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Electrochemical synthesis of nickel(II) complexes of tosylamides: crystal structures of [(4-methylphenyl)sulfonyl]-imino-1H-pyridine], 2,2′-bipyridine bis{[(4-methylphenyl) sulfonyl]-2-pyridyl-amide}nickel(II) and 1,10-phenanthroline bis{[(4-methylphenyl) sulfonyl]-2-pyridyl-amide}nickel(II)

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Abstract

The complex [NiL_2] has been synthesised by the electrochemical oxidation of nickel in an acetonitrile solution of [(4-methylphenyl)sulfonyl]-imino-1H-pyridine (HL). When the oxidation was carried out in the presence of neutral ligands L′ (pyridine, 2,2′-bipyridine or 1,10-phenanthroline) the complexes [NiL_2py_2], [NiL_2bipy] and [NiL_2phen] were obtained. The crystal structures of [(4-methylphenyl)sulfonyl]-imino-1H-pyridine, 2,2′-bipyridine bis{[(4-methylphenyl)sulfonyl]-2-pyridyl-amide}nickel(II) and 1,10-phenanthroline bis{[(4-methylphenyl) sulfonyl]-2-pyridyl-amide}nickel(II) were determined by X-ray diffraction methods. In the monomeric complexes, the nickel atom is in a distorted octahedral environment defined by the amide and pyridyl nitrogen atoms of the two ligands and the two bipyridine or phenanthroline nitrogen atoms. The vibrational and electronic spectra of the complexes are discussed and are shown to agree with the structures. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Electrochemical synthesis; Nickel (II) complexes; Amide complexes; X-ray

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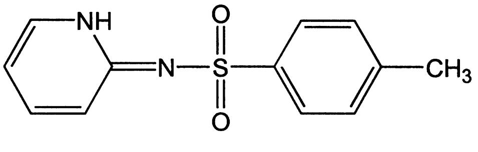
1. Introduction

It is well known that metal complex formation by the substitution of a metal ion for an amide proton is a very difficult process [1]. However, this process is facilitated by the presence of an additional donor atom on the molecule, permitting the formation of a stable five or six membered chelate ring with the metal ion [2,3], or by the presence in the amide group of groups, such as tosyl, which have a strong inductive electronic effect and thereby increase the acidity of the amide hydrogen.



For these reasons, and as a result of our interest in the metallic complexes of amide ligands, we now report the electrochemical synthesis of a nickel(II) complex with [(4-methylphenyl)sulfonyl]-imino-1H-pyridine (HL), a molecule containing a weakly acidic N–H group and a pyridine ring which can lead to chelation involving the pyridine nitrogen and the deprotonated nitrogen of the amide. We have also prepared mixed complexes containing this anionic ligand and pyridine (py), 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen) by the same method.

2. Experimental

Acetonitrile, dichloromethane, 2-aminopyridine, tosyl chloride, pyridine, 2,2′-bipyridine, 1,10-phenanthroline and all other reagents were commercial products and were used as supplied. Nickel (Aldrich Chemie) was used as 2×2 cm plates.

The parent molecule, HL (1) was prepared by reaction of the amine and the tosyl chloride in a 2:1 ratio in

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dichloromethane. A diluted aqueous solution of K_2CO_3 was added to the mixture until pH 10 and the resultant white product collected by filtration of the organic phase, and dried in vacuo. Anal: C: 58.19%, H: 5.06%, N: 11.33%, S: 12.98%; Calc for $C_{12}H_{12}N_2SO_2$: C: 58.05%, H: 4.88%, N:11.29%, S: 12.91%. ^{1}H NMR (Cl_3CD, ppm) 2.4 -CH_3; 13.6 N–H; 7.8, 7,3 benzene ring; 6.8, 7.4, 7.6, 8.3 pyridine ring. IR (KBr, cm^{-1}): 3230(m); 3127(m); 3056(w); 1915(w); 1866 (w); 1793(w); 1654 (sh); 1635(s); 1534 (m); 1463(w); 1393(m); 1375 (m); 1282 (m); 1086(m); 1035(w); 1020(w); 999(m); 959(m); 807(m); 785(m); 732(w) 704(w); 668(m); 633(w); 613(w); 572(m); 552(m); 515 (w). The product was recrystallised from $CH_3CN/(CH_3)_2CO$ to give crystals suitable for X-ray diffraction crystallography.

