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# Electrochemical synthesis and crystal structures of nickel(II), copper(II), zinc(II) and cadmium(II) complexes with *N*,*N*'-bis[(4-methylphenyl)sulfonyl]ethylenediamine

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#### Abstract

The electrochemical oxidation of anodic metal (nickel, copper, zinc and cadmium) in acetonitrile solutions containing N,N'-bis[(4-methylphenyl)sulfonyl]ethylenediamine H<sub>2</sub>L and an additional nitrogen coligand, such as 1,10-phenanthroline, yielded mixed complexes of general formula [ML(phen)<sub>2</sub>] (M = Ni, Cu, Zn and Cd). The compounds have been characterized by microanalysis, IR and UV–Vis (Ni, Cu complexes) spectroscopy, FAB mass spectrometry, <sup>1</sup>H NMR spectroscopic studies (Zn, Cd complexes) and EPR spectroscopy (Cu and Ni complexes). All compounds have also been characterized by single crystal X-ray diffraction. The molecular structures of these compounds consist of individual monomeric molecules in which the metal atom is in an [MN<sub>6</sub>] distorted octahedral environment. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Tosyl amide complexes; Electrochemical synthesis; X-ray crystal structures

#### 1. Introduction

The application of an electrolytic procedure for the synthesis of metal complexes has been widely used, especially in the cases of weakly acidic organic ligands in which the acid group is usually a hydroxyl [1-6], an NH pyrrole [7-14] or a thiol group [15-20].

We have now extended our previous work to include the electrochemical synthesis of complexes of ligands of type (I) Scheme 1 bearing two secondary amide groups. Although it is well known that replacement of the





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amide proton by a metal ion is not an easy process [21], in the case of a sulfonamide group the electron-withdrawing effect of the sulfonyl group increases the acidity of the amide hydrogen and makes the substitution of the proton easier [22].

As a result of our continuing interest in the electrochemical synthesis of amide complexes, we describe here the electrochemical synthesis of the nickel, copper, zinc and cadmium(II) complexes  $[ML(phen)_2]$  with N,N'-bis[(4-methylphenyl)sulfonyl]ethylenediamine (H<sub>2</sub>L).

## 2. Experimental

Acetonitrile, ethylenediamine, tosyl chloride, 1,10phenanthroline and all other reagents were commercial products (Aldrich) and were used without further purification. Nickel, copper, zinc and cadmium (Ega Chemie) were used as plates (ca.  $2 \times 2$  cm). The ligand H<sub>2</sub>L Scheme 1, was prepared by slow addition of C<sub>7</sub>H<sub>7</sub>ClO<sub>2</sub>S (6.4 g, 33.4 mmol) to a stirred ice-cold solution of  $C_2H_8N_2$  (1 g, 16.7 mmol) in Py (6 cm<sup>3</sup>). After addition of cold water (10 cm<sup>3</sup>), the mixture was stirred for 1 h. After this time, the oily organic phase was separated and water (10 cm<sup>3</sup>) and EtOH (10 cm<sup>3</sup>) were added. The solid formed was filtered off and recrystallized from a mixture (1:1) of water-EtOH. The purity of the product was checked by elemental analysis, IR and <sup>1</sup>H NMR spectroscopy. Anal. Found: C, 53.0; H, 5.7; N, 7.6; S, 17.7. Calc. for [C<sub>16</sub>H<sub>20</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub>]: C, 52.2; H, 5.5; N, 7.6; S, 17.4%. IR (KBr, cm<sup>-1</sup>): 3275 (s); 3060 (w); 3040 (w); 2970 (w); 2925 (w); 2870 (w); 1915 (w); 1590 (s); 1485 (w); 1455 (s); 1445 (s); 1405 (s); 1330 (s); 1305 (s); 1290 (s); 1235 (w); 1180 (w); 1150 (s); 1090 (s); 1075 (s); 1060 (s); 1015 (w); 872 (s); 815 (s); 750 (s); 705 (w); 665 (s); 610 (w); 565 (s); 550 (s); 495 (w); 475 (w); 410 (w); 395 (w); 310 (w). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm) 2.43 s (-CH<sub>3</sub>); 3.05 s (CH<sub>2</sub>); 7.30 m, 7.71 m ( $C_6H_6$  ring).

# 2.1. Preparation of complexes

The complexes were obtained using an electrochemical procedure. The cell consisted of a tall-form beaker with a rubber bung through which the electrochemical leads entered into the cell. An MeCN solution of the ligand H<sub>2</sub>L and 1,10-phenanthroline (50 cm<sup>3</sup>), containing about 10 mg of tetramethylammonium perchlorate as a current carrier, was electrolysed using a platinum wire as the cathode and a metal plate as the sacrificial anode. Applied voltages of 10–15 V allowed sufficient current flow for smooth dissolution of the metal. As the electrolysis proceeded, the colour of the solution changed and hydrogen gas evolved from the cathode. The cells can be summarised as  $Pt(-)/CH_3CN + H_2L/$ M(+), where M is Ni, Cu, Zn or Cd.

The crystalline solids formed at the bottom of the cell were collected, washed with MeCN, Et<sub>2</sub>O and dried in vacuo. In some cases concentration of the resulting solution was required in other to obtain a solid product.

# 2.1.1. [NiL(phen)<sub>2</sub>]

Electrolysis of a solution (50 cm<sup>3</sup>) of H<sub>2</sub>L (0.206 g, 0.559 mmol), 1,10-phenanthroline (0.222 g, 1.120 mmol) and tetramethylammonium perchlorate (ca. 10 mg) in MeCN, at 20 V and 10 mA for 3 h, dissolved 28 mg of Zn ( $E_f$  = 0.43). At the end of the experiment the brown crystalline solid was filtered off, washed with hot MeCN, Et<sub>2</sub>O, and dried in vacuo. The compound was characterized as [NiL(phen)<sub>2</sub>]·CH<sub>3</sub>CN. *Anal.* Found: C, 61.5; H, 4.6; N, 11.9; S, 8.5. Calc. for [C<sub>42</sub>H<sub>37</sub>N<sub>7</sub>-NiO<sub>4</sub>S<sub>2</sub>]: C, 61.0; H, 4.5; N, 11.9; S, 7.8%. IR (KBr, cm<sup>-1</sup>): 3050 (w); 3010 (w); 2920 (w); 2880 (w); 2815 (w); 1620 (w); 1590 (w); 1570 (w); 1503 (w); 1480 (w); 1440 (w); 1408 (s); 1340 (w); 1250 (s); 1240 (s); 1140 (s);

1120 (s); 1098 (s); 1078 (s); 1020 (w); 1008 (w); 875 (w); 865 (w); 842 (s); 802 (s); 788 (w); 722 (s); 660 (s); 635 (w); 595 (w); 555 (s); 545 (w); 498 (w); 462 (w); 420 (w); 290 (w); 260 (w).

