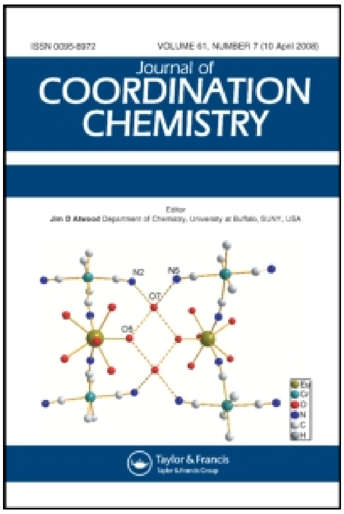

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# SYNTHESIS, SPECTROSCOPIC AND ELECTROCHEMICAL CHARACTERISATION OF NICKEL COMPLEXES WITH TWO $N_2O$ TRIDENTATE, UNSYMMETRICAL SCHIFF BASE LIGANDS

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# SYNTHESIS, SPECTROSCOPIC AND ELECTROCHEMICAL CHARACTERISATION OF NICKEL COMPLEXES WITH TWO $N_2O$ TRIDENTATE, UNSYMMETRICAL SCHIFF BASE LIGANDS

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*(Received 21 June 2000)*

Three nickel(II) complexes of general formula $NiL_2$, where L is a unsymmetrical $N_2O$ ligand prepared by Schiff condensation of propane-1,3-diamine with salicylaldehyde (Hslp), 3-methoxysalicylaldehyde (Hmslp) or 2-hydroxy-1-naphthaldehyde (Hnlp) have been prepared. Characterisation of nickel complexes by spectroscopic methods indicates that they are six-coordinate with the amine group bound to the nickel centre. The accessibility of the +3 and +1 oxidation states for the complexes was evaluated by coupling electrochemical techniques and EPR spectroscopy.

*Keywords*: Nickel complexes; Unsymmetrical Schiff bases; EPR; Cyclic voltammetry

## INTRODUCTION

We have been interested in the redox chemistry of nickel and copper Schiff base complexes with different ligand substituents, and in the effect of these substituents in the accessibility to the +3 and +1 oxidation states for the complexes [1–7]. The rapidly emerging field of hetero-binucleating ligands and the coordination chemistry of the heteronuclear complexes derived from such ligands [8–11], has prompted an extension of our work to study redox

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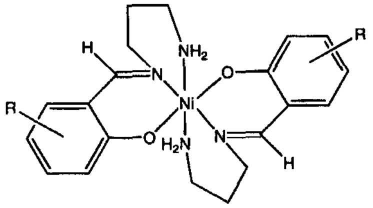
*Corresponding author.

properties in transition metal complexes with ligands that present coordination sites for more than one metal. We are pursuing the synthesis of metal complexes with Schiff bases bearing reactive groups in order to link with other groups that can act as coordination sites to hard metals, and are particularly interested in the functionalisation of Schiff bases complexes with crown ether derivatives, as these groups have a large affinity for alkaline and alkaline-earth metal ions [12, 13]. The interaction of hard cations with transition metal centres when mediated by hetero-binucleating ligands can be studied by using redox and electronic properties of the transition metal ions, and these complexes can ultimately be used as electrochemical sensors for alkaline and alkaline-earth metal ions.

We have already grafted dibenzo 18-crown-6- and benzo-15-crown-5-ether onto tetradentate $N_2O_2$ Schiff base ligands. These ligands were prepared by Schiff condensation of an aldehyde with a tetraamino derivative of dibenzo-18-crown-6 and with a diamino derivative of benzo-15-crown-5, and have the crown ether moiety grafted in a rigid skeleton [14, 15]. We are now pursuing the synthesis of Schiff base ligands functionalised with the same motif, but including the crown ether moiety as flexible appended arms.

