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Synthesis, spectroscopic and electrochemical study of nickel(II) complexes with tetradentate asymmetric Schiff bases derived from salicylaldehyde and methyl-2-amino-1-cyclopentenedithiocarboxylate

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Abstract

New tetradentate ligands with N_2OS coordination spheres were prepared and the corresponding nickel(II) complexes were synthesized and characterized by analytical, spectroscopic and electrochemical methods. The structure of nickel{methyl-2-{*N*-[2-(3′-methoxy-2′-phenolate)methylidynenitrilo]ethyl}aminato(-1)-1-cyclopentenedithiocarboxylate} has been determined by X-ray crystallography. This complex crystallizes in the orthorhombic space group $P2_12_12$ with $a = 11.417$ (3), $b = 13.883$ (4), $c = 12.769$ (3), $Z = 4$ and $R_1 = 0.0539$ for 4641 reflections with $I > 2\sigma(I)$. The UV–Vis and ^{1}H NMR spectroscopic results indicate that the complexes have a square-planar structure in the solid state and in solution. Electrochemical and EPR data show that the complexes are reduced to the correspondent nickel(I) complexes, but that the ligands are non-innocent in the electrochemical oxidation of the complexes.

Keywords: Crystal structures; Electrochemistry; Nickel complexes; Schiff base complexes

1. Introduction

There is currently a great interest in the study of the factors that influence the accessibility of several oxidation states for nickel, specially related to the bio-inorganic role of this metal ion in several redox enzymes [1]. Elucidation of the fundamental structural and electronic factors that influence the relative stability of several oxidation states of the metal may be useful in understanding the enzyme reactivity and in the optimization of the design of model compounds. Further interest in the coordination chemistry of nickel(I) arises from the role of these complexes in several catalytic reactions, such as electrocatalytical [2] and photocatalytical [3] reduction of CO_2, and electrocatalytical reduction of alkyl halides [4].

It has been suggested that the incorporation of both soft and hard donors in the coordination environment of the metal ion may be crucial in the stabilization of oxidation numbers +1 and +3 for nickel [5]. This hypothesis, in conjunction with experimental evidence that the coordination environment of nickel in NiFe hydrogenases [6] and CO-dehydrogenase [7] contains sulphur, nitrogen and/or oxygen donors, resulted in a continuing effort to obtain nickel complexes with this kind of coordination environment. We have synthesized and studied the nickel(II) complexes depicted in Scheme 1, which possess a mixed N_2OS coordination sphere. The corresponding symmetric nickel complexes with ligands derived from salicylaldehyde, [Ni(salen)], and methyl-2-amino-1-cyclopentenedithicarboxylate, [$Ni(cd_2en)$] have been studied by others [8,9], and the results may be compared with those obtained in the present work in order to verify if there are some synergic effects between the two halves of the ligand, which may be responsible for additional accessibility of multiple oxidation states for nickel.

2. Experimental

2.1. Materials

All solvents used in the preparations were reagent grade. Chemicals for the preparations were reagent grade and commercially available, and were used without further purification. The electrochemical measurements were performed in *N,N′*-dimethylformamide (dmf) (Merck, *proanalisi*); tetrabutylammonium perchlorate (TBAP) was prepared by published methods [10]. **CAUTION**: perchlorates are hazardous and may explode.

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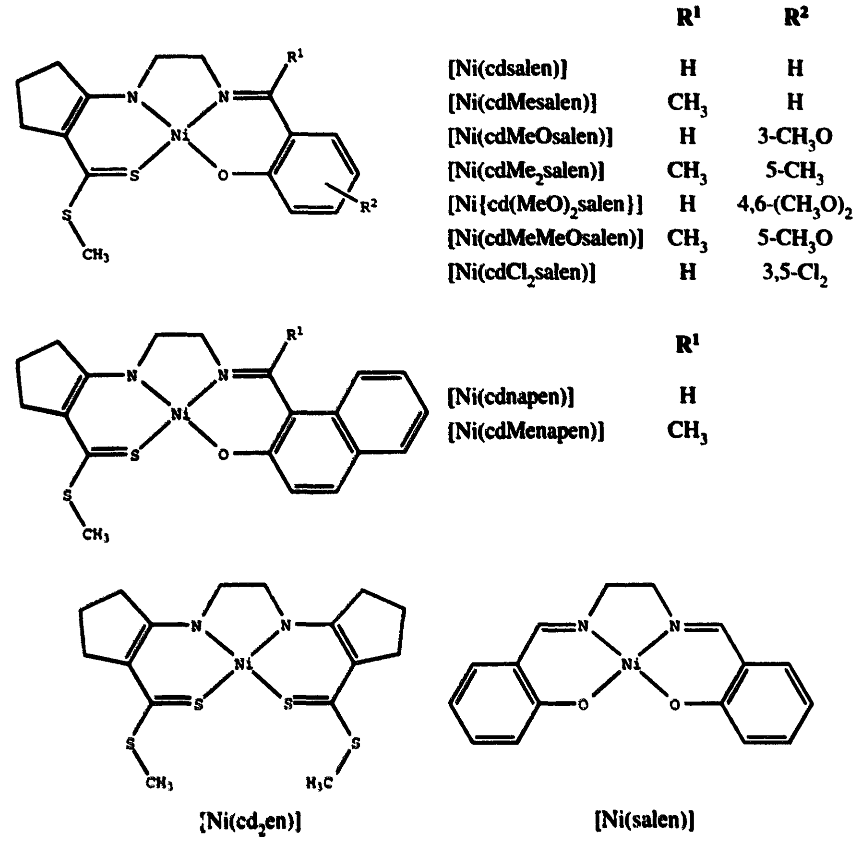

	R¹	R²
[Ni(cdsalen)]	H	H
[Ni(cdMesalen)]	CH_3	H
[Ni(cdMeOsalen)]	H	3-CH_3O
[Ni(cdMe$_2$salen)]	CH_3	5-CH_3
[Ni{cd(MeO)$_2$salen}]	H	4,6-$(CH_3O)_2$
[Ni(cdMeMeOsalen)]	CH_3	5-CH_3O
[Ni(cdCl$_2$salen)]	H	3,5-Cl_2

	R¹
[Ni(cdnapen)]	H
[Ni(cdMenapen)]	CH_3

Scheme 1.

2.2. *Instrumentation*

Elemental analyses (C; H and N) were performed at the Micro Analytical Laboratory, University of Manchester, and at the Departamento de Química da Faculdade de Ciências do Porto. UV/Vis/NIR spectra were recorded on a Shimadzu UV-3101PC spectrometer, NMR spectra on a Brüker AC200 or a Brüker AMX300 spectrometer in deuterochloroform, unless otherwise stated, with tetramethylsilane as internal standard.