Crystals suitable for X-ray diffraction studies were obtained by crystallisation from CH<sub>3</sub>OH–CH<sub>3</sub>CN.

#### 2.1.2. $[CuL(phen)_2]$

An experiment similar to that described above, with Cu as the anode and a solution of  $H_2L$  (0.137 g. 0.372 mmol), 1,10-phenanthroline (0.148 g, 0.747 mmol) and tetramethylammonium perchlorate (ca. 10 mg) in MeCN (50 cm<sup>3</sup>), at 10 mA and 6 V for 2 h, dissolved 45 mg of Cu ( $E_{\rm f} = 0.95$ ). At the end of the experiment the pale green crystalline solid was filtered off, washed with hot MeCN, Et<sub>2</sub>O and dried in vacuo. The compound was characterized as [CuL(phen)<sub>2</sub>]·CH<sub>3</sub>CN. Anal. Found: C, 60.6; H, 2.9; N, 10.8; S, 7.6. Calc. for [C<sub>42</sub>H<sub>37</sub>CuN<sub>7</sub>O<sub>4</sub>S<sub>2</sub>]: C, 60.7; H, 4.5; N, 11.8; S, 7.7%. IR (KBr, cm<sup>-1</sup>): 3040 (w); 3005 (w); 2980 (w); 2930 (w); 2880 (w); 2820 (w); 1615 (w); 1582 (s); 1565 (s); 1500 (s); 1480 (s); 1445 (w); 1420 (s); 1375 (w); 1352 (w); 1340 (w); 1312 (w); 1250 (s); 1215 (s); 1140 (s); 1120 (s); 1090 (s); 1020 (s); 1008 (s); 980 (w); 970 (w); 945 (w); 882 (w); 860 (w); 840 (s); 800 (s); 785 (s); 768 (s); 724 (s); 660 (s); 630 (w); 595 (s); 560 (s); 540 (s); 525 (s); 500 (w); 465 (w); 415 (w); 355 (w); 280 (w); 260 (w); 235 (w).

#### 2.1.3. $[ZnL(phen)_2]$

Electrochemical oxidation of a Zn anode in a solution of H<sub>2</sub>L (0.206 g, 559 mmol), 1,10-phenanthroline (0.222 g, 1.120 mmol) and tetramethylammonium perchlorate (ca. 10 mg) in MeCN (50 cm<sup>3</sup>), at 20 V and 10 mA for 3 h, caused 33 mg of Zn to be dissolved  $(E_{\rm f} = 0.45)$ . At the end of the experiment the brown crystalline solid was filtered off, washed with hot MeCN, Et<sub>2</sub>O and dried in vacuo. The compound was characterized as [ZnL(phen)<sub>2</sub>]·CH<sub>3</sub>CN. Anal. Found: C, 4.5; N, 11.5; S, 8.1. Calc. 60.6; Н. for [C<sub>42</sub>H<sub>37</sub>N<sub>7</sub>O<sub>4</sub>S<sub>2</sub>Zn]: C, 60.5; H, 4.5; N, 11.8; S, 7.7%. IR (KBr, cm<sup>-1</sup>): 3045 (w); 3010 (w); 2920 (w); 2880 (w); 2820 (w); 2240 (w); 1945 (w); 1910 (w); 1880 (w); 1820 (w); 1750 (w); 1615 (w); 1585 (s); 1568 (s); 1502 (s); 1482 (s); 1445 (w); 1420 (s); 1375 (w); 1340 (w); 1315 (w); 1280 (w); 1255 (s); 1240 (s); 1215 (s); 1185 (w); 1140 (s); 1120 (s); 1095 (s); 1080 (s); 1045 (w); 1020 (s); 1008 (s); 975 (w); 942 (w); 880 (w); 860 (w); 843 (s); 805 (s); 788 (s); 770 (w); 722 (s); 657 (s) 635 (w); 595 (w); 550 (s); 525 (w); 498 (w); 460 (w); 415 (w); 395 (w); 355 (w); 280 (w); 235 (w). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm) 2.00 (-CH<sub>3</sub>); 3.51 (CH<sub>2</sub>); 6.21, 6.45 (C<sub>6</sub>H<sub>6</sub> ring); 8.30 (2,9), 7.82 (4,7), 7.69 (5,6), 7.61 (3,8) (phen).

## 2.1.4. $[CdL(phen)_2]$

The electrochemical oxidation of Cd in a solution of the ligand  $H_2L$  (0.206 g, 0.559 mmol) and 1,10-phenan-

throline (0.222 g, 1.120 mmol) in MeCN (50 cm<sup>3</sup>), using a 10 mA current for 3 h, resulted in the dissolution of 57 mg of the metal ( $E_{\rm f} = 0.45$ ). At the end of the electrolysis the yellow solid was filtered off, washed with MeCN, Et<sub>2</sub>O and dried in vacuo. The compound was characterized as [CdL(phen)<sub>2</sub>]. Anal. Found: C, 56.9; H, 4.1; N, 10.2; S, 7.3. Calc. for [C<sub>40</sub>H<sub>34</sub>CdN<sub>6</sub>-O<sub>4</sub>S<sub>2</sub>]: C, 57.24; H, 4.08; N, 10.0; S, 7.6%. IR (KBr, cm<sup>-1</sup>): 3060 (w); 3030 (w); 2970 (w); 2925 (w); 2880 (w); 2820 (w); 2240 (w); 1930 (w); 1890 (w); 1610 (w); 1580 (w); 1560 (w); 1500 (s); 1482 (s); 1435 (w); 1417 (s); 1370 (w); 1355 (w); 1339 (w); 1295 (w); 1250 (s); 1215 (s); 1140 (s); 1120 (s); 1100 (s); 1077 (s); 1040 (w); 1020 (s); 1005 (s); 854 (s); 840 (s); 802 (s); 782 (s); 766 (s); 720 (s); 659 (s); 635 (s); 595 (s); 550 (s); 538 (s); 520 (s); 490 (w); 460 (w); 415 (w); 395 (w); 350 (w); 275 (w); 238 (w); 215 (w). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm) 1.99 (-CH<sub>3</sub>); 3.33 (CH<sub>2</sub>); 6.28, 6.77 (C<sub>6</sub>H<sub>6</sub> ring); 9.21 (2,9), 8.34 (4,7), 7.86 (5,6) and 7.70 (3,8) (phen).