In this work we report the synthesis of nickel(II) complexes of the general formulae $NiL_2$, where L is a $N_2O$ tridentate ligand obtained by Schiff condensation of propane-1,3-diamine with salicylaldehyde (Hslp), methoxy-salicylaldehyde (Hmslp) or 2-hydroxy-1-naphthaldehyde (Hnlp) (Scheme 1). These nickel complexes have amine groups that will enable the reacting with formyl crown-ether derivatives to yield Schiff base nickel complexes with two crown ether moieties as appended arms.



| | | |
|---|---|---|
| I | R=H | $[Ni(slp)_2]$ |
| II | R=3-OCH$_3$ | $[Ni(mslp)_2]$ |
| III | R=$C_6H_6$ | $[Ni(nlp)_2]$ |

SCHEME 1

## EXPERIMENTAL SECTION

### Reagents and Solvents

All solvents and reagents were used as received. Solvents for syntheses were of reagent grade and those for electrochemical measurements of analytical grade. Propane-1,3-diamine, salicylaldehyde and nickel(II) acetate tetrahydrate were from Merck, and 2-hydroxy-1-naphthaldehyde and 3-methoxysalicylaldehyde from Aldrich.

### Physical Measurements

Mass spectra (FAB) were performed at the Department of Chemistry, University of Leicester (UK), and elemental analysis (C, H, N) at the Departamento de Química, Universidade de Aveiro (Portugal).

Infrared spectra (KBr pellets) were recorded in the range 400–4000 $cm^{-1}$ using a Biorad FTS 155 spectrometer. Diffuse reflectance spectra of powder samples were registered on a Shimadzu UV-3101 PC spectrophotometer, in the range 1600–200 nm and using $BaSO_4$ as reference. Room temperature electronic spectra (1100–350 nm) of the Ni(II) complexes in DMF were recorded with a Unicam UV 2 spectrophotometer, using standard 1 cm-quartz cells; complex concentrations used were $1 \times 10^{-3}$ mol $dm^{-3}$ and $1 \times 10^{-5}$ mol $dm^{-3}$. EPR spectra were obtained at 120 K with a Bruker ESP 300 spectrometer (X-band); the magnetic field was calibrated by using $Mn^{2+}$ in MgO, and diphenylpicrylhydrazyl was used as internal reference (dpph; $g = 2.0037$).

Cyclic voltammetry of the nickel(II) complexes ($1 \times 10^{-3}$ mol $dm^{-3}$) was performed in DMF using an Autolab PGSTAT20 potentiostat/galvanostat. The electrochemical cell was a closed standard three-electrode cell connected to a solution reservoir through a teflon tube. A Pt disk electrode with an area of 0.0314 $cm^2$ was used as the working electrode, a Pt gauze electrode as the counter electrode and a Ag/AgCl (1 mol $dm^{-3}$ NaCl) as the reference electrode. The ferrocene/ferrocinium redox couple was used as internal standard; under the experimental conditions used, $E_{1/2}$ for $Fc/Fc^+$ couple was 0.48 V in DMF. Prior to use, the Pt working electrode was polished with an aqueous suspension of 0.05 µm alumina (Beuhler) on a Master-Tex (Beuhler) polishing pad, then rinsed with water and acetone and dried in an oven. All solutions were de-aerated and delivered to the cell by a stream of argon. In the cyclic voltammetry experiments, scan rates in the interval 0.1 to 2 $V s^{-1}$ were used and the potential limits were −2.0 and 1.3 V.

Electrolysis were carried out at a controlled potential in a three electrode cell, using a Pt gauze as the working electrode, a Pt foil as counter electrode and a Ag/AgCl (1 mol dm$^{-3}$ NaCl) as reference electrode.

## Synthesis of the Nickel Complexes

### *Bis[o-[N-(3-aminopropylformimidoyil]phenolate-O,N,N]nickel, [Ni(slp)$_2$] (I)*

The synthesis has been reported by Elder [16]; the complex was obtained by addition of nickel acetate tetrahydrate (5.00 g; 0.020 mol) to the condensation product of salicylaldehyde (5.30 g; 0.043 mol) and propane-1,3-diamine (17.70 g; 0.24 mol) in ethanolic solution. Yield 6.71 g (81.2%).

*Anal.* Found(%): C, 55.8; H, 7.6; N, 12.1. Calc. for $NiC_{20}H_{26}N_4O_2 \cdot H_2O \cdot C_2H_5OH$: C, 55.4; H, 7.2; N, 11.7; *m/z* 647 (18.1%), 470 (5.9), 413 ($M^+$ +H, 38.5), 307 (3.3), 235 (100), 205 (6.7), 179 (20.7), 154 (26.7).