Electrochemical measurements were made with a PAR 362 using solutions ≈ 1×10^{-3} mol dm^{-3} in complex and 0.1 mol dm^{-3} in TBAP. Cyclic voltammetry was performed in dmf using a three-electrode cell, with a platinum microsphere as working electrode, a platinum foil as counter electrode and an Ag/AgCl (1 mol dm^{-3} NaCl) reference electrode. In all cases, ferrocene (Fc) was used as an internal standard, and under the experimental conditions employed $E_{1/2}$ of the Fc^+/Fc couple is 485 mV. All potentials are reported relative to Ag/AgCl (1 mol dm^{-3} NaCl).

Controlled potential electrolysis of the nickel(II) complexes was performed using strictly anaerobic conditions in a three-electrode cell, with a platinum gauze working electrode, a platinum foil counter electrode and an Ag/AgCl (1 mol dm^{-3} NaCl) reference electrode. The potential applied was approximately 50 mV more negative than the cathodic peak potential determined in the voltammetric experiments.

EPR spectra were obtained with a Bruker ESP 300E spectrometer (9 GHz) in a dual cavity, using diphenylpicrylhydrazyl (dpph; $g = 2.0037$) as an external standard; the magnetic field was calibrated by use of Mn^{2+} in MgO. Spectra were obtained at 77 K, using sealed quartz tubes.

2.3. *Synthesis*

Methyl-2-{*N*-(2′-aminoethane}-amino-1-cyclopentenedithiocarboxylate (Hcden) was prepared by published methods [11,12].

2.3.1. *General procedure for the synthesis of the ligands*

All the ligands used in this work were prepared by addition of the equimolar amount of the appropriate salicylaldehyde to a methanolic solution of Hcden. The yellow products obtained were recrystallized from methanol–chloroform, 1:1 vol./vol.

2.3.1.1. *Methyl-2-{N-[2-(2′-hydroxyphenyl)methylidynenitrilo]ethyl}amino-1-cyclopentenedithiocarboxylate, H$_2$cdsalen*

Yield 79.8%. λ_{max}(dmf)/nm 314 (logϵ_{max} 4.15) and 398 (4.36); δ_H (200 MHz; $CDCl_3$) 1.82 (2 H, m), 2.59 (3 H, s), 2.65–2.79 (4 H, m), 3.72 (2 H, t), 3.85 (2 H, t), 6.64–6.97 (2 H, m), 7.23–7.36 (2 H, m), 8.40 (1 H, s, CH=N), 12.38 (1 H, br s, NH) and 12.88 (1 H, br s, OH) (Found:

C, 59.4; H, 6.27; N, 8.55; S, 20.0%. $C_{16}H_{20}N_2OS_2$ requires C, 60.0; H, 6.29; N, 8.74; S, 20.0%).

2.3.1.2. *Methyl-2-{N-[2-(2'-hydroxyphenyl)ethylidynenitrilo]ethyl}amino-1-cyclopentenedithiocarboxylate, H$_2$cdMesalen*

Yield 63.4%. λ_{max}(dmf)/nm 313 ($\log\epsilon_{max}$ 4.12) and 398 (4.36); δ_H (300 MHz; $CDCl_3$) 1.85 (2 H, m), 2.36 (3 H, s), 2.58 (3 H, s), 2.73 (2 H, t), 2.79 (2 H, t), 3.76–3.85 (4 H, m), 6.82 (1 H, t), 6.94 (1 H, d), 7.30 (1 H, t), 7.53 (1 H, d), 12.45 (1 H, br s, NH) and 15.4 (1 H, br s, OH) (Found: C, 60.0; H, 6.58; N, 8.28; S, 19.6%. $C_{17}H_{22}N_2OS_2$ requires C, 61.0; H, 6.63; N, 8.37; S, 19.2%).

2.3.1.3. *Methyl-2-{N-[2-(2'-hydroxy-3'-methoxyphenyl)-methylidynenitrilo]ethyl}amino-1-cyclopentenedithiocarboxylate, H$_2$cdMeOsalen*

Yield 78.4%. λ_{max}(dmf)/nm 313 ($\log\epsilon_{max}$ 4.11) and 398 (4.38); δ_H (200 MHz; $CDCl_3$) 1.80 (2 H, m), 2.56 (3 H, s), 2.64–2.77 (4 H, m), 3.75 (2 H, t), 3.86 (2 H, t), 3.90 (3 H, s, OCH_3), 6.79–6.97 (3 H, m), 8.39 (1 H, s, CH=N), 12.36 (1 H, br s, NH) and 13.27 (1 H, br s, OH) (Found: C, 57.9; H, 6.17; N, 8.16; S, 18.3%. $C_{17}H_{22}N_2O_2S_2$ requires C, 58.2; H, 6.33; N, 7.99; S, 18.3%).

2.3.1.4. *Methyl-2-{N-[2-(2'-hydroxy-5'-methylphenyl)-ethylidynenitrilo]ethyl}amino-1-cyclo-pentenedithiocarboxylate, H$_2$cdMe$_2$salen*

Yield 63.8%. λ_{max}(dmf)/nm 315 ($\log\epsilon_{max}$ 4.15) and 398 (4.40); δ_H (200 MHz; $CDCl_3$) 1.84 (2 H, m), 2.29 (3 H, s), 2.33 (3 H, s), 2.57 (3 H, s), 2.68–2.82 (4 H, m), 3.78–3.82 (4 H, m), 6.83 (1 H, d), 7.10 (1 H, d), 7.30 (1 H, s), 12.44 (1 H, br s, NH) and 15.16 (1 H, br s, OH) (Found: C, 62.0; H, 6.98; N, 8.07; S, 18.2%. $C_{18}H_{24}N_2OS_2$ requires C, 62.0; H, 6.94; N, 8.04; S, 18.4%).

2.3.1.5. *Methyl-2-{N-[2-(2'-hydroxy-4',6'-dimethoxyphenyl)methylidynenitrilo]ethyl}amino-1-cyclopentenedithiocarboxylate, H$_2$cd(MeO)$_2$salen*

Yield 62.8%. λ_{max}(dmf)/nm 289 (sh), 312 ($\log\epsilon_{max}$ 4.38) and 398 (4.39); δ_H (200 MHz; $CDCl_3$) 1.81 (2 H, m), 2.57 (3 H, s), 2.62–2.79 (4 H, m), 3.47–3.73 (4 H, m), 3.77 (3 H, s, OCH_3), 3.78 (3 H, s, OCH_3), 5.76 (1 H, d) 5.98 (1 H, d), 8.54 (1 H, s, CH=N), 12.38 (1 H, br s, NH) and 14.18 (1 H, br s, OH) (Found: C, 56.5; H, 6.39; N, 7.43; S, 16.7%. $C_{18}H_{24}N_2O_3S_2$ requires C, 56.8; H, 6.36; N, 7.36; S, 16.9%).

