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Note

# Synthesis of the ligand N,N'-bis(2-tert-butylthiobenzenylidene)-diethylenetriamine; its reactivity with nickel(II) salts

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#### Abstract

The synthesis of the Schiff base ligand N,N'-bis(2-tert-butylthiobenzenylidene)-diethylenetriamine (<sup>t</sup>Bu<sub>2</sub>L1) and its reactivity with nickel(II) salts is described. Reaction of <sup>t</sup>Bu<sub>2</sub>L1 with nickel chloride results in two different complexes, depending on the temperature of the reaction mixture. The green paramagnetic five-coordinate complex [Ni(<sup>t</sup>Bu<sub>2</sub>L1)Cl<sub>2</sub>] forms on reaction at room temperature, whereas at reflux temperature the red diamagnetic [Ni(L1\*)]Cl · H<sub>2</sub>O is formed. In the ligand L1\* one of the imine groups is hydrolysed, and the protecting tert-butyl group of the remaining thiobenzylidene is lost, resulting in a new tetradentate N<sub>3</sub>S thiolato ligand. [Ni(L1\*)]Cl · H<sub>2</sub>O crystallises in the monoclinic space group  $P2_1/c$ , with Ni–N distances of 1.860(7), 1.941(8) and 1.914(7) Å and a Ni–S distance of 2.131(3) Å. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structures; Nickel complexes; Five-coordinate complexes; Schiff base complexes

## 1. Introduction

The structural characterisation of the active site of the [Ni–Fe] hydrogenase enzyme, extracted from *Desulfovibrio Gigas* [1], by which the catalytic site was revealed to contain a heterodimetallic nickel–iron cluster in a sulfur rich environment, has renewed interest in the chemical modelling of [Ni–Fe] hydrogenases. A large amount of modelling chemistry had already been reported prior to the publication of the X-ray structure [2,3], when it was believed that the active site contained mononuclear nickel.

The compounds described in this paper were synthesised as part of a research in modelling the heterodinuclear Ni-Fe active site of hydrogenases. It was decided that ligands containing mixed N/S donor groups would be used preferentially to provide greater synthetic control. Previous work resulted in mononuclear compounds with square planar cis NiN<sub>2</sub>S<sub>2</sub> chromophores [4,5]. However, reaction of these complexes with suitable iron complexes did not result in the desired Ni-Fe heterodinuclear compounds; therefore, several new ligands were designed and synthesised. This has resulted in an interesting dinuclear iron compound as a good structural model for Fe-only hydrogenases [6]. A schematic drawing of the target ligand described in this paper is given in Fig. 1. Loss of the protecting tertiary butyl groups upon complexation with nickel salts should lead to a five-coordinated nickel complex bound to two imino-nitrogens, one secondary amine and two thiolato-sulfur donors, which then would be available for bridging to a second metal ion.

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Fig. 1. The protected ligand N,N'-bis(2-tert-butylthiobenzenylidene)diethylenetriamine.

# 2. Experimental

# 2.1. Materials

Starting materials were obtained from Aldrich. All procedures were performed in a nitrogen or argon atmosphere using solvents that were degassed on a vacuum system prior to use. 2-Tert-butyl-thiobenzalde-hyde was prepared according to a literature procedure [7].

## 2.2. Physical methods

Infrared spectra (KBr pellets) were recorded in the range 4000-400 cm<sup>-1</sup> using a Perkin–Elmer FT-IR Paragon spectrophotometer controlled by a PC using PE Grams analyst software. Nuclear magnetic resonance spectra were recorded on a Bruker dpx300 MHz spectrometer. Ligand field spectra of the solids (300–2000 nm, diffuse reflectance) were taken on a Perkin–Elmer 330 spectrophotometer equipped with a data station. Microanalysis measurements were performed at the Microanalytical Laboratory of the University College, Dublin.

# 2.3. Ligand synthesis

To a solution of 2-tert-butyl-thiobenzaldehyde (1.0 g, 5.15 mmol) in 40 ml ethanol (98%) was added a solution of diethylenetriamine (0.28 ml, 2.58 mmol) in 20 ml ethanol (98%) and the mixture was heated under reflux for 1 h in the presence of CaSO<sub>4</sub> as a drying agent. The resultant bright yellow solution was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent evaporated, leaving a yellow oil (<sup>1</sup>Bu<sub>2</sub>L1). The yellow oil could only be isolated in a crude form, and was used for further reactions in this form. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  = 9.11 (2H, s, HC=N), 8.01 (2H, m), 7.53 (2H, m), 7.38 (4H, m), 3.80 (4H, t, CH<sub>2</sub>), 3.02 (4H, t, CH<sub>2</sub>), 1.24 (18H, s, <sup>1</sup>Bu).