IR (KBr) ($\nu$/cm$^{-1}$): 3439(b), 3335, 3262, 2909, 1640, 1594, 1538, 1474, 1446, 1391, 1331, 1307, 1238, 1197, 1141, 1086, 1021, 971, 934, 892, 846, 758, 735, 638, 583, 500, 440.

### *Bis[o-[N-(3-aminopropylformimidoyil]-6-methoxyphenolate-O,N,N]nickel, [Ni(mslp)$_2$] (II)*

The compound was prepared using the procedure described for (I), but using 3-methoxysalicylaldehyde (6.10 g; 0.040 mol), propane-1,3-diamine (17.6 g; 0.24 mol) and nickel acetate tetrahydrate (4.99 g; 0.020 mol). The resulting yellow-brown compound was re-crystallised from acetonitrile and dried under vacuum; yield 5.57 g (58.9%).

*Anal.* Found(%): C, 54.5; H, 6.5; N, 11.7. Calc. for $NiC_{22}H_{30}N_4O_4 \cdot 1/2H_2O$: C, 54.6; H, 6.5; N, 11.6; *m/z*: 737 (16.3%), 530 (4.1), 473 ($M^+$ + H, 50.7), 421 (1.1), 307 (4.4), 265 (100), 208 (17.8), 154 (25.2).

IR(KBr) ($\nu$/cm$^{-1}$): 3466(b), 3307, 3240, 3172, 2931, 2845, 1636, 1598, 1541, 1476, 1442, 1398, 1333, 1233, 1221, 1169, 1139, 1083, 1061, 1022, 987, 953, 728, 619, 593, 537.

### *Bis[o-[N-(3-aminopropylformimidoyil]naphtholate-O,N,N]nickel, [Ni(nlp)$_2$] (III)*

This complex was prepared by a modification of that referred to above. A warmed ethanolic solution of 2-hydroxy-1-naphthaldehyde (6.90 g;

0.040 mol) was added drop-wise during 2.5 h to a stirred solution of propane-1,3-diamine (17.7 g; 0.24 mol) in ethanol (ca. 60°C); after the addition was complete, nickel(II) acetate tetrahydrate (4.99 g; 0.020 mol) was added to the mixture. The resulting mixture was refluxed and after 2 h water (20 $cm^3$) was added. The resulting brown-yellow solid was taken up in ethanol (ca. 100 $cm^3$), the suspension was refluxed for 2 h, and the solids were then collected by filtration and washed with ethanol and diethyl ether. The compound was re-crystallised from *N*,*N*-dimethylformamide, washed with methanol and dried under vacuum; yield 6.50 g (63.3%).

*Anal.* Found(%): C, 61.3; H, 6.7; N, 11.3. Calc. for $NiC_{28}H_{30}N_4O_2 \cdot H_2O \cdot$ dmf: C, 61.6; H, 6.5; N, 11.6; *m*/*z*: 797 (10.0%), 570 (3.7), 513 ($M^+$ +H, 25.2), 359 (6.3), 285 (100), 229 (25.2), 184 (4.8), 154 (16.3).

IR(KBr) ($\nu/cm^{-1}$): 3345, 3276, 2905, 1622, 1589, 1543, 1506, 1460, 1432, 1409, 1386, 1344, 1307, 1257, 1243, 1183, 1141, 1091, 1058, 1021, 984, 955, 887, 832, 744, 647, 578, 523, 500, 458.

### Oxidation/Reduction of Nickel(II) Complexes

Chemical oxidation of the complexes was performed by addition of a 20% molar excess of iodine to a solution of the complexes in DMF. Reduction was also performed in DMF using excess of 5% Na(Hg) amalgam. All manipulations of the oxidised and reduced solutions were made under anaerobic conditions, and the resulting oxidised/reduced solutions were transferred to EPR tubes and frozen in liquid nitrogen.