2.3.1.6. *Methyl-2-{N-[2-(2'-hydroxy-5'-methoxyphenyl)-ethylidynenitrilo]ethyl}amino-1-cyclopentenedithiocarboxylate, H$_2$cdMeMeOsalen*

Yield 77.7%. λ_{max}(dmf)/nm 289 (sh), 313 ($\log\epsilon_{max}$ 4.05) and 397 (4.37); δ_H (200 MHz; $CDCl_3$) 1.84 (2 H, m), 2.33 (3 H, s), 2.57 (3 H, s), 2.69–2.83 (4 H, m), 3.74–3.87 (7 H, m, CH_2 and OCH_3), 6.85–6.96 (2 H, m) 7.04 (1 H, d), 12.45 (1 H, br s, NH) and 14.77 (1 H, br s, OH) (Found: C, 58.7; H, 6.65; N, 7.53; S, 17.6%. $C_{18}H_{24}N_2O_2S_2$ requires C, 59.3; H, 6.64; N, 7.68; S, 17.6%).

2.3.1.7. *Methyl-2-{N-[2-(3',5'-dichloro-2'-hydroxyphenyl)methylidynenitrilo]ethyl}amino-1-cyclopentenedithiocarboxylate, H$_2$cdCl$_2$salen*

Yield 98.0%. λ_{max}(dmf)/nm 314 ($\log\epsilon_{max}$ 4.08) and 397 (4.30); δ_H (200 MHz; $CDCl_3$) 1.83 (2 H, m), 2.58 (3 H, s), 2.63–2.79 (4 H, m), 3.75 (2 H, t), 3.88 (2 H, t), 7.17 (1 H, s) 7.41 (1 H, s), 8.33 (1 H, s, CH=N), 12.28 (1 H, br s, NH) and 13.85 (1 H, br s, OH) (Found: C, 49.6; H, 4.53; N, 7.34; S, 16.6; Cl, 18.4%. $C_{16}Cl_2H_{18}N_2OS_2$ requires C, 49.4; H, 4.66; N, 7.20; S, 16.5; Cl, 18.2%).

2.3.1.8. *Methyl-2-{N-[2-(2'-hydroxynaphthyl)methylidynenitrilo]ethyl}amino-1-cyclopentenedithiocarboxylate, H$_2$cdnapen*

Yield 71.0%. λ_{max}(dmf)/nm 313 ($\log\epsilon_{max}$ 4.27), 398 (4.37) and 429 (sh); δ_H (200 MHz; $CDCl_3$) 1.72 (2 H, m), 2.54 (3 H, s), 2.56–2.66 (4 H, m), 3.72–3.86 (4 H, m), 6.99 (1 H, d) 7.26 (1 H, t), 7.42 (1 H, t), 7.63–7.76 (2 H, m), 7.87 (1 H, d), 12.49 (1 H, br s, NH) and 14.56 (1 H, br s, OH) (Found: C, 64.2; H, 5.94; N, 7.51; S, 17.2%. $C_{20}H_{22}N_2OS_2$ requires C, 64.8; H, 5.98; N, 7.51; S, 17.3%).

2.3.1.9. *Methyl-2-{N-[2-(2'-hydroxynaphthyl)ethylidynenitrilo]ethyl}amino-1-cyclopentenedithiocarboxylate, H$_2$cdMenapen*

Yield 77.3%. λ_{max}(dmf)/nm 313 ($\log\epsilon_{max}$ 4.05), 338 (sh) and 400 (4.02); δ_H (200 MHz; $CDCl_3$) 1.76 (2 H, m), 2.56 (3 H, s), 2.60 (3 H, s), 2.68–2.78 (4 H, m), 3.80–3.85 (4 H, m), 7.01 (1 H, d) 7.26 (1 H, t), 7.40 (1 H, t), 7.60–7.69 (3 H, m) and 12.53 (1 H, br s, NH) (Found: C, 61.3; H, 6.38; N, 7.05; S, 16.4%. $C_{21}H_{24}N_2OS_2$ requires C, 65.6; H, 6.29; N, 7.28; S, 16.7%).

2.3.2. *General procedure for nickel(II) complexes*

To a solution of the appropriate ligand (0.1 mmol) in 10 cm^3 of chloroform/methanol 2:1 vol./vol., was added a solution of nickel acetate tetrahydrate (0.25 g, 0.1 mmol) in 10 cm^3 of methanol. The solution was stirred for 15 min and then allowed to stand at room temperature for 24 h. The resulting green or brown powder was recrystallized from acetonitrile/methanol 1:1 vol./vol.

2.3.2.1. *Nickel{methyl-2-{N-[2-(2'-phenolate)-methylidynenitrilo]ethyl}aminato(-1)-1-cyclopentenedithiocarboxylate, [Ni(cdsalen)]*

Yield 99.8%. δ_H (200 MHz; $CDCl_3$) 1.82 (2 H, m), 2.48 (2 H, t), 2.62 (2 H, t), 2.67 (3 H, s), 3.26 (2 H, t), 3.53 (2 H, t), 6.49 (1 H, t), 6.79 (1 H, d), 7.04–7.13 (2 H, m) and 7.68 (1 H, s, CH=N) (Found: C, 50.5; H, 5.47; N, 7.48%. $C_{16}H_{18}N_2OS_2Ni$ requires C, 51.0; H, 5.35; N, 7.43%).

2.3.2.2. Nickel{methyl-2-{N-[2-(2'-phenolate)ethylidynenitrilo]ethyl}aminato(-1)-1-cyclopentenedithiocarboxylate, [Ni(cdMesalen)]

Yield 41.8%. δ_H (200 MHz; $CDCl_3$) 1.84 (2 H, m), 2.44 (3 H, s), 2.49 (2 H, t), 2.62 (2 H, t), 2.68 (3 H, s), 3.22 (2 H, t), 3.55 (2 H, t), 6.52 (1 H, t), 6.85 (1 H, d), 7.10 (1 H, t) and 7.49 (1 H, d) (Found: C, 52.1; H, 5.01; N, 7.20%. $C_{17}H_{20}N_2OS_2Ni$ requires C, 52.2; H, 5.15; N, 7.16%).

2.3.2.3. Nickel{methyl-2-{N-[2-(3'-methoxy-2'-phenolate)methylidynenitrilo]ethyl}aminato(-1)-1-cyclopentenedithiocarboxylate, [Ni(cdMeOsalen)]

Yield 78.4%. δ_H (200 MHz; $CDCl_3$) 1.85 (2 H, m), 2.51 (2 H, t), 2.64 (2 H, t), 2.69 (3 H, s), 3.23 (2 H, t), 3.53 (2 H, t), 3.75 (3 H, s OCH_3), 6.44 (1 H, t), 6.65–6.78 (2 H, m) and 7.77 (1 H, s, CH=N) (Found: C, 49.9; H, 5.00; N, 6.74; S, 15.5%. $C_{17}H_{20}N_2O_2S_2Ni$ requires C, 50.2; H, 5.45; N, 6.88; S, 15.7%).