# 2.4. Preparation of the complexes

## 2.4.1. $[Ni(^{t}Bu_{2}L1)Cl_{2}]$

The yellow oil of crude ligand N,N'-bis(2-tert-butylthiobenzenylidene)-diethylenetriamine was dissolved in 10 ml ethanol (98%) and a solution of NiCl<sub>2</sub> · 6H<sub>2</sub>O (0.61 g, 2.58 mmol) in 10 ml ethanol (98%) was added. The mixture was stirred for 10 min during which time a bright green precipitate began to form. The precipitate was collected on microfine filter paper (1.12 g, 85% yield based on NiCl<sub>2</sub> · 6H<sub>2</sub>O). *Anal.* Calc. for C<sub>26</sub>H<sub>37</sub>Cl<sub>2</sub>N<sub>3</sub>-NiS<sub>2</sub>: C, 53.35; H, 6.37; N, 7.18; Ni, 10.0; S, 10.96. Found: C, 53.23; H, 6.55; N, 7.07; Ni, 10.0; S, 10.6%. IR (KBr)  $\nu$  (cm<sup>-1</sup>): 3266 (w), 2960 (m), 2929 (m), 2863 (m), 1636 (vs), 1584 (s), 1458 (s), 1434 (m), 1423 (w), 1385 (s), 1363 (s), 1328 (w), 1292 (w), 1274 (w), 1206 (w), 1166 (vs), 1126 (m), 1104 (m), 1062 (w), 1044 (m), 1032 (m), 972 (w), 955 (m), 929 (vs), 849 (w), 817 (w), 764 (vs), 700 (w), 627 (w), 572 (w), 500 (m), 444 (w). Vis-NIR (solid-state reflectance, D<sub>2</sub> lamp): bands at 5.8 × 10<sup>3</sup>, 8.8 × 10<sup>3</sup>, 15.4 × 10<sup>3</sup>, and 24.9 × 10<sup>3</sup> cm<sup>-1</sup>.

# 2.4.2. $[Ni(L1^*)]Cl \cdot H_2O$

The yellow oil of ligand N, N'-bis(2-tert-butylthiobenzenylidene)-diethylenetriamine was dissolved in 10 ml ethanol (98%) and a solution of NiCl<sub>2</sub> · 6H<sub>2</sub>O (0.61 g, 2.58 mmol) in 10 ml ethanol (98%) was added. The mixture was heated under reflux conditions for 1 h. After 5 min a bright green precipitate formed, but this redissolved after half an hour of further heating, during which time the solution turned a deep red colour. The solution was left to cool and on slow evaporation, red crystals of  $[Ni(L1^*)]Cl \cdot H_2O$  were formed (0.53 g, 63%) yield based on NiCl<sub>2</sub>  $\cdot$  6H<sub>2</sub>O). Anal. Calc. for C<sub>11</sub>H<sub>18</sub>ClN<sub>3</sub>NiOS: C, 39.50; H, 5.42; N, 12.56; S, 9.59 Found: C, 39.57; H, 5.40; N, 12.21; S, 9.75%. IR (KBr)  $v (cm^{-1})$ : 3425 (m), 3363 (m), 3212 (m), 3157 (m), 1608 (vs), 1587 (s), 1535 (s), 1462 (m), 1428 (w), 1409 (m), 1325 (w), 1250 (m), 1220 (m), 1190 (s), 1128 (w), 1096 (m), 1058 (m), 1050 (s), 981 (s), 964 (m), 879 (w), 828 (w), 768 (s), 722 (w), 645 (w), 587(m), 494 (w), 448 (w). Vis-NIR (solid-state reflectance, D<sub>2</sub> lamp): bands at  $23.4 \times 10^3$  and  $18.9 \times 10^3$  cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>3</sub>OD)  $\delta$ (ppm) = 8.14 (1H, s, HC = N), 7.64 (1H, d, J = 8.1 Hz),7.46 (1H, dd, J = 8.0 and 1.3 Hz), 7.23 (1H, td, J = 7.2and 1.5 Hz), 7.04 (1H, td, J = 8.0 and 1.1 Hz), 4.00-3.87 (2H, m), 3.1-2.5 (6H, several multiplets).