2.1. Electrochemical synthesis

The electrochemical procedure was similar to that described by Odlhan and Tuck [4]. The cell was a 100 cm^3 beaker fitted with a rubber bung through which the electrochemical leads entered the cell. The nickel anode was suspended from a platinum wire, and another platinum wire formed the cathode. The tosyl parent (HL) and the additional ligand (py, bipy or phen) were dissolved in acetonitrile–dichloromethane and a small amount of tetraethylammonium perchlorate (ca. 20 mg) was added as current carrier. Direct current was obtained from a purpose-built d.c. power supply. In all cases, hydrogen was evolved at the cathode. The cells can be summarised as: $Pt_{(-)}/CH_3CN+HL+(\text{py, bipy or phen})/Ni_{(+)}$.

[NiL_2] (**2**). Electrolysis of an acetonitrile–dichloromethane (25+25 cm^3) solution containing HL (200 mg, 0.81 mmol) and tetraethylammonium perchlorate (ca. 20 mg) at 10 mA and 12 V for 2 h dissolved 21.2 mg of nickel ($E_f=0.48$). At the end of the experiment the green/blue crystalline solid was filtered, washed with acetonitrile and diethyl ether, dried in vacuo, and crystallised from CH_3CN. The compound was characterised as [NiL_2].H_2O: Anal. Found: H, 3.91%; C, 50.21%; N 10.48%; S, 10.83%. Calc. for [$C_{24}H_{24}N_4O_5S_2Ni$]: H, 4.23%; C, 50.46%; N 9.81%; S, 11.22%. IR(KBr, cm^{-1}) 2360(vw); 1733(w); 1384(w); 1590(s); 1563(w); 1506(m); 1457(m); 1318(m); 1267(m); 1137(m); 1091(m); 1041(w); 1012(m); 991(m); 818(w); 793(m); 769(s); 748(w); 709(m); 668(m); 651(m); 577(m) 553(m); 418(w).

[NiL_2py_2] (**3**). Electrolysis of an acetonitrile–dichloromethane (25+25 cm^3) solution containing HL (190.0 mg, 0.77 mmol), pyridine (127 mg, 1.60 mmol) and tetraethylammonium perchlorate (ca. 20 mg) at 10 mA and 7 V for 2 h dissolved 18.3 mg of nickel ($E_f=0.42$). At the end of the experiment the solid product was filtered, washed with hot acetonitrile and diethyl ether and dried in vacuo. The compound was characterised as [NiL_2py_2]: Anal. Found: H, 4.36%; C, 57.16%; N 11.52%; S, 8.43%. Calc. for [$C_{34}H_{32}N_6O_4S_2Ni$]: H, 4.53%; C, 57.40%; N 11.81%; S, 9.01%. IR (KBr, cm^{-1}): 3061(w); 1595(s); 1559(m); 1464 (s); 1267(m); 1133(s); 1091(m); 1020(m); 988(m); 780(m); 759(m); 703(m); 662(s) 631(w); 577(m); 555(m); 531(m); 437(m).

[NiL_2bipy] (**4**). Electrolysis of an acetonitrile–dichloromethane (25+25 cm^3) solution containing HL (200.3 mg, 0.81 mmol), 2,2′-bipyridine (53.2 mg, 0.40 mmol) and tetraethylammonium perchlorate (ca. 20 mg) at 10 mA and 14 V for 2 h dissolved 20.5 mg of nickel ($E_f=0.47$). At the end of the experiment the blue-grey solid was filtered, washed with hot acetonitrile and diethyl ether and dried in vacuo. This solid was recrystallised from $(CH_3)_2CO/CH_3CN$ to give crystals suitable for X-ray diffraction. The compound was characterised as [NiL_2bipy].$(CH_3)_2CO$. Anal. Found: C, 57.57%; H, 4.66%; N, 11.38%; S, 7.89%. Calc. for [$C_{37}H_{36}N_6NiO_5S_2$]: C, 57.90%; H, 4.73%; N, 10.95%; S, 8.36%. IR (KBr, cm^{-1}): 3094(vw); 3060(vw); 1706(m); 1592(s); 1559(w); 1461(s); 1438(s); 1319(s); 1140(s); 1112(w) 1089(m); 1043(w); 1010(m); 984(m); 813(w); 773(m); 735(m); 709(w); 668(m); 657(m); 577(s); 553(m).