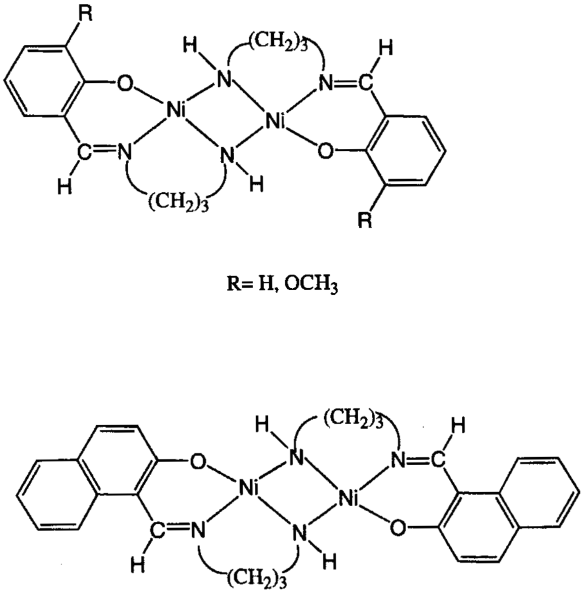
## RESULTS AND DISCUSSION

Metal complexes were prepared by template synthesis using the method of Elder [16], as the ligands could not be isolated due to purification difficulties. To prevent formation of the symmetric ligand during Schiff condensation, a large excess of diamine has to be used, and thus at the end of the reaction it is difficult to isolate the $N_2O$ Schiff base in high purity. We have also tried to isolate the ligands by removing the nickel atom from the prepared complexes using dimethylglioxime, but with no success. After removal of red nickel dimethylglyoxime complexes, yellow solids were obtained that were shown by $^1H$ NMR to be the symmetrical ligands. These results indicate that in solution and in the absence of excess diamine, the unsymmetrical ligands exist in equilibrium with the parent aldehyde and diamine, which can combine *via* a new path and form the symmetrical ligand.

## Mass Spectra

The mass spectrum of [Ni(slp)$_2$] is similar to that reported in the literature [16], and shows the peak of the complex molecular ion (MH$^+$) at *m*/*z* 413, and a peak at *m*/*z* 470 that corresponds to binuclear complex [Ni$_2$(slp)$_2$]$^+$, formed from two fragments of [Ni(slp)$_2$] (Scheme 2). Two peaks at *m*/*z* 179 and 235 are also observed and that correspond to [Ni(slp)]$^+$ and (H$_2$slp)$^+$. The latter fragment corresponds to the protonated ligand and is an indication that the asymmetric N$_2$O ligand has been prepared and is bound to nickel.

The other complexes show fragments with *m*/*z* values that correspond to similar type of fragments observed for [Ni(slp)$_2$], what suggest that all three complexes have similar structures in which nickel is bound to the N$_2$O asymmetric ligands. The mass spectrum of [Ni(mslp)$_2$] exhibits peaks at *m*/*z* 473, 265 and 209 which correspond to (MH$^+$), [Ni(mslp)]$^+$ and (H$_2$mslp)$^+$, respectively; the spectrum also shows a less intense peak at *m*/*z* 530 corresponding to binuclear species [Ni$_2$(mslp)$_2$]$^+$. Similarly, the mass spectrum of [Ni(nlp)$_2$] shows the peak at 513 associated with (MH$^+$), and other peaks at 570, 285 and 229 corresponding to binuclear species [Ni$_2$(nlp)$_2$]$^+$, to [Ni(nlp)]$^+$ and the protonated ligand (H$_2$nlp)$^+$, respectively (Scheme 2).



R= H, OCH$_3$

SCHEME 2

## Infrared Spectra

The spectra of the three complexes in the region 4000–1600 cm$^{-1}$ are similar and all show two very sharp bands in the region 3350–3240 cm$^{-1}$ due to symmetric and anti-symmetric stretching of $-NH_2$. The observation of two sharp bands suggests binding of the terminal amino groups to nickel, and is an indication that the ligands act as tridentate and that the complexes are six-coordinate [16, 17]. This result is important as these complexes could be four-coordinate with the amine groups not bound to the metal, as has been observed for nickel complexes with similar ligands but with substituents in the amine nitrogen atoms [18, 19].

