both approaches were explored with complexes  $[\text{Ni}_2\text{L2}](\text{CF}_3\text{SO}_3)_2$  and  $[\text{Ni}_2\text{L3}](\text{CF}_3\text{SO}_3)_2$  (for electrochemical attempts see ref. 17) but only the products of chemical oxidations could be isolated from solution.

A range of chemical oxidants were tested with the red dinickel(II) dithiolate complexes  $[\text{Ni}_2\text{L2}](\text{CF}_3\text{SO}_3)_2$  and  $[\text{Ni}_2\text{L3}](\text{CF}_3\text{SO}_3)_2$ . The initial colour changes observed on adding the oxidant to an MeCN solution of  $[\text{Ni}_2\text{L2}](\text{CF}_3\text{SO}_3)_2$  under an argon atmosphere are listed in Table 2. The most promising oxidants were cerium(IV) ammonium nitrate (CAN) and  $\text{I}_2$ .

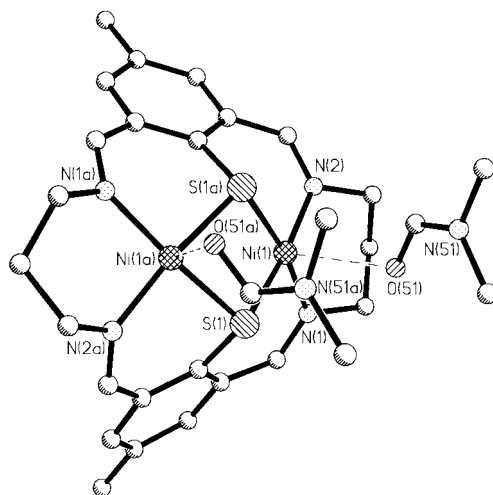
The black complex  $[\text{Ni}_2\text{L2}][\text{Ce}(\text{NO}_3)_6]$  was subsequently isolated in excellent yield (85%) by adding one equivalent of the strong oxidant CAN to an ice-cooled solution of  $[\text{Ni}_2\text{L2}](\text{CF}_3\text{SO}_3)_2$  in MeCN. The infrared spectrum of  $[\text{Ni}_2\text{L2}][\text{Ce}(\text{NO}_3)_6]$  confirmed the presence of an imine stretch  $\{1625 \text{ cm}^{-1}$  cf.  $1624 \text{ cm}^{-1}$  for  $[\text{Ni}_2\text{L2}](\text{CF}_3\text{SO}_3)_2\}$  indicating that the integrity of the macrocycle is retained throughout the oxidation process. The presence of the cerium hexanitrate anion is indicated by a nitrate band in the infrared spectrum at  $1380 \text{ cm}^{-1}$ <sup>161</sup> and was confirmed by elemental analysis. The black solid,  $[\text{Ni}_2\text{L2}][\text{Ce}(\text{NO}_3)_6]$ , is not stable indefinitely but slowly changes to a red colour over a period of weeks. In DMF solution (it is not soluble enough to be studied in any other solvents) this colour change occurs much more quickly. The UV/Vis spectrum of  $[\text{Ni}_2\text{L2}][\text{Ce}(\text{NO}_3)_6]$  in DMF is very similar to that of both the one electron electrochemical oxidation product of  $[\text{Ni}_2\text{L2}](\text{CF}_3\text{SO}_3)_2$  (in MeCN) and the product obtained by adding one equivalent of CAN to a MeCN solution of  $[\text{Ni}_2\text{L2}](\text{ClO}_4)_2$ .<sup>17</sup> Initially the solution is black and there is a broad band at 870 nm. The solution decays quite rapidly, over ca. 24 hours, from black to red. The UV/Vis spectrum of the resulting red solution indicates that the major product of the decay process is  $[\text{Ni}_2\text{L2}]^{2+}$ , with a band at  $\approx 510 \text{ nm}$ . The slow diffusion of diethyl ether vapour into this red DMF solution yields red single crystals. The infrared spectrum of the red crystals still features an imine band at  $1625 \text{ cm}^{-1}$  indicating that the macrocycle remains intact. The crystal structure of this red product was determined and it was found to be the complex  $[\text{Ni}_2\text{L2}](\text{NO}_3)_2 \cdot 2\text{DMF}$  (*vide infra*). Microanalysis of the remaining crystals is also consistent with this formula.