[NiL_2phen] (**5**). Electrolysis of an acetonitrile–dichloromethane (25+25 cm^3) solution containing HL (220.4 mg, 0.89 mmol), 1,10-phenanthroline (80.0 mg, 0.44 mmol) and tetraethylammonium perchlorate (ca. 20 mg) at 10 mA and 10 V for 2 h dissolved 20.2 mg of nickel ($E_f=0.46$). At the end of the experiment the blue-grey solid was filtered, washed with hot acetonitrile and diethyl ether and dried in vacuo. This solid was recrystallised from $(CH_3)_2CO/CH_3CN$ and crystals suitable for X-ray diffraction were obtained. The compound was characterised as [NiL_2phen]: Anal. Found: C, 58.61%; H, 4.05%; N, 11.51%; S, 8.90%. Calc. for [$C_{36}H_{30}N_6O_4S_2Ni$]: C, 58.95%; H, 4.12%; N, 11.46%; S, 8.74%. IR (KBr, cm^{-1}): 3056(vw); 3025(vw); 1652(m); 1589(s); 1557(m); 1520(m); 1495(w); 1457(m); 1134(m); 1010(m); 844(m); 776(m); 728(m); 707(m); 675(m); 655(m); 577(m); 552(m).

2.2. Physical measurements

The C, N, H and S contents of the compounds were determined on a Carlo-Erba EA 1108 microanalyser. IR spectra were recorded as KBr mulls on a Bruker Vector-22 spectrophotometer. The ^{1}H NMR spectra were recorded on a Bruker ARX-400 MHz spectrometer using Cl_3CD as solvent. 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

The data collection was on a SIEMENS Smart CCD area-detector diffractometer with graphite-monochromated Mo K_α radiation, $\lambda=0.71073$ Å at room temperature.

All the structures were solved by direct methods [5] and

Table 1
Summary of crystal data and structure refinement

Compound	HL (**1**)	$[NiL_2bipy]\cdot(CH_3)_2CO$. (**4**)	$[NiL_2phen]$ (**5**)
Empirical formula	$C_{24}H_{24}N_4O_4S_2$	$C_{37}H_{36}N_6O_5S_2Ni$	$C_{36}H_{30}N_6NiO_4S_2$
Formula weight	496.59	767.55	733.49
Crystal system/space group	Monoclinic/$P2_1/c$ (No. 14)	Orthorhombic/$P2_12_12_1$ (No. 19)	Orthorhombic/$P2_12_12_1$ (No. 19)
Unit cell dimensions	$a=10.8142(5)$ Å $b=15.1088(7)$ Å $c=14.7701(7)$ Å $\beta=104.1583(13)°$	$a=10.247(2)$ Å $b=14.298(5)$ Å $c=25.199(7)$ Å	$a=10.46150(10)$ Å $b=14.0533(2)$ Å $c=25.7907(4)$ Å
Volume	2340.0(2) $Å^3$	3692(2) A^3	3791.71(9) $Å^3$
Z	4	4	4
Density (calculated)	1.410 Mg/m^3	1.381 Mg/m^3	1.285 Mg/m^3
Absorption coefficient	0.267 mm^{-1}	0.689 mm^{-1}	0.666 mm^{-1}
$F(000)$	1040	1600	1520
Crystal size/colour	0.60×0.25×0.15 mm/White	0.35×0.15×0.10 mm/grey-blue	0.30×0.25×0.15 mm/grey-blue
Theta range for data collection	1.94 to 28.30°.	1.62 to 28.29°	1.58 to 28.39°
Index ranges	$-10\leq h\leq 14$, $-20\leq k\leq 20$, $-19\leq l\leq 19$	$-13\leq h\leq 13$, $-19\leq k\leq 10$, $-33\leq l\leq 33$	$-12\leq h\leq 13$, $-18\leq k\leq 16$, $-26\leq l\leq 34$
Reflections collected	12281	19790	21155
Independent reflections	5713 [$R(int)=0.1015$]	9077 [$R(int)=0.1900$]	9373 [$R(int)=0.1102$]
Reflections observed	2256	3177	4448
Criterion for observation	$>2\sigma(I)$	$>2\sigma(I)$	$>2\sigma(I)$
Data/restraints/parameters	5713/0/403	9077/0/460	9373/0/442
Goodness-of-fit on F^2	0.915	1.018	0.957
Final R indices [$I>2\sigma(I)$]	$R_1=0.0672$, $wR_2=0.1298$	$R_1=0.0903$, $wR_2=0.1415$	$R_1=0.0834$, $wR_2=0.1793$
Absolute structure parameter		−0.03(3)	0.03(3)
Largest diff. peak and hole	0.300 and −0.558 e $Å^{-3}$	0.532 and −0.615 e $Å^{-3}$	0.650 and −0.713 e A^{-3}