2.3.2.4. Nickel{methyl-2-{N-[2-(5'-methyl-2'-phenolate)ethylidynenitrilo]ethyl}aminato(-1)-1-cyclopentenedithiocarboxylate, [Ni(cdMe$_2$salen)]

Yield 63.8%. δ_H (200 MHz; $CDCl_3$) 1.81 (2 H, m), 2.20 (3 H, s), 2.40 (3 H, s), 2.45 (2 H, t), 2.61 (2 H, t), 2.67 (3 H, s), 3.23 (2 H, t), 3.56 (2 H, t), 6.73 (1 H, d), 6.92 (1 H, d) and 7.15 (1 H, s) (Found: C, 53.3; H, 5.47; N, 6.76; S, 15.6%. $C_{18}H_{22}N_2OS_2Ni$ requires C, 53.4; H, 5.97; N, 6.91; S, 15.8%).

2.3.2.5. Nickel{methyl-2-{N-[2-(4',6'-dimethoxy-2'-phenolate)methylidynenitrilo]ethyl}aminato(-1)-1-cyclopentenedithiocarboxylate, [Ni{cd(MeO)$_2$salen}]

Yield 62.8%. δ_H (200 MHz; $CDCl_3$) 1.84 (2 H, m), 2.51 (2 H, t), 2.64 (2 H, t), 2.68 (3 H, s), 3.20 (2 H, t), 3.47 (2 H, t), 3.71 (3 H, s, OCH_3), 3.76 (3 H, s, OCH_3), 5.61 (1 H, s), 5.96 (1 H, s) and 8.10 (1 H, s, CH=N) (Found: C, 49.4; H, 4.95; N, 6.28; S, 15.0%. $C_{18}H_{22}N_2O_3S_2Ni$ requires C, 49.5; H, 5.07; N, 6.41; S, 14.7%).

2.3.2.6. Nickel{methyl-2-{N-[2-(5'-methoxy-2'-phenolate)ethylidynenitrilo]ethyl}aminato(-1)-1-cyclopentenedithiocarboxylate, [Ni(cdMeMeOsalen)]

Yield 77.7%. δ_H (200 MHz; $CDCl_3$) 1.84 (2 H, m), 2.41 (3 H, s), 2.44 (2 H, t), 2.63 (2 H, t), 2.67 (3 H, s), 3.20 (2 H, t), 3.52 (2 H, t), 3.73 (3 H, s, OCH_3) and 6.80–6.86 (3 H, m) (Found: C, 50.9; H, 5.30; N, 6.46; S, 15.2%. $C_{18}H_{22}N_2O_2S_2Ni$ requires C, 51.3; H, 5.74; N, 6.65; S, 15.2%).

2.3.2.7. Nickel{methyl-2-{N-[2-(3',5'-dichloro-2'-phenolate)methylidynenitrilo]ethyl}aminato(-1)-1-cyclopentenedithiocarboxylate, [Ni(cdCl$_2$salen)]

Yield 98.0%. δ_H (300 MHz; $CDCl_3$) 1.84 (2 H, m), 2.55–2.69 (4 H, m), 2.63 (3 H, s), 3.33 (2 H, t), 3.67 (2 H, t), 7.40 (1 H, s), 7.43 (1 H, s) and 8.28 (1 H, s, CH=N) (Found: C, 42.9; H, 3.99; N, 6.15; S, 14.2%. $C_{16}H_{16}N_2OS_2Cl_2Ni$ requires C, 43.1; H, 4.07; N, 6.28; S, 14.4%).

2.3.2.8. Nickel{methyl-2-{N-[2-(2'-naphtholate)-methylidynenitrilo]ethyl}aminato(-1)-1-cyclopentene-dithiocarboxylate, [Ni(cdnapen)]

Yield 71.0%. δ_H (200 MHz; $CDCl_3$) 1.84 (2 H, m), 2.51 (2 H, t), 2.64 (2 H, t), 2.69 (3 H, s), 3.26 (2 H, t), 3.65 (2 H, t), 6.98 (1 H, d), 7.24 (1 H, t), 7.40 (1 H, t), 7.52–7.63 (2 H, m), 7.84 (1 H, d) and 8.57 (1 H, s, CH=N) (Found: C, 55.9; H, 5.68; N, 6.36; S, 15.3%. $C_{20}H_{20}N_2OS_2Ni$ requires C, 56.2; H, 5.98; N, 6.56; S, 15.0%).

2.3.2.9. Nickel{methyl-2-{N-[2-(2'-naphtholate)-ethylidynenitrilo]ethyl}aminato(-1)-1-cyclopentene-dithiocarboxylate, [Ni(cdMenapen)]

Yield 77.3%. δ_H (200 MHz; $CDCl_3$) 1.83 (2 H, m), 2.50 (2 H, t), 2.60 (3 H, s), 2.64 (2 H, t), 2.68 (3 H, s), 3.22 (2 H, t), 3.72 (2 H, t), 6.96 (1 H, d), 7.19 (1 H, t), 7.35 (1 H, t), 7.45–7.55 (2 H, m) and 7.62 (1 H, d) (Found: C, 56.7; H, 5.29; N, 6.19; S, 14.5%. $C_{21}H_{22}N_2OS_2Ni$ requires C, 57.2; H, 5.48; N, 6.35; S, 15.0%).

2.4. Chemical reduction of the nickel(II) complexes

Typically the chemical reduction of the nickel(II) complexes was performed by adding 5.0 g of sodium amalgam (1% w/w Na/Hg) to 10 cm^3 of solutions $\approx 1 \times 10^{-3}$ mol dm^{-3} of the desired nickel(II) complex in dmf, using strictly anaerobic conditions.

2.5. Crystallography

2.5.1. X-ray data collection and reduction

Green needles of [Ni(cdMeOsalen)].0.5(*p*-dioxane) were formed by slow evaporation of a *p*-dioxane/dichloromethane solution. The crystal-cell dimension determination and data collection were performed on a STOE-IPDS diffractometer, using Mo Kα radiation (λ = 0.71073 Å), at 293 K. A summary of crystal data, experimental details and refinement results are listed in Table 1.