#### 2.2. Physical measurements

Microanalyses were performed using a CHNS Carlo Erba 1108 elemental analyser. IR spectra were recorded in KBr mulls on a Bruker IFs 66v spectrophotometer. FAB mass spectra were recorded on a Kratos-MS-50T spectrometer connected to a DS90 data system using 3-nitrobenzylalcohol (3-NBA) as a matrix. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker WM 350 MHz using CDCl<sub>3</sub> or DMSO-d<sub>6</sub> as solvents. Chemical shifts were determined against TMS. Solid state electronic spectra were recorded on a Shimadzu UV 3101 PC. Magnetic measurements were made using a DMS VSM 1160 instrument.

#### 2.3. Crystal structure determination

Crystals of [NiL(phen)<sub>2</sub>], [CuL(phen)<sub>2</sub>], [ZnL(phen)<sub>2</sub>] and [CdL(phen)<sub>2</sub>] were mounted on glass fibres on a SIEMENS Smart CCD area-detector diffractometer. Data collections were carried out under ambient conditions using Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å, graphite monochromator).

All the structures were resolved by direct methods and refined by full-matrix least-squares based on  $F^2$ [23]. Data were corrected for absorption using SADABS [24]. No anomalies were encountered in the refinement of any of the structures. Neutral atom scattering factors and anomalous dispersion factors were taken from the International Tables for X-ray Crystallography [25]. The crystal data and summary of data collection and structure refinement for these compounds are given in Table 1. Significant bond distances and angles for [NiL(phen)<sub>2</sub>],  $[CuL(phen)_2],$  $[ZnL(phen)_2]$ and [CdL(phen)<sub>2</sub>] are given in Tables 2-5. Complete crystallographic details are given in the Supporting Information. ORTEP diagrams of the molecules are shown in Figs. 1-4.

# 2.4. EPR measurements of [CuL(phen)<sub>2</sub>] and [NiL(phen)<sub>2</sub>]

The powder and frozen THF solution spectra of [CuL(phen)<sub>2</sub>] and the powder spectrum of [NiL(phen)<sub>2</sub>] were obtained using an EMX EPR spectrometer from Bruker, equipped with a rectangular resonant cavity and 100 kHz field modulation and N2 Temperature Controller system. The EPR spectra were obtained at 120 K (room temperature for the Ni compound) under the following conditions: 0.1 mT (0.4 mT) amplitude modulation, 10 mW microwave power, and first and second harmonic detection. In order to improve the signal-to-noise ratio of the second harmonic measurements, an average of 64 scans was recorded and a detailed superhyperfine splitting from nitrogen nuclei interactions was obtained. A g-marker of MgO-Cr(III) (g = 1.9797) was used to obtain the microwave frequency for both samples. The positions and linewidths of the resonance for the Cu compound were calculated by numerical simulation of the powder spectra using the QPOW program [26,27] with the Spin Hamiltonian composed of Zeeman, Hyperfine and Superhyperfine interactions. For the Ni compound the Spin Hamiltonian involves the zero field splitting and Zeeman interaction and to estimate the value of the zero field splitting it was also necessary to measure the EPR spectrum at the Q-band using a Varian E-line spectrometer. EPR spectra and simulations for the copper compound are shown in Fig. 5 and the EPR parameters are given in Table 6. The EPR spectra for the nickel compound at both frequencies (X- and Q-band) are shown in Fig. 6.

#### 3. Results and discussion

#### 3.1. Electrochemical synthesis of complexes

The anodic oxidation of nickel, copper, zinc or cadmium in the presence of  $H_2L$  and 1,10-phenanthroline is a simple and efficient route to obtain compounds of composition [ML(phen)<sub>2</sub>], where L is the dianion resulting of the deprotonation of the two amide groups of ligand  $H_2L$ . In all cases, the product formed was easily separated as a crystalline product by filtration. These compounds are insoluble in common organic solvents and have melting points greater than 250 °C.

The values of the electrochemical efficiency, defined as the amount of metal dissolved per Faraday of charge, were close to 0.5 in the cases of the Ni, Zn and Cd complexes. This fact, along with the evolution of Table 1

Summary of crystal data and structure refinement

Compound	[NiL(phen) <sub>2</sub> ]	[CuL(phen) <sub>2</sub> ]	[ZnL(phen) <sub>2</sub> ]	[CdL(phen) <sub>2</sub> ]
Empirical formula	C <sub>42</sub> H <sub>37</sub> N <sub>7</sub> NiO <sub>4</sub> S <sub>2</sub>	C <sub>42</sub> H <sub>37</sub> CuN <sub>7</sub> O <sub>4</sub> S <sub>2</sub>	C <sub>42</sub> H <sub>37</sub> N <sub>7</sub> O <sub>4</sub> S <sub>2</sub> Zn	C <sub>40</sub> H <sub>34</sub> CdN <sub>6</sub> O <sub>4</sub> S
Formula weight	826.62	831.44	833.28	839.26
Temperature (K)	293(2)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	Cc	<i>C</i> 2	<i>C</i> 2	C2/c
Unit cell dimensions				
a (Å)	9.53490(10)	17.32590(10)	17.1584(5)	20.9098(2))
b (Å)	16.4785(3)	9.31180(10)	9.4354(3)	13.4262(2)
<i>c</i> (Å)	25.0886(4)	13.2776(2)	13.3009(3)	14.6961(2)
α (°)	90.00(-)	90.00(-)	90.00(-)	90.00(-)
β (°)	94.0817(4)	113.0240(10)	113.1350(10)	122.7430(10)
γ (°)	90.00(-)	90.00(-)	90.00(-)	90.00(-)
$V(Å^3)$	3931.94(10)	1971.50(4)	1980.20(10)	3470.20(8)
Ζ	4	2	2	4
$D_{\text{calc}} (\text{mg m}^{-3})$	1.396	1.401	1.398	1.606
Absorption coefficient (mm <sup>-1</sup> )	0.652	0.712	0.777	0.804
<i>F</i> (000)	1720	862	864	1712
Crystal size (mm)	$0.45 \times 0.30 \times 0.05$	$0.40 \times 0.30 \times 0.15$	$0.20 \times 0.15 \times 0.10$	$0.45 \times 0.40 \times 0.20$
Colour	Brown-red	Green	Light brown	Yellow
$\theta$ range for data collection (°)	1.63-28.26	2.44-28.27	1.66–28.27	1.91-28.27
Index ranges	$-12 \le h \le 12, -9 \le k \le 21,$	$-22 \le h \le 21, -11 \le k \le 12,$	$-22 \le h \le 20, -12 \le k \le 10,$	$-18 \le h \le 27, -17 \le k \le 14,$
	$-33 \le l \le 33$	$-12 \le l - \le 17$	$-16 \le l - \le 17$	$-19 \le l \le 17$
Reflections collected	13 226	6809	6810	12 422
Reflections observed	13 226	6809	6810	12 422
Independent reflections	8886 $[R_{int} = 0.0508]$	4023 $[R_{int} = 0.0219]$	4013 $[R_{int} = 0.0484]$	4280 $[R_{int} = 0.0195]$
Criterion for observation	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
Data/restraints/parameters	8886/2/508	4023/1/255	4013/1/260	4280/0/308
Final R indices $[I > 2\sigma(I)]$	0.0433/0.0867	0.0298/0.0650	0.0522/0.0826	0.0237/0.0592
Goodness-of-fit on $F^2$	0.793	0.979	1.003	1.026
Largest difference peak and hole (e $Å^{-3}$ )	0.485  and  -0.665	0.388 and -0.270	0.289  and  -0.455	0.336 and -0.486