refined by a full-matrix least-squares based on F^2 [6]. Non hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealised positions and refined with isotropic displacement parameters, except those from the free ligand which were located. The SQUEEZE program [7] was used to correct the reflection data for the diffuse scattering due to disordered solvent found in the $[NiL_2phen]$ complex. Correct absolute structures of both complexes were determined by using the Flack parameter. Atomic scattering factors and anomalous dispersion corrections for all atoms were taken from International Tables for X-ray Crystallography [8]. Details of crystal data and structural refinement are given in Table 1.

3. Results and discussion

Anodic oxidation of nickel metal in the presence of (4-methylphenyl)sulfonyl]-imino-1H-pyridine, alone or dissolved with the coligands pyridine (py), 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen) yields crystalline products with formula $[NiL_2]$, $[NiL_2py_2]$, $[NiL_2bipy]$ and $[NiL_2phen]$, respectively. The values of the electrochemical efficiency, defined as the amount of metal dissolved per number of Faradays, were close to 0.5 mol F^{-1} in all cases. This value is compatible with the mechanism,

$$\text{Cathode: } HL + 2e^- \rightarrow 2L^- + H_2$$

$$\text{Anode: } Ni \rightarrow Ni^{2+} + 2e^-$$

The overall reactions can be described as

$$Ni + 2HL \rightarrow [NiL_2] + H_2$$

$$Ni + 2HL + nL' \rightarrow [NiL_2L'_n] + H_2.$$

3.1. Description of the structure of HL, (1).

Fig. 1 shows a view of **1** together with the atomic

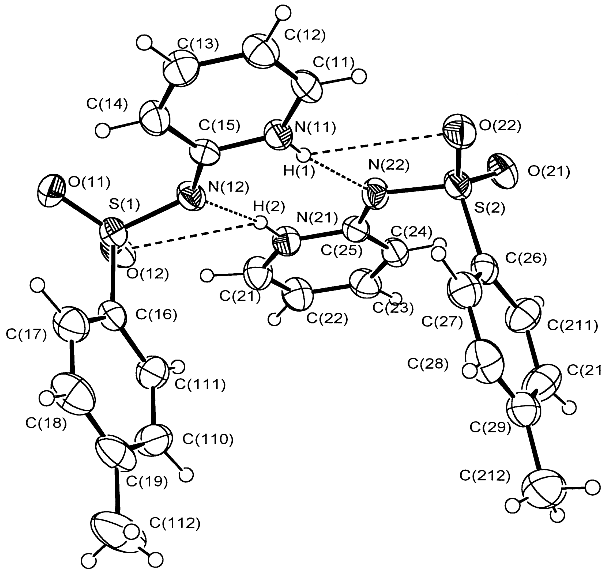


Fig. 1. ORTEP draw of the compound HL (**1**) showing the atom label scheme and the hydrogen bonds.