The bands at 1640 cm$^{-1}$ (I), 1636 cm$^{-1}$ (II) and 1622 cm$^{-1}$ (III) are assigned to the C=N stretch, and the observed values correlate with the increasing reduced mass of the complexes. Group vibration patterns below 1600 cm$^{-1}$ show different for each complex due to the different substituents in the aldehyde moiety.

## Electronic Spectra

Powder reflectance spectra are very similar and show one low intense broad band in the near-infrared with shoulders in the low and high frequency regions, and two more shoulders in the high intensity charge transfer bands that extend into the UV region (Fig. 1). The observation of low intense *d–d* bands at $\lambda > 500$ nm clearly indicates that the complexes are six-coordinate [18–20], and confirms that amine group is bound to metal.

For each complex, the electronic spectra in DMF are similar to the corresponding reflectance spectra, although less well resolved. This result suggests that the complexes have the same structure in the solid state and in

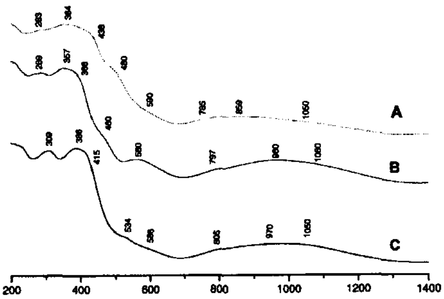


FIGURE 1 Powder reflectance spectra of (A) $[Ni(mslp)_2]$; (B) $[Ni(slp)_2]$; (C) $[Ni(nlp)_2]$.

DMF solution, with the unsymmetrical Schiff base acting as a tridentate ligand.

Spectra in DMF exhibit three low intensity *d–d* bands ($6.0 < \varepsilon < 24\,\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$): one broad band in the near-infrared, another as a shoulder in the high frequency region of this band, and the third band as a shoulder in the high intensity charge transfer bands ($\varepsilon > 5000\,\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$) that extends in the UV region. The broad band observed in the near-IR can be de-convoluted into two bands as summarised in the Table I.

The observation of more than the three *d–d* transitions predicted for $O_h$ symmetry indicate that the symmetry of the complexes is lower than $O_h$, as expected for *bis* complexes with asymmetric tridentate ligands of $N_2O$ type, but as either a tetragonal or trigonal distortion can cause the first band to be split [20], on the basis of the electronic spectra it is not possible to distinguish between them. However, by assuming an $O_h$ symmetry and using the maximum of the broad band in the NIR as an estimate for the frequency of the lowest energy *d–d* transition, an approximate value of $10Dq$ can be calculated for the complexes [20]. The values are practically identical for the three complexes ($\approx 10\,400\,\mathrm{cm^{-1}}$) and are comparable to those found for other nickel(II) complexes with similar ligands but with substituted amines [18, 19], and for nickel(II) complexes where the metal ion is surrounded by a $N_4O_2$ set of donor atoms [20–22]. As a final comment, it must be noted that with any of the ligands used, the complexes can exist in five isomeric forms, one with meridional binding and four with facial binding [16], but that on the basis of the electronic data no information on the isomers formed can be gained.

## Redox Chemistry of the Complexes

### *Oxidation*

The complexes exhibit oxidation processes in the potential range 0–1.3 V, but which are only observable with high scan rates ($\upsilon = 0.5–2\,\mathrm{V\,s^{-1}}$): [Ni(mslp)$_2$] shows two anodic waves at 0.98 and 0.64 V and two

TABLE I Electronic data for the nickel(II) complexes

| *Complexes* | $\lambda_{max}$/*nm* ($\varepsilon$/*dm*$^3$ *mol*$^{-1}$ *cm*$^{-1}$) | | | | | |
|---|---|---|---|---|---|---|
| [Ni(slp)$_2$] | 378 (18275) | 551 (13.8) | 796 (7.2) | 955 (14.5) | | |
| | | 551[a] | 786 | 904 | 1049 | |
| [Ni(mslp)$_2$] | 383 (4770) | 566 (12.4) | 795 (6.40) | 956 (10.9) | | |
| | | 550[a] | 790 | 900 | 1032 | |
| [Ni(nlp)$_2$] | 398 (18730) | 413 (17695) | 574 (23.5) | 790 (14.2) | 958 (20.0) | |
| | | | 555[a] | 798 | 885 | 1000 |