hydrogen from the cathode, is compatible with the mechanism:

Cathode:  $H_2L + 2e^- \rightarrow L^{-2} + H_2$ Anode:  $M + L^{-2} + 2$  phen  $\rightarrow [ML(phen)_2] + 2e^-$ M = Ni, Zn, Cd.

An  $E_{\rm f}$  value close to 1.0 mol F<sup>-1</sup> was found in the synthesis of the copper complex, and this shows that the anodic oxidation leads initially to a Cu(I) compound. However, the analytical data show that the complex is [CuL(phen)<sub>2</sub>]. This observation suggests that the ligand oxidises the Cu(I) to Cu(II) in solution as soon as it is formed.

Cathode: 
$$H_2L + 1e^- \rightarrow 1/2H_{2(g)} + HL^-$$
  
Anode:  $Cu \rightarrow Cu^+ + 1e^-$   
 $HL^- + Cu^+ + phen \rightarrow [CuL(phen)_2] + 1/2H_{2(g)}$ 

This behaviour has been previously observed in the synthesis of other copper complexes by an electrochemical procedure [6].

#### 3.2. Structure of [NiL(phen)<sub>2</sub>]

Fig. 1 shows the molecular structure of  $[NiL(phen)_2]$  together with the atom labelling scheme adopted. Selected bond distances and angles are given in Table 2. The complex crystallises with four formula units and four acetonitrile molecules in the cell.

As can be seen in Fig. 1, monomeric  $[NiL(phen)_2]$  has a highly distorted octahedral coordination around Ni(II). The coordination sphere involves four nitrogen atoms belonging to two bidentate 1,10-phenanthroline ligands and two amide nitrogen atoms of the dianionic ligand N,N'-bis(p-toluenesulfonyl)ethylenediamide.

The arrangement of the 1,10-phenanthroline ligands is such that the equatorial plane is formed by two nitrogen atoms of one phenanthroline molecule, one nitrogen atom of the other phenanthroline molecule and one of the nitrogen atoms from the dianionic ligand. The inner coordination sphere is completed by two additional nitrogen atoms, one from the dianionic ligand and other from a phenanthroline molecule. The four 'in plane' atoms N(2), N(3), N(5) and N(6) are not

Table 2 Selected bond lengths (Å) and angles (°) for [NiL(phen)<sub>2</sub>]

Bond lengths				
Ni(1) - N(2)	2.083(3)	Ni(1)–N(1)	2.085(3)	
Ni(1)–N(5)	2.109(3)	Ni(1)-N(3)	2.116(3)	
Ni(1)–N(4)	2.131(3)	Ni(1)-N(6)	2.135(3)	
S(1)–O(2)	1.446(3)	S(1)–O(1)	1.458(2)	
S(1) - N(1)	1.571(3)	S(1)–C(3)	1.785(4)	
S(2)–O(3)	1.450(2)	S(2)–O(4)	1.452(3)	
S(2)–N(2)	1.573(3)	S(2)-C(10)	1.795(3)	
N(1)-C(1)	1.473(4)	N(2)–C(2)	1.480(4)	
N(3)–C(17)	1.315(4)	N(3)-C(21)	1.365(4)	
N(4)–C(26)	1.317(5)	N(4)–C(22)	1.368(4)	
N(5)-C(29)	1.321(4)	N(5)-C(33)	1.369(4)	
N(6)–C(38)	1.314(4)	N(6)-C(34)	1.367(4)	
Bond angles				
N(2)-Ni(1)-N(1)	80.89(10)	N(2)-Ni(1)-N(5)	94.62(10)	
N(1)-Ni(1)-N(5)	95.51(11)	N(2)-Ni(1)-N(3)	95.68(11)	
C(1)-N(1)-Ni(1)	109.84(19)	N(1)-Ni(1)-N(3)	94.79(11)	
S(1)-N(1)-Ni(1)	129.07(16)	N(5)-Ni(1)-N(3)	166.45(11)	
N(2)–Ni(1)–N(4)	96.93(10)	C(2)-N(2)-Ni(1)	109.74(18)	
N(1)–Ni(1)–N(4)	172.92(11)	S(2)-N(2)-Ni(1)	129.88(16)	
N(5)–Ni(1)–N(4)	91.37(10)	N(3)-Ni(1)-N(4)	78.68(11)	
C(17) - N(3) - Ni(1)	127.9(2)	N(2)-Ni(1)-N(6)	172.72(11)	
C(21) - N(3) - Ni(1)	113.5(2)	N(1)-Ni(1)-N(6)	97.05(10)	
N(5)–Ni(1)–N(6)	78.58(10)	C(26)–N(4)–Ni(1)	129.4(2)	
N(3)–Ni(1)–N(6)	91.43(10)	C(22)-N(4)-Ni(1)	112.7(2)	
N(4)–Ni(1)–N(6)	85.92(10)	C(29)–N(5)–Ni(1)	128.0(2)	
C(33)–N(5)–Ni(1)	113.9(2)	C(38)–N(6)–Ni(1)	129.7(2)	
C(34) - N(6) - Ni(1)	113.0(2)			