Table 2
Selected bond lengths [Å] and angles [°] for HL (**1**)

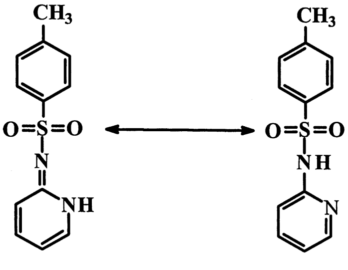
S(1)–O(11)	1.433(3)	S(1)–O(12)	1.435(3)
S(1)–N(12)	1.611(3)	S(1)–C(16)	1.767(4)
N(11)–C(11)	1.339(5)	N(11)–C(15)	1.362(5)
N(12)–C(15)	1.346(4)	C(14)–C(15)	1.406(5)
S(2)–O(22)	1.439(3)	S(2)–O(21)	1.451(3)
S(2)–N(22)	1.600(3)	S(2)–C(26)	1.762(4)
N(21)–C(21)	1.358(5)	N(21)–C(25)	1.364(5)
N(22)–C(25)	1.354(5)	C(24)–C(25)	1.411(6)
O(11)–S(1)–O(12)	117.7(2)	O(11)–S(1)–N(12)	114.0(2)
O(12)–S(1)–N(12)	104.9(2)	O(11)–S(1)–C(16)	107.5(2)
O(12)–S(1)–C(16)	106.6(2)	N(12)–S(1)–C(16)	105.2(2)
C(11)–N(11)–C(15)	124.2(4)	C(15)–N(12)–S(1)	123.1(3)
N(11)–C(11)–C(12)	121.3(4)	N(12)–C(15)–N(11)	114.0(3)
N(12)–C(15)–C(14)	130.7(4)	N(11)–C(15)–C(14)	115.2(4)
O(22)–S(2)–O(21)	117.3(2)	O(22)–S(2)–C(26)	107.4(2)
O(21)–S(2)–N(22)	113.9(2)	O(21)–S(2)–C(26)	107.0(2)
N(22)–S(2)–C(26)	105.6(2)	O(22)–S(2)–N(22)	105.0(2)
C(21)–N(21)–C(25)	123.8(4)	C(25)–N(22)–S(2)	122.1(3)
C(22)–C(21)–N(21)	119.7(5)	N(22)–C(25)–N(21)	113.4(4)
N(22)–C(25)–C(24)	130.7(4)	N(21)–C(25)–C(24)	115.8(4)

Table 3
Hydrogen bonds in the asymmetric unit of the ligand

Atoms: A···HD	d(D–H)	d(H..A)	d(D..A)	<DHA
N(12)···H(2)–N(21)	0.90(4)	2.01(4)	2.909(5)	169.9°
N(22)···H(1)–N(11)	0.83(4)	2.13(4)	2.959(5)	172.4°
O(12)···H(2)–N(21)	0.90(4)	2.78(4)	3.266(5)	115.3°
O(22)···H(1)–N(11)	0.83(4)	2.86(4)	3.330(4)	117.7°

number scheme. Selected bond lengths and angles with the estimated deviations are listed in Table 2. The bond distances and bond angles are similar to those found in other N-2-pyridinyl benzenesulfonamide derivatives [9–12].

The most relevant feature is the presence of the hydrogen atom on the N-pyridine ring, indicating that the free ligand is the imido tautomer (I) rather than the amido tautomer (II).



I **II**

Both, the phenyl and the pyridine rings are almost planar, with the largest deviations being 0.012(3) and 0.008(3) Å, respectively. The interplanar angles of 83.69(10)° and 87.62(11)° are similar to those found in other sulfonamides [11]. In addition, the molecules of [(4-methylphenyl)sulfonyl]-imino-1H-pyridine are associated by intermolecular hydrogen bonds between the atoms in two independent molecules of the unit cell, leading to the formation of a dimer. These hydrogen bonds are between the pyridine nitrogen atom of one molecule and the amide nitrogen atom of the other neighbour. In addition, one oxygen atom of the sulfone group [O(22), O(12)] of one molecule is involved in a hydrogen bond with the nitrogen of the pyridine ring [N(11), N(21)] of the other, so each H(N) atom is participating in a bifurcated hydrogen bond with the N_{amide} and one oxygen atom of the other molecule in the asymmetric unit. These bond lengths and angles are given in Table 3.