[a] Obtained by deconvolution of the experimental spectra.

corresponding low intense cathodic waves at 0.87 and 0.41 V ($v = 1\,\mathrm{V\,s^{-1}}$), whereas [Ni(nlp)$_2$] and [Ni(slp)$_2$] show anodic waves at 0.91 and 0.75 V ($v = 1\,\mathrm{V\,s^{-1}}$), respectively, but with no cathodic counterparts. In the positive potential limit, the voltammograms of all complexes show the beginning of strong anodic waves that must be associated with an irreversible oxidation of the ligand.

Analysis of CV data in the two processes observed for [Ni(mslp)$_2$] reveals: (a) a linear dependence of $i_p$ with $v^{1/2}$; (b) anodic-cathodic peak potential separations that are higher than that of the Fc$^+$/Fc couple; and (c) $i_{pc}/i_{pa}$ ratios that are smaller than 1. These results suggest that the two processes are diffusion-controlled, but with a large degree of irreversibility [23]. [Ni(nlp)$_2$] and [Ni(slp)$_2$] show irreversible processes in this potential range. To eliminate an eventual influence of irreversible ligand oxidation in the metal complex oxidation processes, potential ranges with lower positive limits were tried (0 – 0.85 V). For [Ni(mslp)$_2$] and [Ni(nlp)$_2$] no changes were observed in the oxidation processes, but for [Ni(slp)$_2$] a diffusion-controlled *quasi*-reversible process was observed with $E_{1/2} = 0.41$ V ($v = 1\,\mathrm{V\,s^{-1}}$).

Frozen solutions of the electro-oxidised solutions are EPR silent, as expected due to the high degree of irreversibility associated with the oxidation processes. All compounds were also chemically oxidised with excess of iodine and their frozen solutions exhibit EPR spectra, albeit with low intensity signals, and with $g$ values typical of metal centred oxidised species, $g_{av} = 2.11 - 2.12$ (Tab. II). The spectra are of rhombic type and, apparently, with no hyperfine splitting in any of three $g$ regions (Fig. 2A). The $g$ tensor has low anisotropy and the values are within the range observed for low spin six-coordinate Ni(III) complexes [1 – 3, 5 – 7, 24 – 26]. The similarity between the $g$ features of the Ni(III) species with those of analogous Ni(III) complexes can be use to support the following orientation scheme for the tensor axes: $g_1 = g_x$, $g_2 = g_y$ and $g_3 = g_z$, where $g_1$ and $g_3$ refer to the lowest and highest

TABLE II EPR data for oxidised and reduced nickel species

| *Complexes* | $g_x$ | $g_y$ | $g_z$ | $g_{av}$[a] |
|---|---|---|---|---|
| [Ni$^{III}$(slp)$_2$] | 2.19 | 2.15 | 2.03 | 2.12 |
| [Ni$^{III}$(mlp)$_2$] | 2.18 | 2.14 | 2.02 | 2.11 |
| [Ni$^{III}$(nlp)$_2$] | 2.19 | 2.13 | 2.03 | 2.12 |
| | $g_{\parallel}$ | $g_{\perp}$ | | $g_{av}$[a] |
| [Ni$^{I}$(slp)$_2$] | 2.53 | 2.04 | | 2.20 |
| [Ni$^{I}$(mlp)$_2$] | 2.54 | 2.05 | | 2.21 |
| [Ni(nlp)$_2$]$^-$ | | | 2.00[b] | |

[a] Calculated as $1/3(g_x + g_y + g_z)$.

[b] Radical type spectrum.