The metal free macrocycle  $(\text{L}3')^{2+}$  was isolated in a number of forms, in low overall yield (13%), from the slow evaporation of a solution of  $[\text{Ni}_2\text{L3}](\text{CF}_3\text{SO}_3)_2$  in MeCN which had been treated with an excess of the oxidant  $\text{I}_2$  (Fig. 2). The product consisted of dark brown single crystals together with a few red single crystals. The crystal structures of both a brown and a red

**Table 3** Selected bond lengths (Å) and angles (°) for  $[\text{Ni}_2\text{L2}](\text{NO}_3)_2 \cdot 2\text{DMF}$ 

Ni(1)–N(1)	1.9250(16)	Ni(1)–S(1)#1	2.1837(7)
Ni(1)–N(2)	1.9351(16)	Ni(1)···Ni(1)#1	3.2136(9)
Ni–S(1)	2.1820(8)	S(1)···S(1)#1	2.833(1)
N(1)–Ni(1)–N(2)	94.28(7)	S(1)–Ni(1)–S(1)#1	80.92(2)
N(1)–Ni(1)–S(1)	92.63(5)	C(1)–S(1)–Ni(1)	104.14(7)
N(2)–Ni(1)–S(1)	172.70(5)	C(1)–S(1)–Ni(1)#1	101.29(7)
N(1)–Ni(1)–S(1)#1	169.83(5)	Ni(1)–S(1)–Ni(1)#1	94.80(2)
N(2)–Ni(1)–S(1)#1	91.91(5)		

Symmetry transformations used to generate equivalent atoms: #1  $-x, y, -z + 1/2$ .

**Fig. 5** Perspective view of the cation of  $[\text{Ni}_2\text{L2}](\text{NO}_3)_2 \cdot 2\text{DMF}$  (hydrogen atoms and nitrate ions omitted for clarity).

crystal were determined. The brown crystal was found to be the metal free macrocycle salt  $(\text{L}3')(\text{I}_2)(\text{I}_2)_5$  and the red crystal was found to be  $(\text{L}3')(\text{I}_3)_2$  (*vide infra*). In both cases the macrocyclic cation  $(\text{L}3')^{2+}$  is present. Microanalysis of the crystalline products of different oxidation reactions gave iodine contents in the range 10–12 iodine atoms per macrocycle. The infrared spectrum of the mixed material has an imine band at  $1617 \text{ cm}^{-1}$  indicative of an intact macrocycle. No triflate bands were present.

These polyiodide salts of the macrocyclic cation  $(\text{L}3')^{2+}$  are practically insoluble in common solvents, including  $\text{H}_2\text{O}$ ,  $\text{CHCl}_3$ , MeCN and DMF, significantly limiting attempts at further characterisation. Oxidation of closely related thiolate ligands to isothiazole ring containing derivatives by the weak oxidant  $\text{I}_2$  has been reported.<sup>16</sup>

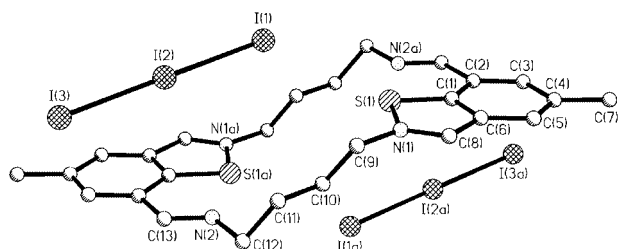
### Crystal structures of $[\text{Ni}_2\text{L2}](\text{NO}_3)_2 \cdot 2\text{DMF}$ , $(\text{L}3')(\text{I}_3)_2$ and $(\text{L}3')(\text{I}_2)(\text{I}_2)_5$