*3.1.1. Description of the structures of [NiL$_2$bipy] (**4**) and [NiL$_2$phen] (**5**)*

The molecular structures of **4** and **5** are shown in Figs. 2 and 3. Selected bond lengths and angles are given in Tables 4 and 5, respectively. The complexes are isostructural, with the nickel atom in a highly distorted octahedral

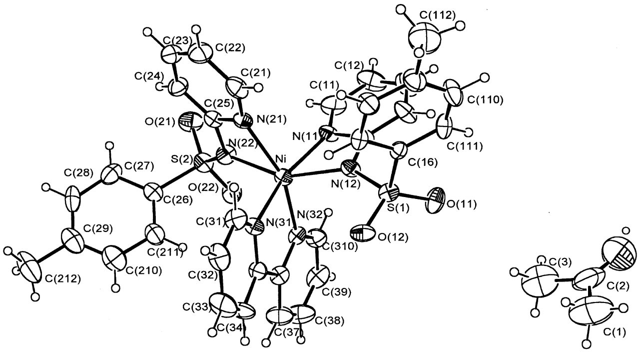


Fig. 2. ORTEP drawing of [NiL$_2$bipy](CH$_3$)$_2$CO (**4**). The ellipsoids correspond to 30% probability.

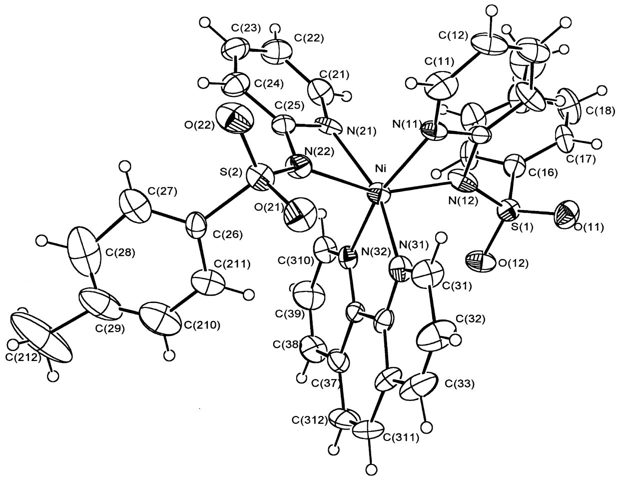


Fig. 3. ORTEP drawing of [NiL$_2$phen] (**5**). The ellipsoids correspond to 30% probability.

Table 4
Selected bond lengths [Å] angles [°] for [NiL$_2$bipy]·(CH$_3$)$_2$CO (**4**)

Ni–N(32)	2.047(5)	Ni–N(31)	2.061(5)
Ni–N(11)	2.089(5)	Ni–N(22)	2.101(7)
Ni–N(12)	2.104(6)	Ni–N(21)	2.142(6)
S(1)–N(12)	1.601(7)	N(11)–C(15)	1.349(3)
N(11)–C(11)	1.352(3)	N(12)–C(15)	1.403(8)
S(2)–N(22)	1.580(7)	S(1)–C(16)	1.762(6)
N(21)–C(21)	1.329(3)	N(21)–C(25)	1.357(3)
N(22)–C(25)	1.393(8)	S(2)–C(26)	1.771(7)
N(31)–C(31)	1.324(3)	N(31)–C(35)	1.333(3)
N(32)–C(310)	1.336(3)	N(32)–C(36)	1.364(3)
N(32)–Ni–N(31)	79.8(2)	N(32)–Ni–N(11)	98.6(2)
N(31)–Ni–N(11)	163.3(2)	N(32)–Ni–N(22)	99.1(2)
N(31)–Ni–N(22)	102.8(3)	N(11)–Ni–N(22)	93.9(3)
N(32)–Ni–N(12)	97.1(3)	N(31)–Ni–N(12)	100.5(2)
N(11)–Ni–N(12)	63.1(2)	N(22)–Ni–N(12)	153.6(3)
N(32)–Ni–N(21)	159.0(2)	N(31)–Ni–N(21)	93.3(2)
N(11)–Ni–N(21)	93.6(2)	N(22)–Ni–N(21)	62.9(2)
N(12)–Ni–N(21)	103.7(3)	N(12)–S(1)–C(16)	105.8(3)
C(15)–N(12)–S(1)	121.4(5)	N(11)–C(15)–N(12)	105.6(5)
C(14)–C(15)–N(12)	131.6(5)	N(22)–S(2)–C(26)	105.1(4)
C(25)–N(22)–S(2)	123.7(6)	N(21)–C(25)–N(22)	107.2(5)
C(24)–C(25)–N(22)	130.3(5)		