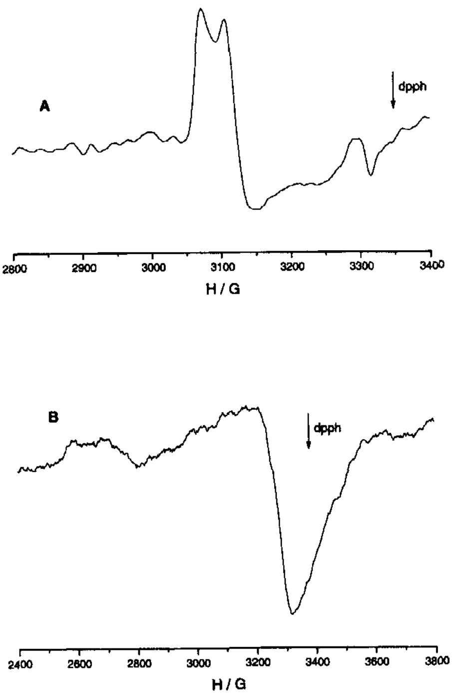


FIGURE 2 Frozen solution X-band EPR spectra at −140°C of (A) a chemically oxidised solution of $[Ni(mslp)_2]$ and (B) an electrochemically reduced solution of $[Ni(mslp)_2]$.

magnetic field $g$ values, respectively (Tab. II) [1−3, 5−7, 24−26]. The observation that $g_x$, $g_y > g_z$ is consistent with axial elongation and with a $[^2A_1(d_z2)]^1$ ground state [27]. In this context, the non-observance of hyperfine splittings due to nitrogen atoms in all $\underline{g}$ regions, and specially in $g_z$, may suggest that the axial positions are occupied by oxygen atoms.

## *Reduction*

The complexes exhibit different reduction behaviour in the potential range 0 to −2.0 V, with the complex with highest $\pi$ delocalisation, $[Ni(nlp)_2]$, showing an irreversible reduction process at −0.96 V ($v = 1\ V\,s^{-1}$). The cyclic voltammograms for the other two compounds, $[Ni(mslp)_2]$ and $[Ni(slp)_2]$, are similar and exhibit one cathodic wave at ca. −1.48 V and two low intensity anodic waves at ca. −1.36 and −0.84 V ($v = 1\ V\,s^{-1}$), thus indicating that the reduction processes are associated not only with electron transfer but also with chemical reactions involving the reduced species [23].

Electrolysed solutions of $[Ni(nlp)_2]$ in DMF are EPR silent, whereas the other complexes exhibit spectra apparently of axial type, with large $g$ tensor anisotropy and $g_{av} = 2.20-2.21$ typical of Ni(I) species (Fig. 2B and Tab. II) [4–6, 28–31], thus implying that the first step in the reduction process involves metal centred reduction.

The complexes have also been reduced chemically with excess Na(Hg) amalgam and their frozen solution EPR spectra recorded. For [Ni(nlp)$_2$], only a radical type spectrum was observed, what indicates that the reduction process involves ligand based processes, as has been observed for other nickel(II) complexes in which the ligands have high $\pi$-delocalisation [28–31]. For the other complexes, frozen solution EPR spectra are similar to those obtained after electrolysis and are typical of Ni(I) complexes with a $d_{x^2-y^2}$ ground state [4–6, 28–31]: they show no detectable hyperfine splitting in any of the $g$ regions and have $g_{\|} > g_{\perp}$ (Fig. 2B). On the basis of the EPR spectra it is not possible to assign a geometry for the reduced Ni(I) complexes, as both square planar, square pyramidal and distorted octahedral geometries originate axial EPR spectra with $g_{\|} > g_{\perp}$, and the ranges of $g$ values overlap, a situation well documented for the iso-electronic copper(II) complexes [32, 33]. Usually, geometry assignments in copper complexes are made by mapping copper hyperfine couplings and $g$ values in the so-called Peisach diagrams [33, 34], but for natural abundance nickel systems this analysis can not be done because the nuclear magnetic moment is zero, and thus it is not possible to ascertain if the amine groups are coordinated to the nickel centre after reduction.

The electrochemical behaviour of the reported six-coordinate nickel complexes with $N_2O$ asymmetric ligands is to be contrasted with that of the homologous square planar nickel complexes with the corresponding symmetrical ligands. The latter are reversible oxidised and reduced at the metal centre in the potential range used [1–7]. The different redox behaviour can be attributed to the presence of a high reactive amine group in the $N_2O$ asymmetric ligands, which can undergo intra-molecular redox reactions upon oxidation/reduction of the metal centre.

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