2.6. Structure solution and refinement

The structure of [Ni(cdMeOsalen)].0.5(*p*-dioxane) was solved with SHELXS-86 [13] program by direct methods and the atomic positional and thermal parameters (anisotropic non-hydrogen atoms, except C18 and C19) were refined by full-matrix least-squares on F^2 with SHELXL-93 [14]. As the solvent molecule is disordered the atoms C18 and C19 were refined isotropically, and O3 was refined anisotropically. Hydrogen-atom positions were calculated by idealized positions, except for hydrogen bonded to C7, which was located from the difference Fourier map. Atomic scattering factors were from International Tables for X-ray Crys-

Table 1
Crystal data, data-collection and structure-refinement parameters of [Ni(cdMeOsalen)]·0.5 *p*-dioxane

Crystal shape	prismatic needle
Chemical formula	$C_{19}H_{24}N_2NiO_3S_2$
Formula weight	451.21
Crystal system	orthorhombic
Space group	$P2_12_12$
Unit-cell dimensions	
a (Å)	11.417(3)
b (Å)	13.883(4)
c (Å)	12.769(3)
α (°)	90
β (°)	90
γ (°)	90
Volume of unit cell (Å^3)	2023.9(9)
Z	4
Density (calc.) (g cm^{-3})	1.481
$F(000)$	944
Absorption coefficient (cm^{-1})	11.62
θ range for data collection (°)	5.01–28.27
Range of h, k, l	$-15 \rightarrow 13$, $-18 \rightarrow 18$, $-16 \rightarrow 16$
Reflections collected	14598
Independent reflections	4905 ($R_{int} = 0.0869$)
Data/restraints/parameters	4641/0/239
Goodness-of-fit on F^2 [b]	1.043
Final R indices [$I > 2\sigma(I)$] [a]	$R_1 = 0.0569$, $wR_2 = 0.1481$
R indices (all data)	$R_1 = 0.0767$, $wR_2 = 0.1823$
Absolute structure parameter	$-0.02(2)$
Extinction coefficient	0.046(6)
Largest diff. peak and hole (e Å^{-3})	0.586 and -0.701

[a] $R = (\Sigma \| F_o | - | F_c \|)/\Sigma | F_o |$; $wR = [(\Sigma w(F_o^2 - F_c^2)^2/(\Sigma F_o^2)^2]^{1/2}$.
[b] $[(\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$, n is the number of reflections and p the number of refined parameters.

tallography [15] and molecular graphics from SCHAKAL [16].

3. Results and discussion

Methyl-2-{*N*-(2′-aminoethane)}-amino-1-cyclopentene-dithiocarboxylate is a convenient starting material for the synthesis of asymmetric ligands containing N_2SO coordination spheres. Schiff base condensation of the methyl-dithiocarboxylate ester with several substituted salicylaldehydes yields the desired ligand in a facile manner and with high yields.

Nickel(II) complexes of the ligands depicted in Scheme 1 have been prepared and characterized by the usual methods: elemental analysis, NMR and absorption electronic spectroscopy in Nujol mulls and dmf solutions.

3.1. Molecular structure

The molecular structure of [Ni(cdMeOsalen)].0.5(*p*-dioxane) is shown in Fig. 1, in conjunction with the numbering scheme used. Relevant bond lengths, bond angles, deviations from best coordination plane and dihedral angles between ONiN and SNiN planes are given in Table 2. Full lists of bond lengths, bond angles and anisotropic displacement parameters are available as supplementary material.

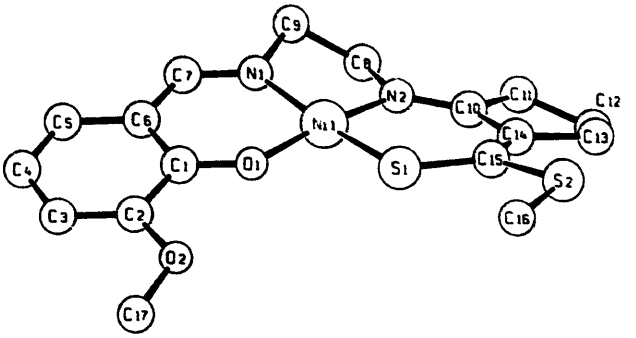

Fig. 1. Molecular structure of [Ni(cdMeOsalen)] showing the atom numbering scheme.

The compound crystallizes in the space group $P2_12_12$ (orthorhombic symmetry), with an asymmetric unit constituted by a molecule of complex and half molecule of *p*-dioxane. The complex has a N_2OS coordination sphere, with the two nitrogens coordinated in a *cis* configuration. The coordination around nickel is essentially square-planar with a small tetrahedral distortion (dihedral angle of 11.81° between coordination planes NNiO and NNiS). The ligand is not planar, adopting a distorted umbrella conformation, and the dimethylene bridge shows a δ-twisted conformation, with C8 and C9 displaced by 0.271 and −0.451 Å, respectively, from the least-squares NiN_2OS plane.

Bond lengths and bond angles of the present complex are similar to those reported for the related complexes [Ni(salen)] [17] and [Ni(cd$_2$en)] [18], with the only significant differences occurring in the metal–ligand distances: Ni–N and Ni–O bond lengths are 0.01–0.03 Å longer than in [Ni(salen)] and in [Ni(cd$_2$en)], while the Ni–S bond length is 0.015 Å shorter than in [Ni(cd$_2$en)]. A similar pattern was reported for the asymmetric complexes [Ni(cdsalen)] [19] and [Ni(cdnapen)] [20]. In addition, bond lengths and bond angles within the ligand are indicative of a strong delocalization of π-electron density in both NO and NS six-membered chelate rings, suggesting that the dithioester fragment behaves essentially as a Schiff base ligand, coordinating via an imine nitrogen and a thiolate sulphur.

Molecular structures of [Ni(cdsalen)] [19] and [Ni(cdnapen)] [20] have been determined and may be compared with the structure of [Ni(cdMeOsalen)]. Some selected structural parameters for the three related complexes are collected in Table 2. The most striking difference lies in the extent of tetrahedral distortion, which is more pronounced in the present complex than in the other two, which have an almost planar structure. Bond lengths and bond angles are almost independent of the different NO fragments, although the Ni–S bond length is slightly longer in [Ni(cdsalen)].

3.2. Electronic spectra

The electronic spectra of the nickel(II) complexes in Nujol mulls and in dmf are similar and show one broad low-energy

Table 2
Selected bond lengths (Å) and bond angles (°) for [Ni(cdsalen)], [Ni(cdMeOsalen)] and [Ni(cdnapen)] [a]