Red crystals of  $[\text{Ni}_2\text{L2}](\text{NO}_3)_2 \cdot 2\text{DMF}$  were grown by the slow diffusion of diethyl ether vapour into a red DMF solution of  $[\text{Ni}_2\text{L2}][\text{Ce}(\text{NO}_3)_6]$  and the crystal structure determined (Fig. 5, Table 3). The asymmetric unit consists of one half of the complex with the other half generated by a two fold rotation. The crystal structure revealed two square planar nickel(II) ions within the macrocycle which are bridged by two thiolate sulfur atoms from the macrocycle. The other two coordination sites on each nickel ion are occupied by imine nitrogen atoms, thus giving each nickel(II) ion an  $\text{N}_2\text{S}_2$  coordination sphere. Each nickel atom has an additional interaction with an oxygen donor atom from a DMF solvent molecule [Ni(1)–O(51) 2.575 Å] (Fig. 5). There are two nitrate counter anions, presumably resulting from the decomposition of  $\text{Ce}(\text{NO}_3)_6$ . In order to accommodate the geometries of the two nickel ions the complex adopts a bowed shape with the two aromatic rings almost perpendicular

**Table 4** Selected bond lengths (Å) and angles (°) for (L3')(I<sub>3</sub>)<sub>2</sub>

S(1)–C(1)	1.725(4)	I(1)–I(2)	2.9510(7)
S(1)–N(1)	1.748(3)	I(2)–I(3)	2.9221(7)
C(1)–C(6)	1.397(5)	S(1)⋯I(1)	3.9463(11)
C(6)–C(8)	1.423(5)	I(3)⋯I(3)#2	3.9711(09)
C(8)–N(1)	1.315(5)	S(1)⋯S(1)#1	5.0408(19)
N(2)–C(13)	1.281(5)		
I(3)–I(2)–I(1)	177.004(11)	N(1)–C(8)–C(6)	112.8(3)
C(1)–S(1)–N(1)	88.18(16)	C(8)–N(1)–S(1)	115.1(3)
C(6)–C(1)–S(1)	113.8(3)	C(13)–N(2)–C(12)	119.7(3)
C(1)–C(6)–C(8)	110.2(3)		

Symmetry transformations used to generate equivalent atoms: #1  $-x, y - 1, -z + 2$ ; #2  $1 - x, -3 - y, 3 - z$ .

**Fig. 6** Perspective view of (L3')(I<sub>3</sub>)<sub>2</sub> (hydrogen atoms omitted for clarity).

[81.50(5)°] to each other. This lengthens the S⋯S distance minimising repulsive S⋯S interactions. There are  $\pi$ – $\pi$  interactions between adjacent macrocycles, with the phenyl rings being an average of 3.44 Å apart.

Red crystals of the metal free macrocycle (L3')(I<sub>3</sub>)<sub>2</sub> were grown by slow evaporation of a solution of [Ni<sub>2</sub>L3](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> in MeCN treated with an excess of I<sub>2</sub> and the crystal structure determined (Fig. 6, Table 4). The asymmetric unit consists of one half of the complex with the other half generated by inversion. Ligand oxidation has occurred to form two five membered isothiazole rings within each macrocycle (Fig. 6). The macrocycle adopts a stepped conformation with the two phenyl rings being parallel to each other, as required by the symmetry operation.

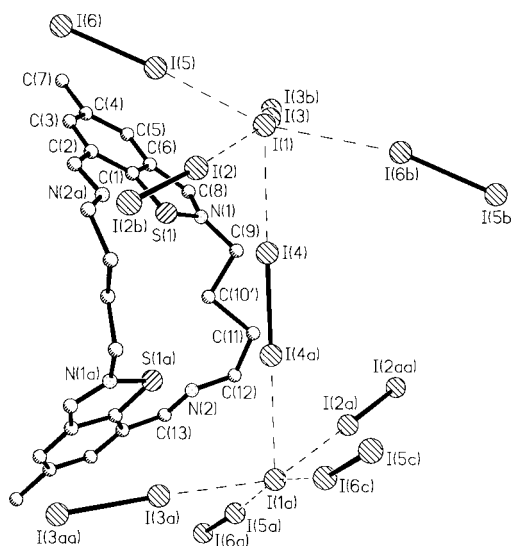
The anions are triiodide ions, formed from the reaction of the excess iodine with the iodide formed during the ligand oxidation reaction. The triiodide ions are linear [I(1)–I(2)–I(3) 177.00(1)°] and symmetrical [I(1)–I(2) 2.9510(7), I(2)–I(3) 2.9221(7) Å]. These values are typical for discrete triiodide anions:<sup>62</sup> no significant interactions involving these anions are observed (Table 4, *vide infra*).