This type of complex,  $[Ni(L1^*)]X$ , can be synthesised using different nickel salts (X = ClO<sub>4</sub>, BF<sub>4</sub>, and with PF<sub>6</sub> after ion exchange).  $[Ni(L1^*)](BF_4)$ : *Anal*. Calc. for C<sub>11</sub>H<sub>16</sub>BF<sub>4</sub>N<sub>3</sub>NiS: C, 35.92; H, 4.38; N, 11.42; S, 8.72. Found: C, 35.69; H, 4.35; N, 11.01; S, 8.94%.  $[Ni(L1^*)](PF_6)$ : *Anal*. Calc. for C<sub>11</sub>H<sub>16</sub>F<sub>6</sub>N<sub>3</sub>NiPS: C, 31.0; H, 3.8; N, 9.9; S, 7.5. Found: C, 30.98; H, 3.73; N, 9.87; S, 7.43%.

## 2.5. Crystal structure determination

## 2.5.1. Crystal data

C<sub>11</sub>H<sub>18</sub>ClN<sub>3</sub>NiOS, M = 334.5, monoclinic space group  $P2_1/c$ , a = 11.285(2), b = 12.980(2), c = 10.092(2)Å,  $\beta = 110.356(12)^\circ$ , V = 1386.0(4) Å<sup>3</sup>, Z = 4,  $D_{calc} = 1.603$  g cm<sup>-3</sup>, T = 150 K,  $\mu = 17.3$  cm<sup>-1</sup>, F(000) = 696.0, Mo Kα radiation,  $\lambda = 0.71073$  Å.

# 2.5.2. Data collection and refinement

An orange crystal of [Ni(C<sub>11</sub>H<sub>16</sub>N<sub>3</sub>S)]Cl·H<sub>2</sub>O suitable for X-ray structure determination was mounted on a Lindemann-glass capillary and transferred into the cold nitrogen stream on an Enraf-Nonius CAD4-T diffractometer on rotating anode. The data were collected using Mo K $\alpha$  radiation, with a graphite monochromator ( $\lambda = 0.71073$  Å). Accurate unit cell parameters and an orientation matrix were determined by least-squares refinement of the setting angles of 25 well-centered reflections (SET4) in the range  $8.3 < \theta <$ 15.2°. Data were collected in  $\omega - 2\theta$  scan mode with scan angle  $\Delta \omega = 1.18 + 0.35 \tan \theta^{\circ}$ . Intensity data of 4373 reflections were measured, of which 2437 were independent ( $R_{int} = 0.10$ ). Data were corrected with the DELABS option in PLATON [8]. The structure was solved with automated Patterson techniques (DIRDIF92 [9]) and refined on  $F^2$  using SHELXL93 [10]. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in the refinement on calculated positions, riding on their carrier atoms except those on H<sub>2</sub>O that were located from a difference map and refined freely. Isotropic displacement parameters for hydrogen atoms were fixed on values related to the equivalent isotropic displacement parameter of the atom they are attached to. Convergence was reached at  $wR_2 = 0.1416$ ,  $w^{-1} = \sigma^2(F_o^2) +$ where  $P = (\max(F_o^2, 0) + 2F_c^2)/3$ ,  $(0.0318P)^2$ ,  $R_1 = 0.0751$  for 1230  $F_0 > 2\sigma(F_0)$ , S = 1.02 for 169 parameters. No residual density was found outside -0.50 and 0.53 e Å<sup>-3</sup>. Neutral atom scattering factors and anomalous dispersion corrections were taken from the International Tables for Crystallography [11]. Geometrical calculations and illustrations were performed with PLATON [8].

## 3. Results and discussion

The ligand <sup>t</sup>Bu<sub>2</sub>L1 was synthesised and reacted with nickel salts in an attempt to form a five-coordinate species which contained two cis thiolato groups, as has been reported for a similar ligand with aliphatic thiolate groups [12]. The thiolate groups in L1 would be formed by deprotection of the thioether groups as has been observed in the synthesis of [N, N'-bis(2-thiobenzenylidene)ethylenediaminato]nickel(II) [4,5]. On mixing an alcoholic solution of nickel chloride and the ligand <sup>t</sup>Bu<sub>2</sub>L1, a bright green precipitate formed and was collected. The infrared spectrum of this compound suggests that the tertiary butyl groups are still present. No NMR spectrum could be recorded of this complex because of paramagnetism. The ligand field data of this compound show that the nickel ion probably is in a distorted square pyramidal environment [13–15]. Microanalysis data suggest a formulation of [Ni('Bu<sub>2</sub>L1)Cl<sub>2</sub>]. Assuming that the unprotected thioether groups are too weak donors to be coordinated to the nickel ion, a five-coordinate environment consisting of three nitrogen donors from the ligand and two chloride ions is anticipated. The bulkiness of the pendant 2-tert-butylbenzenylidene groups would thereby prevent the formation of an octahedral coordination geometry. Several structures of five-coordinate nickel ions with sterically demanding tridentate ligands have been reported [14,16].