Table 3 Selected bond lengths (Å) and angles (°) for  $[CuL(phen)_2]$ 

Bond lengths			
Cu(1)–N(1)	2.020(2)	Cu(1)–N(2)	2.1142(19)
Cu(1)–N(3)	2.3489(17)	S(1)-O(1)	1.4445(17)
S(1)–O(2)	1.4491(17)	S(1)-N(1)	1.571(2)
S(1)-C(2)	1.784(2)	N(1)-C(1)	1.467(3)
N(2)-C(9)	1.331(3)	N(2)-C(13)	1.359(3)
N(3)-C(18)	1.316(3)	N(3)-C(14)	1.347(3)
C(17)-C(18)	1.403(3)	C(1)-C(1) # 1	1.522(5)
C(19)-C(20)	1.343(4)	C(2)–C(3)	1.378(4)
N(90)-C(90)	1.124(9)		
Bond angles			
$N(1)-Cu(1)-N(1) \neq 1$	82.30(11)	N(1)-Cu(1)-N(2)	168.21(7)
N(1) # 1-Cu(1)-N(2)	97.65(7)	N(1) # 1-Cu(1)-	168.21(7)
		N(2) # 1	
N(2)-Cu(1)-N(2) # 1	84.82(10)	N(1)-Cu(1)-N(3)	93.96(7)
N(1) # 1-Cu(1)-N(3)	97.13(7)	N(2)-Cu(1)-N(3)	74.32(7)
N(2) # 1-Cu(1)-N(3)	94.64(7)	N(3)-Cu(1)-N(3) # 1	165.26(9)
C(1)-N(1)-Cu(1)	110.51(14)	N(3)-C(14)-C(13)	117.66(2)
S(1)-N(1)-Cu(1)	129.56(12)	C(15)-C(14)-C(13)	119.6(2)
C(9)-N(2)-Cu(1)	123.39(16)	C(16)-C(15)-C(14)	117.0(2)
C(13)-N(2)-Cu(1)	118.68(15)	C(16)-C(15)-C(20)	123.1(2)
C(18)–N(3)–Cu(1)	130.12(15)	C(17)-C(16)-C(15)	119.9(2)
C(14)–N(3)–Cu(1)	111.35(14)	C(16)-C(17)-C(18)	119.0(2)
N(90)-C(90)-C(91)	180.00(4)		

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

coplanar; N(3) and N(5), which are trans to each other, lie -0.094(1) and -0.107(1) Å, respectively, below the least-squares plane through the four atoms, while N(2) and N(6) are +0.092(1) and +0.109(1) Å, respectively, above this plane; the nickel atom lies nearly in the plane, sitting 0.063(1) Å above it. This lack of planarity gives rise to N(3)–Ni–N(5) and N(2)–Ni(1)– N(6) angles of 166.42(10) and 172.71(11)°, respectively.

Further distortion is provided by the small bite of the 1,10-phenanthroline ligands [78.70(10) and 78.53(10)°] and the dianionic ligand  $[N_{amide}-Ni-N_{amide}, 80.89(10)°]$ . This situation causes the angles defined by the two trans nitrogen atoms and the nickel atom to be very different from the expected values of 180° [166.42(10) and 172.94(11)°] and also means that the angles determined by the Ni and two *cis* nitrogen atoms differ from 90° [78.53(10)–97.05(10)°].

The Ni-N<sub>amide</sub> bond distances [2.083(3) and 2.085(3) Å] do not differ significantly from those of the octahe-1,10-phenanthroline complex dral bis{[(4-methylphenyl)sulfonyl]-2-pyridylamide}nickel(II), 2.095(6) and 2.096(6) Å [28], but they are significantly greater than those found in tetracoordinated nickel(II) amide complexes; for example, 1.916(3) A in the tetrahedral complex [N,N' - bis(2' - pyridinecarboxamido)-1,2-ethane]nickel(II) [29] and 1.904(3) Å in the square-planar complex bis{4-methyl-N-(2-pyridin-2-yl-ethyl)benzenesulfonamide}nickel(II) [30]. This change in bond length is due to a change in the coordination number from 4 to 6. The Ni-N<sub>phen</sub> bond distances, 2.116(3), 2.131(3), 2.109(3) and 2.134(3) Å, are similar to those found in other octahedral nickel(II) phenanthroline complexes; for example, 2.121(5) and 2.136(5) Å in 1,10-phenanthroline bis{[2-(2-pyrrole)methylimino]-4-methylphenolato}nickel (II) [31].

The 1,10-phenanthroline ligands are essentially planar, with no atom deviating from the least-squares plane by more than 0.046 Å. The bond lengths and angles within the ligand are similar to those found in other 1,10-phenanthroline complexes. The N<sub>phen</sub>-Ni–N<sub>phen</sub> angles of 78.70(10) and 78.53(10)° are similar to those reported for other bidentate complexes of phenanthroline [28,31,32]. The phenanthroline molecules are almost perpendicular to one another, with a dihedral angle of 80.13(4)°, and form dihedral angles with the equatorial plane of 6.98(11) and 81.94(5)°.

#### 3.3. Structure of [CuL(phen)<sub>2</sub>]

Fig. 2 shows the molecular structure of  $[CuL(phen)_2]$  together with the labelling scheme used. Selected bond distances and angles with estimated standard deviations are given in Table 3.

In  $[CuL(phen)_2]$  the copper atom is located on a twofold axis and is hexacoordinated by the two amide

Table 4

Selected bond lengths (Å) and angles (°) for [ZnL(phen)<sub>2</sub>]

Bond lengths			
Zn(1)-N(1)	2.092(4)	Zn(1)-N(2)	2.202(3)
Zn(1)-N(3)	2.247(4)	S(1)–O(2)	1.445(3)
S(1)–O(1)	1.446(3)	S(1) - N(1)	1.556(4)
S(1)-C(2)	1.781(4)	N(1)-C(1)	1.471(6)
N(2)-C(9)	1.331(5)	N(2)–C(13)	1.354(5)
N(3)-C(18)	1.335(6)	N(3)-C(14)	1.352(5)
Bond angles			
$N(1)-Zn(1)-N(1) \neq 1$	81.7(2)	N(1)-Zn(1)-N(2)	99.90(14)
$N(1)-Zn(1)-N(2) \neq 1$	95.35(13)	N(1) # 1-Zn(1)-	99.90(13)
		N(2) # 1	
N(2)-Zn(1)-N(2) # 1	159.81(19)	N(1)-Zn(1)-N(3)	169.59(14)
		#1	
N(1) # 1-Zn(1)-N(3)	98.61(12)	N(2)-Zn(1)-N(3)	90.44(13)
#1		#1	
N(2) # 1-Zn(1)-N(3)	74.32(13)	N(1)-Zn(1)-N(3)	98.61(12)
#1			
N(1) # 1-Zn(1)-N(3)	69.59(14)	N(2)-Zn(1)-N(3)	74.32(13)
N(2) # 1-Zn(1)-N(3)	90.44(13)	N(3) # 1-Zn(1)-	83.0(2)
		N(3)	
C(1)-N(1)-Zn(1)	108.9(3)	S(1)-N(1)-Zn(1)	128.7(2)
C(9)-N(2)-Zn(1)	125.3(3)	C(13)-N(2)-Zn(1)	116.3(3)
C(18)–N(3)–Zn(1)	128.6(3)	C(14)-N(3)-Zn(1)	114.6(3)