Brown crystals of the metal free macrocycle (L3')(I<sub>2</sub>(I<sub>2</sub>))<sub>5</sub> were grown by slow evaporation of a solution of [Ni<sub>2</sub>L3]–(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> in MeCN treated with an excess of I<sub>2</sub> and the crystal structure determined (Fig. 7, Table 5). The asymmetric unit consists of one half of the complex with the other half generated by a two fold rotation. Ligand oxidation has occurred to form two five membered isothiazole rings within each macrocycle (Fig. 7). The macrocycle adopts a bowed shape with the two aromatic rings almost perpendicular [79.95(5)°] to each other. Two iodide ions act as the anions. The iodide ion, I(1), formed during the ligand oxidation reaction, interacts with neighboring iodine molecules (excess iodine was used in the oxidation) to form a polyiodide array.<sup>62,63</sup> Consistent with this, the iodine bond lengths (I–I 2.751–2.803 Å) are longer than those observed for free iodine in the vapour phase (2.667 Å)<sup>64</sup> or in the solid phase (2.715 Å),<sup>65</sup> due to donation of electron density from the iodide into the  $\sigma^*$  antibonding orbital on the iodine molecule.<sup>62</sup> The iodine⋯iodine distances of 3.317–3.5008 Å are typical of those observed for polyiodides.<sup>62,63</sup> There are no significant interactions between the isothiazole sulfur and the iodide or iodine (Table 5). The shortest I⋯S distance,

**Table 5** Selected bond lengths (Å) and angles (°) for (L3')(I<sub>2</sub>(I<sub>2</sub>))<sub>5</sub>

S(1)–C(1)	1.724(19)	I(5)–I(6)	2.780(2)
S(1)–N(1)	1.746(14)	I(1)⋯I(2)	3.5008(2)
C(6)–C(8)	1.43(2)	I(1)⋯I(3)	3.3863(2)
C(8)–N(1)	1.31(2)	I(1)⋯I(4)	3.4368(2)
N(2)–C(13)	1.32(2)	I(1)⋯I(5)	3.3175(2)
C(13)–C(2)#3	1.45(2)	I(1)⋯I(6)#4	3.7190(2)
I(2)–I(2)#1	2.751(2)	S(1)⋯I(4)	3.9988(5)
I(3)–I(3)#2	2.794(2)	S(1)⋯S(1)#1	4.7730(2)
I(4)–I(4)#3	2.803(3)	I(1)⋯I(6)#5	4.922
C(1)–S(1)–N(1)	89.0(7)	C(8)–C(6)–C(1)	108.8(15)
C(2)–C(1)–C(6)	119.8(17)	N(1)–C(8)–C(6)	113.8(15)
C(2)–C(1)–S(1)	127.6(14)	C(8)–N(1)–C(9)	122.8(15)
C(6)–C(1)–S(1)	112.6(13)	C(8)–N(1)–S(1)	115.8(12)
C(5)–C(6)–C(8)	132.4(16)	C(9)–N(1)–S(1)	121.0(11)
C(5)–C(6)–C(1)	118.8(16)		

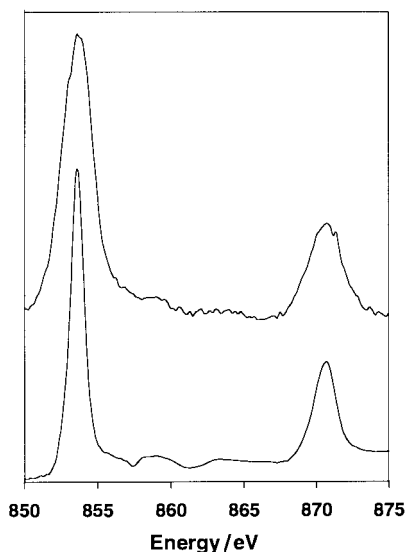
Symmetry transformations used to generate equivalent atoms: #1  $-x + 1, y, -z + 3/2$ ; #2  $-x + 2, -y + 1, -z + 1$ ; #3  $-x + 2, y, -z + 3/2$ ; #4  $x + 1/2, y + 1/2, z$ ; #5  $1 - x, 1 - y, 1 - z$ .