Complex	[Ni(cdsalen)]	[Ni(cdMeOsalen)]	[Ni(cdnapen)](A)	[Ni(cdnapen)](B)
Ni1–O1	1.860(4)	1.863(3)	1.853(2)	1.851(2)
Ni1–N2	1.867(5)	1.867(4)	1.863(3)	1.864(3)
Ni1–N1	1.872(5)	1.871(3)	1.856(3)	1.859(3)
Ni1–S1	2.163(3)	2.1552(12)	2.156(2)	2.154(2)
S1–C15	1.725(6)	1.709(5)	1.707(4)	1.709(4)
O1–C1	1.311(7)	1.297(5)	1.308(4)	1.298(4)
N1–C7	1.295(7)	1.289(6)	1.298(4)	1.303(4)
N2–C10	1.313(7)	1.294(6)	1.313(4)	1.315(4)
Bond angles				
O1–Ni1–N1	94.0(2)	93.1(2)	92.7(2)	92.5(1)
N2–Ni1–N1	86.3(2)	87.1(2)	87.2(1)	87.4(1)
O1–Ni1–S1	81.9(2)	83.23(10)	82.29(8)	82.49(8)
N2–Ni1–S1	98.0(2)	97.86(11)	97.8(1)	97.6(1)
O1–Ni1–N2	178.1(2)	172.6(2)	179.6(1)	179.4(1)
N1–Ni1–S1	174.09(14)	169.32(13)	175.00(9)	174.98(9)
Dihedral angle between O1–Ni1–N1 and S1–Ni1–N2 planes				
α	4.40(17)	11.81(6)	4.71(40)	5.18(17)
Deviations from least-squares Ni–N1–N2–O1–S1 coordination plane				
Ni1	0.021(2)	0.025(2)	−0.0027(4)	−0.0032(4)
N1	−0.055(2)	−0.156(2)	−0.0056(27)	−0.0064(29)
N2	0.049(2)	0.139(2)	0.0049(27)	0.0057(28)
O1	0.054(2)	0.152(2)	0.0054(25)	0.0063(26)
S1	−0.048(2)	−0.135(2)	−0.0048(11)	−0.0055(11)
C8	−0.258(8)	0.271(6)		
C9	0.249(8)	−0.451(7)		

[a] Parameters for [Ni(cdsalen)] and [Ni(cdnapen)] obtained respectively from Refs. [19] and [20]. [Ni(cdnapen)] contains two crystallographic independent molecules, here referred to as molecules A and B.

Table 3
Band maxima of the UV/Vis/NIR spectra of the nickel(II) complexes [a]

Complex	λ/nm (ϵ/mol^{-1} dm^3 cm^{-1})	
	dmf	Nujol
[Ni(cdsalen)]	407.7 (3.87×10^3); 428.1 (2.58×10^3); 461.4 (2.34×10^3); 606.8 (101)	434.8; 486.8; 621.9
[Ni(cdMesalen)]	409.0 (3.02×10^3); 428.1 (1.85×10^3); 469.5 (9.24×10^2); 606.1(125)	435.9; 483.6; 612.7
[Ni(cdMeOsalen)]	416.5 (3.75×10^3); 430.5 (2.06×10^3); 466.9 (8.43×10^2); 613.9 (97)	433.3; 473.5; 628.1
[Ni(cdMe$_2$salen)]	417.9 (3.59×10^3); 431.8 (1.80×10^3); 469.0 (6.73×10^2); 607.9 (161)	407.2; 442.5; 612
[Ni(cd(MeO)$_2$salen)]	379.5 (2.40×10^3); 419.1 (4.52×10^3); 473.0 (1.41×10^3); 601.3 (110)	431.6; 454.5; 475.0; 597.7
[Ni(cdMeMeOsalen)]	413.2 (3.46×10^3); 436.9 (2.75×10^3); 466.0 (2.48×10^3); 615.0 (183)	419.3; 448.8; 483.1; 621.5
[Ni(cdCl$_2$salen)]	405.5 (3.38×10^3); 428.4 (1.97×10^3); 466.0 (2.82×10^3); 609.8 (104)	451 [b]; 480 [b]; 511 [b]; 607.5
[Ni(cdnapen)]	418.2 (4.35×10^3); 434.4 (3.12×10^3); 465.8 (2.01×10^3); 603.9 (147)	441.1; 481 [b]; 509 [b]; 613.1
[Ni(cdMenapen)]	400.3 (4.06×10^3); 427.7 (4.06×10^3); 456.2 (3.04×10^3); 599.2 (293)	411.2; 438.6; 471.5; 589.6
[Ni(cd$_2$en)] [c]	420 (4.50×10^3); 442 (6.50×10^3); 478 (4.00×10^3); 658 (130)	452.5; 641
[Ni(salen)] [d]	390 (4.56×10^3); 405 (7.17×10^3); 440 (3.86×10^3); 540 (230)	370; 410; 430; 540

[a] Molar extinction coefficients are shown in brackets, in mol^{-1} dm^3 cm^{-1}.
[b] Inflection.
[c] Obtained from Ref. [9].
[d] Obtained from Ref. [8].

band at $\lambda\approx$ 599–615 nm, followed by several high-intensity bands at higher energy. Band maxima and calculated extinction coefficients are presented in Table 3.

The low-energy band is typical of d–d transitions in square-planar nickel(II) complexes with mixed coordination spheres containing nitrogen and sulphur atoms [21], suggesting that all the nickel(II) complexes studied remain approximately square-planar, even in strong donor solvents. This is in accordance with the ^{1}H NMR spectra obtained in d_7-dmf, CD_3CN and $CDCl_3$, which show that the complexes are diamagnetic in these solvents; only minor differences between the spectra of the complexes and of the free proligands are observed. Consequently, coordination of solvent molecules is very weak or non-existent.

The three bands observed in the region 470–400 nm are probably due to S–Ni and O–Ni LMCT transitions, and occur at energies similar to those found for the corresponding symmetric nickel(II) complexes [Ni(cd$_2$en)] [9] and [Ni(salen)] [8] (Table 3).

Analysis of the results presented in Table 3 shows that the positions of the d–d and LMCT bands are not very sensitive to the different substituents of the ligand, and may not be directly related to the electron donor/acceptor ability of the substituent. This behaviour has been observed for square-planar copper(II) complexes and was explained by the possible existence of both electronic and structural effects induced by the substituents, which may have opposite effects [22]. Comparison of the molecular structure of [Ni(cdsalen)] [19], and [Ni(cdMeOsalen)] shows that, for the asymmetrical complexes reported here, introduction of substituents in the phenolate ring may induce different tetrahedral distortions, which may be opposite to the electronic substituent effect. Consequently, and in the absence of structural data for all the complexes, it is not possible to rationalize the small differences in band position for all the nickel(II) complexes studied.

3.3. Cyclic voltammetry

The voltammetric behaviour of the nickel(II) complexes and the parent ligands was studied in dmf solutions in the potential range +1.4 to −2.1 V and selected results are summarized in Table 4.

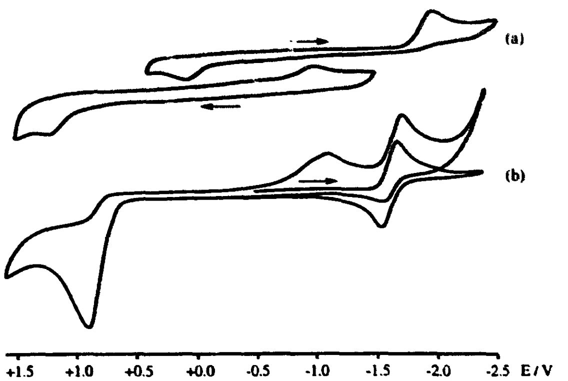

Fig. 2. Cyclic voltammograms of the following solutions: (a) 1 mM H_2cdsalen and 0.1 M TBAP in dmf; (b) 1 mM [Ni(cdsalen)] and 0.1 M TBAP in dmf; employing a scan rate of 200 mV s^{-1} at a platinum electrode vs. Ag/AgCl reference electrode.