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

#### Table 5

Selected bond lengths (Å) and angles (°) for [CdL(phen)<sub>2</sub>]

Bond lengths			
Cd(1)-N(1)	2.2827(14)	N(2)-C(9)	1.323(2)
Cd(1)-N(3)	2.3866(14)	N(2)-C(20)	1.354(2)
Cd(1)-N(2)	2.4103(14)	N(3)-C(18)	1.326(2)
S(1)–O(1)	1.4410(14)	N(3)-C(19)	1.350(2)
S(1)–O(2)	1.4481(14)	$C(1)-C(1) \neq 1$	1.518(3)
S(1)–N(1)	1.5669(14)	C(2)–C(3)	1.381(2)
S(1)–C(2)	1.7817(17)	C(2)–C(7)	1.391(3)
N(1)-C(1)	1.465(2)		
Bond angles			
N(1)-Cd(1-N(1) # 1	77.08(7)	N(1)-Cd(1)-N(3)	104.74(5)
N(1) # 1-Cd(1)-N(3)	95.74(5)	N(3)-Cd(1)-N(3) # 1	153.81(7)
$N(1)-Cd(1)-N(2) \neq 1$	164.42(5)	N(1) # 1-Cd(1)-N(2)	100.81(5)
		#1	
N(3)-Cd(1)-N(2) # 1	90.82(5)	C(1)-N(1)-Cd(1)	107.75(10)
N(3) # 1-Cd(1)-N(2)	69.66(5)	S(1)-N(1)-Cd(1)	126.46(8)
#1			
N(3) # 1-Cd(1)-N(2)	90.82(5)	C(9)-N(2)-C(20)	118.54(15)
N(2) # 1-Cd(1)-N(2)	85.27(7)	C(9)-N(2)-Cd(1)	125.23(12)
O(1)–S(1)–O(2)	116.71(9)	C(20)-N(2)-Cd(1)	116.21(11)

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

nitrogen atoms of the dianionic ligand and by four nitrogen atoms of two bidentate 1,10-phenanthroline molecules. This environment is similar to that found in  $[NiL(phen)_2]$ , but with an important difference. In the  $[NiL(phen)_2]$  compound all the Ni–N distances are quite similar, 2.083(3)–2.134(3) Å, whereas in the copper complex two of the Cu–N bond distances are

greater, 2.3489(17) Å, than the other four, 2.020(2)– 2.1142(19) Å. Therefore, in the  $[CuL(phen)_2]$  complex the coordination polyhedron is best described as an octahedron with the longer Cu–N distances associated with the axial nitrogen atoms. Thus, the equatorial plane is formed by the two amide nitrogen atoms of the tosylamide ligand and two other nitrogen atoms, one from each phenanthroline molecule; the axial positions are occupied by the other nitrogen atoms of each phenanthroline.

The N(1), N(1)\*, N(2) and N(2)\* atoms of the equatorial plane deviate considerably from planarity. The trans equatorial atoms N(1) [N(1\*)] and N(2) [N(2\*)] are both above (below) the least-squares plane by + 0.218(1) Å [-0.203(1) Å], leading to an N(1)–Cu–N(2) angle of 168.21(7)°. The copper atom lies in the best square plane formed by the equatorial atoms. The angle between the apical nitrogen atoms and the copper atom is 165.26(9)°, whereas those formed by the metal and two cis ligands differ from 90°, with values in the range 82.30(11)–97.6(7)°.

Two of the bond distances between the copper atom and the four nitrogen atoms of the 1,10-phenanthroline molecules are significantly longer, 2.3489(17) Å, than the other two, 2.1142(19) Å. The longer distances are associated with the apical nitrogen atoms. The value of 2.1142(19) Å can be considered as normal and is similar to those found in other copper complexes with bidentate 1,10-phenanthroline or 2,2'-bipyridine ligands [33,34]. However, the distance of 2.3489(17) Å is unusually high and is similar to the longest Cu-N distance found in  $[Cu(phen)_3]^{2+}$ , a compound with a very pronounced Jahn-Teller distortion [34]. The Cu-Namide bond length, 2.020(2) Å, is significantly shorter than those generally observed in other hexacoordinated copper complexes with tosylamides, such as bis[(N-4-toluenesulfonyl-2-pyridylaminato-N, N')-pyridyl] copper(II) [35], 2.548 and 2.387 Å. This bond is slightly longer than those reported for tetracoordinated copper complexes involving sulfonamides. For example, 1.999(2) Å bis{4-methyl-N-(2-pyridin-2-ylin square planar ethyl)benzenesulfonamide}copper(II) [30]. However, it is similar to that found in pentacoordinated copper(II) complexes; e.g. 2.041(5) and 2.031(5) Å in [CuL<sub>2</sub>dmf], where HL is N-(p-tolylsulphonyl)-o-phenylenediamine [36], or 2.044(3) Å in  $\{(1,10\text{-phenanthroline})[N-2(\text{oxo-}$ phenyl)-methylidine]-N'-tosylbenzene-1,2-diaminato}copper(II) [32].

Each of the phenanthroline ligands is planar within experimental error; the intraligand bond lengths and angles are similar to those found in other complexes and will not be discussed further.

#### 3.4. Structure of [ZnL(phen)<sub>2</sub>]

The molecular structure of  $[ZnL(phen)_2]$ , along with the atom labelling scheme, is illustrated in Fig. 3.

Selected bond lengths and angles, with estimated standard deviations are given in Table 4. The zinc atom is located on a crystallographic twofold axis and is coordinated to the two amide nitrogen atoms of the dianionic tosylamide ligand and to four nitrogen atoms of two phenanthroline molecules. The coordination polyhedron around the zinc atom is distorted octahedral. The small bite angles of the ligands, particularly in the case of the neutral 1,10-phenanthroline ligand, are the main reason for the distortion. Thus, the values of the N<sub>phen</sub>-Zn- $N_{phen}$  and  $N_{amide}\mathchar`-\mbox{Zn-}\mbox{N}_{amide}$  angles are 74.32(2) and 81.7(2)°, respectively. One of the amide nitrogen atoms, N(1), and one nitrogen atom, N(3)', of a phenanthroline molecule are in trans positions and, consequently, if these are considered as the apical positions then the equatorial plane is formed by the other amide

nitrogen atom of the tosylamide ligand and the other three nitrogen atoms of the 1,10-phenanthroline molecules. Two of the nitrogen atoms of this plane, N(1)\* and N(3), are below the best equatorial square plane by 0.112(2) and 0.138(2) Å, respectively, while N(2) and N(2)\* are above it by 0.138(2) and 0.113(2) Å, respectively. The zinc atom is 0.125(2) Å out of this equatorial plane. The N–Zn–N bond angles within the equatorial plane differ markedly from those of a regular octahedron; cis, 74.32(13)–99.90(13)° and trans, 159.81–169.59(14)°. The axial positions form an angle N–Zn–N of 169.59(14)°. This distortion is caused mainly by the small bite angle, 74.32(13)°, of the phenanthroline ligands.