**Fig. 7** Perspective view of (L3')(I<sub>2</sub>(I<sub>2</sub>))<sub>5</sub> (hydrogen atoms omitted for clarity). Note that nearest neighbour iodine atoms have been generated by symmetry (see Table 5) to show the nature of the polyiodide array and hence this figure does not show the correct ratio of iodine atoms to macrocyclic complex.

I(4)⋯S(1) 3.9988(5) Å, is much longer than the expected value for a sulfur iodine bond [I–S *ca.* 2.6–3.0 Å].<sup>66</sup>

### Electrochemical studies on [Ni<sub>2</sub>L2][Ce(NO<sub>3</sub>)<sub>6</sub>]

Due to the low solubility of [Ni<sub>2</sub>L2][Ce(NO<sub>3</sub>)<sub>6</sub>] in common solvents, electrochemical studies on this complex were limited to those performed in DMF. The decay of the complex occurs even faster in the presence of the supporting electrolyte, with the solutions changing colour from black to red in around 45 min, making a conclusive study (*e.g.* bulk electrolysis, scan rate dependence of the  $E_{1/2}$  *etc.*) impossible.<sup>67</sup> The cyclic voltammogram of [Ni<sub>2</sub>L2][Ce(NO<sub>3</sub>)<sub>6</sub>], freshly dissolved in DMF (*vs.* 0.01 M AgNO<sub>3</sub>/Ag), revealed a series of four approximately one electron processes: two reduction processes at –1.60 (quasi-reversible) and –1.10 V (quasi-reversible) and two oxidation processes at +0.30 V (quasi-reversible) and +0.70 V (irreversible). Characteristic of cyclic voltammograms run in DMF, the two oxidation waves have somewhat smaller peak currents than those observed for the reduction waves.<sup>67</sup> These processes are assigned as largely metal based by comparisons with other dinickel dithiolate macrocycles.<sup>17</sup> All four processes are translated approximately –0.10 V from those observed for [Ni<sub>2</sub>L2]–(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> in DMF and for the electrochemically generated one



**Fig. 8** Nickel L-edge XANES spectra of  $[\text{Ni}_2\text{L}_2][\text{Ce}(\text{NO}_3)_6]$  (top) and  $[\text{Ni}_2\text{L}_2](\text{CF}_3\text{SO}_3)_2$  (bottom).

electron oxidation product of  $[\text{Ni}_2\text{L}_2](\text{CF}_3\text{SO}_3)_2$  in MeCN,<sup>17</sup> implying that the nickel centres in  $[\text{Ni}_2\text{L}_2][\text{Ce}(\text{NO}_3)_6]$  experience a slight change in environment, presumably due to interactions with the cerium nitrate anions (the macrocyclic ligand is unchanged).

A controlled potential electrolysis experiment was performed at  $-0.10$  V vs.  $0.01$  M  $\text{AgNO}_3/\text{Ag}$  on a fresh black DMF solution of  $[\text{Ni}_2\text{L}_2][\text{Ce}(\text{NO}_3)_6]$  and  $0.64$  electron equivalents of charge were transferred ( $I_f = 2\%$  of  $I_i$ ), yielding a red solution. This is less than the expected one electron equivalent of charge, indicating that, as anticipated, some decomposition may have already taken place.