3.3.1. Ligands

A typical voltammogram of the ligands studied is presented in Fig. 2. At potentials ranging from +0.98 to +1.24 V one anodic wave is observed (wave I), corresponding to a totally irreversible charge transfer. Coupled with this anodic wave, one cathodic wave of lower intensity at potentials −1.1 to −1.2 V (wave II) is seen in the reverse scan, except for H_2cdCl$_2$salen which shows two coupled cathodic waves at −0.6 and at −1.6 V. Multiple scanning in the potential range +1.4 to −1.8 V shows that the voltammetric waves are not repeatable, and that current intensities decrease in subsequent cycles. This behaviour is also found in several mercaptans, and has been attributed to the oxidation of the thiol group to the corresponding disulphide, for which the peak at −1.1 V has been ascribed to the reduction of the disulphide to the corresponding thiolate [23]. The decrease in current intensity may be explained by a slow decomposition reaction involving the disulphide species, yielding a solid product that deposits at the electrode surface, as is detected by electrode fouling at the end of the voltammetric experiments.

Cyclic voltammograms obtained in the potential range +0.2 to −2.1 V show one ill-defined cathodic wave at approximately −2.0 V, except for H_2cdnapen and H_2cdMenapen, the voltammograms of which show two con-

Table 4
Voltammetric parameters obtained for the nickel(II) complexes [a]

Complex	E_{pa}(I)	E_{pc}(II)	E_{pc}(III)	E_{pc}(IV)	E_{pa}(IV)	$E_{1/2}$(IV)	ΔE(IV)	i_{pa}/i_{pc}(IV)
[Ni(cdsalen)]	+0.87	−0.94	−1.08	−1.693	−1.605	−1.649	0.088	0.98
[NI(cdMesalen)]	+0.88	−0.92	−1.04	−1.691	−1.613	−1.652	0.078	0.97
[Ni(cdMeOsalen)]	+0.92	−0.50	−1.14	−1.600	−1.515	−1.558	0.085	0.90
[Ni(cdMe$_2$salen)]	+0.82	−0.58/−0.84	−1.24	−1.715	−1.630	−1.672	0.085	0.95
[Ni{cd(MeO)$_2$salen}]	+0.88	−0.86	−1.02	−1.670	−1.580	−1.625	0.090	0.89
[Ni(cdMeMeOsalen)]	+0.81	−0.85	−1.18	−1.706	−1.621	−1.664	0.085	0.95
[Ni(cdCl$_2$salen)]	+0.94	−0.87	−1.22	−1.480	−1.390	−1.435	0.090	0.77
[Ni(cdnapen)]	+0.97	−0.95	−1.35	−1.643	−1.556	−1.600	0.087	0.98
[Ni(cdMenapen)]	+0.90	−0.95	−1.25	−1.663	−1.573	−1.618	0.090	0.94
[Ni(cd$_2$en)]	+0.78			−1.604	−1.524	−1.564	0.080	0.94

[a] Potentials reported in V, relative to Ag/AgCl (1 mol dm^{-3} NaCl) reference electrode and corrected to the Fc^+/Fc couple ($E_{1/2}$ = 0.485 V); $E_{1/2}$ was taken as $(E_{pc}+E_{pa})/2$; i_{pa}; i_{pc} values were baseline corrected.

secutive cathodic waves. In the reverse scan one anodic wave at ≈0.0 V is observed, with a current intensity of approximately 20% of that of the cathodic peak, with the exception of $H_2cd(MeO)_2salen$, $H_2cdMeMeOsalen$ and H_2cdCl_2salen, for which no anodic wave is detected. Cyclic voltammograms obtained for H_2cd_2en and other related ligands containing the methyl-2-aminocyclopentenedithiocarboxylate fragment show a reduction behaviour similar to the present ligands (see supplementary material), in contrast to H_2salen and substituted derivatives, which do not show any reduction wave before solvent discharge. Thus, the cathodic wave observed may be assigned to the reduction of the methyl-2-aminocyclopentenedithiocarboxylate fragment.

3.3.2. Nickel(II) complexes

The oxidation behaviour is similar to that observed for the ligands, but with E_{pa} values 0.2 to 0.4 V more negative than for the corresponding free ligands (Fig. 2). Similarly, after several voltammetric cycles a solid product is deposited at the surface of the electrode. This observation suggests that the oxidation of these nickel(II) complexes is a ligand-based process that leads to decomposition of the complex. The same type of electrochemical behaviour was observed for [Ni(cd₂en)] [9], but is in contrast to the behaviour of nickel(II) complexes with Schiff bases derived from salicylaldehyde and naphthaldehyde, which show a reversible one-electron oxidation process with the formation of nickel(III) complexes [8,24].

The cyclic voltammograms obtained in the potential range 0.0 to −2.1 V are indicative of a reversible heterogeneous electron transfer occurring at potentials in the range −1.44 to −1.67 V (Fig. 2). The cathodic–anodic peak separation is comparable to that observed for the Fc^+/Fc couple under the same experimental conditions. Study of the dependence of the voltammetric parameters with scan rate in the interval 10–500 mV s^{-1} shows: (a) a linear relationship of $i_{pa,pc}$ with $v^{1/2}$, and (b) a small dependence of $E_{pc,pa}$ with scan rate ($E_{pa,pc}$ is proportional to $i_{pa,pc}$) that may be attributed solely to ohmic potential drop due to the high resistance of the solvent used. The ratios i_{pa}/i_{pc} are close to unity, except for $[Ni(cdCl_2salpd)]$, which exhibits i_{pa}/i_{pc} ratios always less than 0.8. This latter behaviour may be explained by additional errors involved in the determination of anodic peak currents, due to the proximity of the cathodic wave associated with ligand reduction. EPR spectra of the electrochemically reduced solutions show that the redox process corresponds in all cases to a Ni^{II}/Ni^{I} conversion (see Section 3.4).

Cyclic voltammograms of [Ni(salen)] and $[Ni(cd_2en)]$ solutions in dmf/TBAP 0.1 mol dm^{-3} were also recorded in the interval 0.0 to −2.1 V and for both complexes a reversible redox process is observed with $E_{1/2}$ values of −1.70 and −1.56 V, respectively, in agreement with previously reported values [9,25].