Two different Zn–N bond distances are observed; the bonds involving amide nitrogen atoms, 2.092(4) Å, are



Fig. 1. Perspective view of [NiL(phen)<sub>2</sub>] (50% probability displacement ellipsoids).



Fig. 2. Perspective view of [CuL(phen)<sub>2</sub>] (50% probability displacement ellipsoids).



Fig. 3. Perspective view of [ZnL(phen)<sub>2</sub>] (50% probability displacement ellipsoids).



Fig. 4. Perspective view of [CdL(phen)<sub>2</sub>] (50% probability displacement ellipsoids).

significantly shorter than those involving phenanthroline nitrogen atoms, 2.202(3) and 2.247(4) Å. These latter bonds are slightly longer than those found in other octahedral zinc compounds that contain phenanthroline; e.g. in  $[Zn(pyS)_2phen]$  [37] [average value 2.182(7) Å] or in  $[Zn(O_2C_6H_4)(phen)_2]$  [38] (2.189 Å). The Zn-N<sub>amide</sub> bond distances, 2.092(4) Å, are greater than those found in tetrahedral compounds containing anionic nitrogen atoms; e.g. 1.962(5) Å in bis{*N*-[(2pyrrolyl)methylidyne]-*N'*-tosylbenzene-1,2-diaminato}zinc(II) [39]. However, this distance is shorter than those found in the octahedral amide zinc(II) complex  $[Zn(C_7H_4NO_3S)_2(H_2O)_4]$ , 2.201(2) Å, where  $C_7H_4NO_3S$ is the anion of saccharine [40].

Each 1,10-phenanthroline ligand is essentially planar, with no atom deviating from the least-squares plane by more than 0.050 Å. In addition, the bond lengths and angles within the ligand are similar to those found in

other 1,10-phenanthroline complexes. The phenanthroline molecules are almost perpendicular to one another, dihedral angle of  $80.26(5)^\circ$ , and form dihedral angles with the equatorial plane of 81.12(6) and  $7.86(13)^\circ$ .

#### 3.5. Structure of [CdL(phen)<sub>2</sub>]

A perspective view of the molecular structure of  $[CdL(phen)_2]$ , along with the atom labelling scheme, is illustrated in Fig. 3. Selected bond distances and angles with estimated standard deviations are given in Table 5.

The structure of  $[CdL(phen)_2]$  shows that the cadmium atom is located on a twofold axis and is coordinated to the nitrogen atoms of two bidentate 1,10-phenanthroline molecules and to the amide nitrogen atoms of the dianionic ligand in a distorted octahedral  $[CdN_6]$  coordination environment. The Cd–N<sub>amide</sub> bond lengths are shorter, 2.2827(14) Å, than the Cd– $N_{phen}$  bond lengths, 2.3866(14) and 2.4103(14) Å, probably because in the former case the ligand is anionic, whereas the other ligands are neutral.

The Cd– $N_{amide}$  bond length is quite similar to those found in other hexacoordinated complexes of cadmium(II); e.g. 2.234(12) and 2.280(10) Å in 1,10-phenanthroline bis{[(4-methylphenyl)sulfonyl]-2-pyridylamide}- cadmium(II) [41]. The Cd– $N_{phen}$  bond lengths, 2.3866(14) and 2.4103(14) Å, are slightly longer than those found in the above complex, 2.304(11) and 2.374(10) Å.

The trans atoms N(1') and N(2) of the equatorial plane described by [N(2)N(3)N(1')N(3')] are below the least-squares plane by -0.1689(5) and -0.23338(8) Å,



Fig. 5. EPR spectra of the  $[CuL(phen)_2]$  as: (a) solid state powder sample and (b and c) as a tetrahidrofurane (THF) solution. Spectra were measured at 120 K, 0.1 mT of amplitude modulation as a first and second harmonic and 10 mW of microwave power. The second harmonic measurement was done with 64 scans to improve signal-to-noise ratio. The spectral simulations are presented as dot lines.

Table 6						
EPR parameters e	extracted by compu-	ing simulation fron	n EPR spectr	a of the sample	[CuL(phen) <sub>2</sub> ] as a j	powder and THF solution

Type of sample	Nuclei	$g_x \pm 0.0003$	$g_y \pm 0.0003$	$g_z \pm 0.0003$	$A_x$ (MHz)	$A_y$ (MHz)	$A_z$ (MHz)	$\Delta H_x$ (MHz)	$\Delta H_y$ (MHz)	$\Delta H_z$ (MHz)
Powder	Cu(II) N-equatorial N-apical	2.0470	2.1030	2.2580	5 20 5	5 12 5	408 5 15	45	50	360
THF solution	Cu(II) N-equatorial N-apical	2.0530	2.0860	2.2830	5 35 5	5 35 5	438 5 35	25	25	25

The Cu(II) ion are coordinated by four equatorial nitrogen nuclei and two apical nitrogen nuclei. The EPR measurements was done at temperature of 120 K.



Fig. 6. EPR spectra of the [NiL(phen)<sub>2</sub>] as a solid state powder sample: is the spectrum at X-band (a) and (b) Q-band. Spectra were measured at 293 K, 0.4 mT of amplitude modulation and 10 mW of microwave power. A Cr(III), as impurity in MgO crystal, was used as g-marker.

respectively, while N(3) and N(3') are above it by + 0.2309(8) and + 0.1718(6) Å, respectively. This situation leads to an N(1)–Cd–N(2') angle of 164.42(5)°. The cadmium atom is 0.140(1) Å out of the equatorial plane.

The 1,10-phenanthroline ligands are planar, with dihedral angles between them of  $77.81^{\circ}$  and dihedral angles between them and the equatorial plane of 8.92(6) and  $81.19(3)^{\circ}$ .

### 3.6. Spectroscopic studies

The v(NH) band in the free ligands appears at 3275 cm<sup>-1</sup> but is not observed in the IR spectra of the complexes. This observation indicates that the amide hydrogen atoms are lost during the electrochemical process. In addition, the spectra of the complexes also show bands at 1510, 850, and 730 cm<sup>-1</sup> due to the coordinated phenanthroline molecules [42]. All these data are in accordance with a hexacoordinated geometry for these complexes.