On repeating the synthesis but this time heating the mixture under reflux conditions in order to remove the protecting tertiary butyl groups, the same green precipitate was observed initially, but after half an hour of heating, the precipitate had redissolved and a red solution had formed. On cooling and after slow evaporation of the solvent, red crystals of  $[Ni(L1^*)]Cl \cdot H_2O$ were formed. The infrared spectra of this complex showed that the tertiary butyl groups had indeed been removed. In addition, broad peaks in the 3500-3100 cm<sup>-1</sup> region of the infrared spectrum, indicative of OH or NH groups were apparent. The red complex is diamagnetic and its NMR spectrum in MeOD was recorded, which confirmed the absence of tert-butyl groups, but which showed the presence of only one aromatic group per C4 backbone. Single crystal diffraction studies showed that the ligand was partially decomposed, with one of the imine groups being hydrolysed. A projection of the crystal structure of  $[Ni(L1^*)]Cl \cdot H_2O$  is given in Fig. 2, and selected bond distances and angles are given in Table 1. The structure shows that the nickel ion is in a square planar environment, formed by a primary and a secondary amine, an imino nitrogen and a thiolate group. The bond distances and angles are in the normal range for low-spin divalent nickel. The bond distances in the aliphatic chain of the ligand are somewhat shortened, due to



Fig. 2. A PLUTON projection of the compound  $[Ni(L1^*)]Cl \cdot H_2O$ .

Table 2

Table 1										
Selected	bond	lengths	(Å)	and	angles	(°)	for	[Ni(L1	*)]Cl ·	$H_2O$

Ni(1)-S(10)	2.131(3)	Ni(1)–N(21)	1.941(8)
Ni(1)-N(18)	1.860(7)	Ni(1)-N(24)	1.914(7)
S(10)–Ni(1)–N(18)	98.5(2)	N(18)-Ni(1)-N(21)	86.1(3)
S(10)-Ni(1)-N(21)	175.2(2)	N(18)-Ni(1)-N(24)	171.1(3)
S(10)-Ni(1)-N(24)	89.2(2)	N(21)-Ni(1)-N(24)	86.3(3)

Hydrogen bond distances (Å) and angles (°) in $[\mathrm{Ni}(\mathrm{L1}^*)]\mathrm{Cl}\cdot\mathrm{H}$	20

D–H···A	D…A	D–H	Н…А	D–H…A
N(24)-H(24a)-O(30)	2.895(10)	0.92(1)	2.005(10)	162.4(8)
N(24)-H(24b)-Cl(2)	3.280(7)	0.921(9)	2.385(7)	164.1(8)
O(30)-H(31)-Cl(2) <sup>a</sup>	3.166(7)	0.98(2)	2.21(4)	164(9)
O(30)-H(32)-Cl(2) <sup>b</sup>	3.208(7)	0.98(8)	2.27(8)	160(7)

<sup>a</sup> Symmetry operations: x, 1/2 - y, -1/2 + z.

<sup>b</sup> Symmetry operations: 1-x, -1/2+y, 1/2-z.

positional disorder (puckering), resulting in a rather high *R*-value. However, no attempt was made to calculate a disorder model. The thermal motion observed in the aliphatic chain explains the complex splitting patterns observed in the NMR spectra of this compound. The hydrogen atoms originating from the water molecule and the primary amine are all involved in an extended hydrogen bonding network. The distances and angles in these hydrogen bonds are given in Table 2. The non-coordinated chloride ion is held in its position by three H-bonds, two from the water molecule, and one from the primary amine. An impression of the two-dimensional network which is formed by the hydrogen bonding in [Ni(L1\*)]Cl  $\cdot$  H<sub>2</sub>O is given in Fig. 3.

## 4. Supplementary material

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number CCDC-104981.

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Fig. 3. An impression of the two-dimensional hydrogen bonding network in  $[Ni(L1^*)]Cl \cdot H_2O$ .

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