Our data suggest that there are three factors that contribute to the accessibility of the +1 oxidation state for nickel. First, substitution of phenolate by softer thiolate donors results in a decrease of $E_{1/2}$ values of ≈0.07 V. Secondly, introduction of electron-acceptor substituents also results in more positive $E_{1/2}$ values for the Ni^{II}/Ni^{I} process. This effect is even more pronounced than the observed stabilization of the nickel(I) complexes when the oxygen donor is replaced by a sulphur in the coordination sphere of the complex. As an example, $E_{1/2}$ for $[Ni(cdCl_2salen)]$ is 0.21 V more positive than for [Ni(cdsalen)]. Finally, an increase of the aromatic character of the ligand also results in a relative stabilization of the +1 oxidation state of nickel, but this effect is less important as can be seen by noting that substitution of the phenolate ring by a naphtholate ring {[Ni(cdRsalen)] versus [Ni(cdRnapen)]} only increases the $E_{1/2}$ value by ≈0.05 V.

3.4. EPR of electrochemically and chemically reduced solutions of the nickel(II) complexes

Electrochemical reduction of nickel(II) complexes in dmf was followed by coulometry, under strictly anaerobic conditions and using previously dried solvents. Total charge at the end of the electrolysis corresponds, in all cases, to one-electron reductions of the nickel(II) complexes. During electrolysis, the solutions turn from light green to dark green or blue, and the new solutions exhibit a broad EPR signal, at room temperature, with $g_{iso} \approx 2.12$, thus confirming that the reduction occurs at the metal centre (Fig. 3). Chemical reduction using Na/Hg amalgam yields solutions with identical EPR spectra.

Frozen-solution EPR spectra exhibit a rhombic signal (Table 5, Fig. 3), with $g_1 \gg g_2 \approx g_3$, typical of nickel(I) complexes with a $d_{x^2-y^2}$ or a d_{xy} ground state [26–30]. In the high-field region of the spectra, hyperfine coupling with two magnetically equivalent nitrogen nuclei (^{14}N, $I=1$) is observed, in accordance with the similarity between the two nitrogen donor atoms revealed in the molecular structures of these complexes [19,20].

EPR spectra of the nickel(I) complexes show a significant dependence of the g values with the coordination sphere of the ligand, with a reduction of g values with increasing number of sulphur atoms in the coordination sphere of the complexes, but are almost independent of the substituents of the ligand.

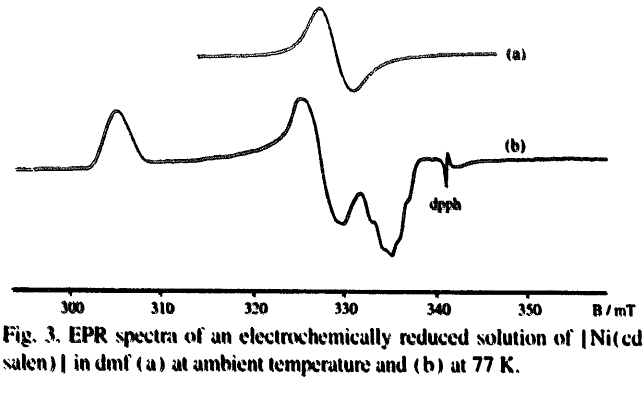

Fig. 3. EPR spectra of an electrochemically reduced solution of [Ni(cdsalen)] in dmf (a) at ambient temperature and (b) at 77 K.

Table 5
Experimental EPR parameters for the nickel(I) complexes [a]

Complex	g_1	g_2	g_3	g_{iso}/g_{med}	$A_2(N)$	$A_3(N)$
[Ni(cdsalen)]	2.238	2.086	2.041	2.122	9.5	10.2
[NI(cdMesalen)]	2.243	2.081	2.042	2.122	8.0	9.8
[Ni(cdMeOsalen)]	2.237	2.087	2.044	2.123		11.5
[Ni(cdMe$_2$salen)]	2.244	2.080	2.043	2.122	9.0	9.3
[Ni{cd(MeO)$_2$salen}]	2.238	2.086	2.043	2.122		11.5
[Ni(cdMeMeOsalen)]	2.243	2.081	2.042	2.122	9.0	9.3
[Ni(cdCl$_2$salen)]	2.240	2.088	2.041	2.123	9.0	9.9
[Ni(cdnapen)]	2.238	2.085	2.040	2.121	9.5	9.8
[Ni(cdMenapen)]	2.235	2.079	2.042	2.119		8.0
[Ni(cd$_2$en)]	2.208	2.070	2.046	2.108		7.0
[Ni(salen)] [b]	2.250	2.081	2.040	2.124		

[a] Hyperfine coupling constants in 10^{-4} cm^{-1}.
[b] Values from Ref. [25].

4. Conclusions

The nickel(II) complexes synthesized in this work were shown to have a mixed donor N_2OS coordination sphere with an approximate square-planar geometry. Cyclic voltammetric studies revealed that in the potential range studied the nickel(II) complexes may be oxidized and reduced, but while the reduction process occurs at the metal centre and yields nickel(I) complexes, the oxidation is probably ligand based.

Spectroscopic characterization of the complexes in solid and in solution shows that the structure of the complexes remains essentially unaltered, even in strong coordinating solvents. Another aspect to be stressed is the relative insensitivity of the spectroscopic characteristics of both nickel(II) and nickel(I) complexes to substituents on the salicylate fragments, in contrast to what is observed for the reduction potentials. Since the spectroscopic properties of the metal complexes are expected to be highly dependent on the energy of the metal orbital involved in σ-interaction with the ligands, these results imply that the dependence of reduction potentials on substituents is related either to the π-acceptor ability of the ligand and/or to a tetrahedral distortion of the nickel(II) complex. Comparing X-ray diffraction and voltammetric results for the present complexes, it is apparent that both factors must be important in the stabilization of the +1 oxidation state for nickel: (a) [Ni(cdsalen)] and [Ni(cdnapen)] show similar tetrahedral distortions, but the latter is reduced at more positive potentials, as expected from its higher π acceptor ability; (b) [Ni(cdMeOsalen)], which has a more pronounced tetrahedral distortion than [Ni(cdsalen)], is more easily reduced, although the electron-donor ability of the substituent would have predicted a more negative reduction potential for the former complex.

Voltammetric data suggest that the replacement of oxygen by sulphur atoms stabilizes the +1 oxidation state for nickel. For the three non-substituted complexes [Ni(salen)], [Ni(cdsalen)] and [Ni(cd$_2$en)] there is an increase of ≈0.07 V in $E_{1/2}$ for the reduction process by each oxygen that is replaced by a sulphur in the coordination sphere. Although it is currently accepted that thiolate ligands stabilize high oxidation states for metal ions, low oxidation states are expected to be unstabilized by this kind of ligand [31,32]. Nevertheless, in ligands like those we report here and that exhibit a strong π delocalization, it is possible that sulphur may act as a strong donor towards metal ions in high oxidation states, and as a π-acceptor towards metal ions in low oxidation states.

5. Supplementary material

Lists of observed and calculated structure factors, complete bond distances and angles, anisotropic thermal parameters for the non-hydrogen atoms, hydrogen atoms parameters and cyclic voltammetry data for the ligands are available from the authors on request.

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