The FAB mass spectra of the compounds show, in all cases, the molecular ion  $[ML(phen)_2]$  (m/z 785, 790, 791 and 839, respectively, for M = Ni, Cu, Zn and Cd), as well as a peak associated with [MLphen] formed by loss

of one phenanthroline ligand from the initial species  $(m/z \ 605, \ 610, \ 611 \ and \ 661, \ respectively, \ for M = Ni, Cu, Zn and Cd). The spectra also show a peak for the [M(phen)<sub>2</sub>] fragment <math>(m/z \ 418, \ 423, \ 424 \ and \ 473, \ respectively, \ for M = Ni, Cu, Zn and Cd) \ formed by loss of the amide ligand and another peak for [Mphen] [<math>m/z \ 238 \ (100\%), \ 243 \ (100\%), \ 244 \ (67\%) \ and \ 294 \ (100\%), \ for M = Ni, Cu, Zn and Cd, \ respectively] \ formed by loss of both the amide ligand and one of the phenanthroline molecules.$ 

In the cases of the zinc and cadmium complexes, the <sup>1</sup>H NMR spectra provide further evidence for the above conclusions. The spectrum of the ligand shows one singlet at 5.30 ppm, which is assigned to the amide proton, and signals at 3.05 and 2.43 ppm, assigned to the methylene and methyl protons, respectively. A multiplet due to the aromatic hydrogen atoms is observed in the range 7.7-7.3 ppm. The spectra of  $[ZnL(phen)_2]$  and  $[CdL(phen)_2]$  show that the signal due to the amide proton is absent, reinforcing the conclusion drawn form the IR spectra that the ligands are coordinated to the metal in their dianionic form.

On the other hand, the signals due to the methylene groups are shifted to low field and the signals due to the 1,10-phenanthroline hydrogen atoms to high field. This can be taken as further evidence for coordination of the amide ligand and coordination of the phenanthroline to the metal centre. This conclusion is supported by the X-ray diffraction structures of  $[ML(phen)_2]$ .

The solid reflectance spectrum of the  $[CuL(phen_2)]$  complex shows an asymmetric band around 13 600 cm<sup>-1</sup>, which is typical of copper(II) species with a hexacoordinated geometry [43] and is in agreement with the structure of  $[CuL(phen)_2]$  established by X-ray diffraction. The magnetic moment of the copper(II) complex (1.91 BM) is close to the spin value for one unpaired electron and within the general range for Cu(II) complexes.

The solid state powder EPR spectrum at 120 K is shown in Fig. 5(a). The main feature is the presence of a non-resolved broad signal in the low field region. This spectrum can be assigned to a distorted octahedral complex with three different g values, as described in Table 6. When the powder sample is dissolved in tetrahydrofuran (THF) and frozen at 120 K, the EPR spectrum shows a detailed hyperfine splitting from the interaction of the unpaired electron spin with the copper nuclear spin and superhyperfine splitting from the nuclear spin of the surrounding nitrogen atoms. Fig. 5(b and c) show these results with the best simulations. The parameters of the best fit are shown in Table 6. The simulation was obtained on the assumption that the four equatorial nitrogen atoms are equivalent and that the two apical ones are equivalent but different from the equatorial ones. The isotropic values  $A_0 =$ 

 $(A_x + A_y + A_z)/3$  for the superhyperfine interactions show that the unpaired electron is more concentrated on the equatorial nitrogen nuclei ( $A_0 = 25$  MHz) than on the apical nuclei ( $A_0 = 15$  MHz), as expected from the crystal data. The  $A_z$  value for the hyperfine interaction with the copper nuclear spin is smaller ( $A_z = 438$ MHz, or 13.8 mT) than the values found in other copper compounds containing nitrogen ligands [43-45]. This could be due to delocalization of the unpaired electron over the six surrounding nitrogen atoms. The unpaired electron could be described as occupying a  $d_{x^2-y^2}$  orbital mixed with the four in-plane p orbitals of the equatorial nitrogen atoms and a  $d_{z^2}$  orbital mixed with the  $p_z$  orbitals of the apical nitrogen atoms. The powder results, where the hyperfine lines are quite collapsed, were simulated using Lorentzian or Gaussian line shapes, as shown in Fig. 5(a). It should be noted that in the low field region the Lorentzian lines gave the best fit, whereas the Gaussian line shapes are better in the high field region. As the dissolved sample do not change ligands, the crystal packing needs to be responsible of the collapsing of the hyperfine EPR lines. The crystal structure shows that the hydrogen atoms H(11)and H(16) are close, 2.62 and 2.56 A, respectively, to the O(2) atom of the neighbouring molecule. These interactions could provide a superexchange pathway that induces the observed line collapse with an angular dependence of the linewidth, as occurs in other crystalline copper compounds [46-48].

The solid state powder EPR spectra of the Ni compound at room temperature are shown in Fig. 6(a and b) (in the X- and Q-band, respectively). Broad non-resolved signals with resonance fields of 156.20 and 1103.60 mT can be observed at microwave frequencies of 9371.91 and 34493.03 MHz, respectively. The spectrum can be explained as resulting from the ion in an octahedral distorted symmetry where the energy levels are lifted by zero field splitting terms. If axial symmetry is assumed, the resonance frequencies will be given by the expression:

 $hv = D \pm g\beta H$ 

corresponding to the transition from the energy level with m = 0 to that with  $m = \pm 1$ . In this expression *h* is the Planck constant,  $\beta$  is the Bohr magneton, *g* is the giromagnetic factor and *D* is a zero field splitting. On using the values of the resonance fields at the X- and Q-band, and assuming a value of g = 2.0, a value of D = 0.167 cm<sup>-1</sup> is obtained. *D* is less than the Zeeman energy values (D < hv) at both microwave frequencies.

The solid state electronic spectrum for the nickel(II) complex [NiL(phen)<sub>2</sub>] shows bands at approximately 10 500, 18 250 and 24 900 cm<sup>-1</sup>, which can be assigned to the transitions  ${}^{3}A_{2g} \rightarrow {}^{4}T_{2g}(v_{1})$ ,  ${}^{3}A_{2g} \rightarrow {}^{4}T_{1g}$  (F) ( $v_{2}$ ) and  ${}^{3}A_{2g} \rightarrow {}^{4}T_{1g}$ (P) ( $v_{3}$ ), respectively [49]. This data is in

accord with a hexacoordinate environment around the nickel atom.

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