#### EPR spectroscopy of $[\text{Ni}_2\text{L}_2][\text{Ce}(\text{NO}_3)_6]$

A fresh sample of  $[\text{Ni}_2\text{L}_2][\text{Ce}(\text{NO}_3)_6]$  was prepared (in MeCN) immediately before carrying out the EPR experiment. This black solid was isolated from the reaction mixture, washed and dried briefly *in vacuo*, then dissolved in DMF, frozen in liquid nitrogen and the EPR spectrum promptly obtained on the DMF glass. The observation of two overlapping axial signals is consistent with the presence of two different nickel(III) ions. The signals at  $g_{\parallel} = 2.04$  and  $g_{\perp} = 2.20$  are closely similar to those derived for the electrochemically oxidised  $[\text{Ni}_2\text{L}_2](\text{CF}_3\text{SO}_3)_2$  reported earlier.<sup>17</sup> However, a second species with  $g_{\perp} = 2.18$  and a complex multiplet centred near  $2.07$  is also observed. The ion is characteristic of  $d^7$  nickel(III), but with axial coordination of solvent (DMF/MeCN) molecule or molecules or possibly an anion present in solution.

#### XANES studies

Nickel L-edge XANES can be used to detect the oxidation state of nickel in complexes and metalloproteins.<sup>24</sup> The nickel L-edge XANES spectra of complexes  $[\text{Ni}_2\text{L}_2](\text{CF}_3\text{SO}_3)_2$  and  $[\text{Ni}_2\text{L}_2][\text{Ce}(\text{NO}_3)_6]$  are shown in Fig. 8. The spectrum of  $[\text{Ni}_2\text{L}_2](\text{CF}_3\text{SO}_3)_2$  is typical of those obtained for related dinickel(II) complexes from this group.<sup>17,19–21,23,24</sup> The spectrum of  $[\text{Ni}_2\text{L}_2][\text{Ce}(\text{NO}_3)_6]$  is consistent with the presence of both a low spin nickel(II) site and a nickel(III) site.<sup>24,68,69</sup> However, it is difficult to completely analyze the  $[\text{Ni}_2\text{L}_2][\text{Ce}(\text{NO}_3)_6]$  spectrum because the  $M_5$  edge for cerium occurs close to the  $L_2$  edge for nickel.

#### Conclusion

The established route to make the masked thiolate head unit **6** on a preparative scale has been refined and successfully extended to include the closely related head units **7** and **8**. Using

this method the range of masked thiolate head units available can in principle be extended still further to include, for example, the masked thiols derived from 2,6-diformyl-4-chlorophenol<sup>70</sup> and 2,6-diformyl-4-trifluoromethylphenol.<sup>71</sup>

The first Schiff-base macrocyclic complex to be derived from the new head unit **7**,  $[\text{Ni}_2\text{L}_1](\text{ClO}_4)_2$ , has been prepared and characterised. As yet the masked thiolate **8** has not been reacted to form metal complexes, however, it could provide an attractive synthetic route to many new ligands as well as an alternative route to tsalen type complexes.<sup>72–75</sup>

Both metal and ligand centred oxidation products of the dinickel(II) dithiolate complexes have been successfully isolated in the course of this work. The unstable black complex  $[\text{Ni}_2\text{L}_2][\text{Ce}(\text{NO}_3)_6]$  proved difficult to characterise and work with, but taken together the results indicate that this product of CAN oxidation is primarily nickel centred: (a) the complex decomposes over time to form the structurally characterised dinickel(II) complex  $[\text{Ni}_2\text{L}_2](\text{NO}_3)_2 \cdot 2\text{DMF}$  with no change to the ligand, (b) the electrochemistry is similar to that of the parent dinickel(II) complex  $[\text{Ni}_2\text{L}_2](\text{CF}_3\text{SO}_3)_2$ , (c) the EPR spectrum indicates the presence of a nickel(III) centre, (d) the UV/Vis spectrum is similar to the electrochemically generated one electron oxidation product of  $[\text{Ni}_2\text{L}_2](\text{CF}_3\text{SO}_3)_2$ , (e) the nickel L-edge XANES studies indicate the presence of a nickel(III) centre. In contrast, the metal free macrocycle  $(\text{L}3')^{2+}$  is the product of ligand centred oxidation. It results, in low yields, from the treatment of the parent dinickel(II) complex with excess iodine and has been conclusively identified by X-ray structure determinations.

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