environment, [NiN$_6$]. Two of the nitrogen atoms belong to a bidentate bipyridine or phenanthroline ligand, and two anionic forms L$^-$ groups each provide an amide and a pyridine nitrogen atom; so that each forms a four-membered chelate ring. The arrangement of the two ligands is such that the two amide nitrogen atoms are in a *cis* arrangement and the two pyridine nitrogen atoms are *trans* to each other. The distortion of the octahedral geometry is mainly due to the small bite of the ligand, with an average angle $\mathrm{N_{py}}$–Ni–$\mathrm{N_{amide}}$ of 63.0(2)° for [NiL$_2$bipy] and 63.8(2)° for [NiL$_2$phen]. These values are similar to those found in other nickel(II) complexes containing four-member N,N-chelate rings; e.g. N–Ni–N, 59.07° and 59.73° in bis(μ_2-hydroxo)-(μ_2-1,2-bis(phenyltriazenidyl) benzene-N,N′,N″,N‴)-bis(1,2-bis(phenyltriazenidyl)benzene)-di-nickel(II) [13] and 66.68° in chloro-(6-methoxymethyl-1,3,6,8,11,14-hexa-azabicyclo(12.2.1)heptadecane-N,N′,N″,N‴,N⁗)-nickel(II)perchlorate [14].

Table 5
Selected bond lengths [Å] angles [°] for [NiL$_2$phen] (**5**)

Ni–N(31)	2.031(6)	Ni–N(32)	2.052(6)
Ni–N(11)	2.063(5)	Ni–N(22)	2.095(6)
Ni–N(12)	2.096(6)	Ni–N(21)	2.110(6)
S(1)–N(12)	1.598(6)	S(1)–C(16)	1.717(8)
N(11)–C(15)	1.355(9)	N(11)–C(11)	1.367(9)
N(12)–C(15)	1.406(8)	N(22)–C(25)	1.361(8)
S(2)–N(22)	1.587(6)	S(2)–C(26)	1.755(8)
N(21)–C(21)	1.335(9)	N(21)–C(25)	1.391(9)
N(31)–C(35)	1.337(9)	N(31)–C(31)	1.358(9)
N(32)–C(36)	1.320(9)	N(32)–C(310)	1.373(8)
N(31)–Ni–N(32)	79.6(2)	N(31)–Ni–N(11)	98.7(2)
N(32)–Ni–N(11)	163.6(2)	N(31)–Ni–N(22)	99.6(2)
N(32)–Ni–N(22)	102.2(2)	N(11)–Ni–N(22)	94.2(3)
N(31)–Ni–N(12)	96.3(2)	N(32)–Ni–N(12)	99.8(2)
N(11)–Ni–N(12)	64.0(2)	N(22)–Ni–N(12)	154.8(2)
N(31)–Ni–N(21)	160.8(2)	N(32)–Ni–N(21)	94.5(2)
N(11)–Ni–N(21)	92.0(2)	N(22)–Ni–N(21)	63.6(2)
N(12)–Ni–N(21)	102.7(2)	N(12)–S(1)–C(16)	107.0(3)
C(11)–N(11)–C(15)	116.1(7)	C(15)–N(12)–S(1)	121.7(5)
N(11)–C(15)–N(12)	105.8(6)	N(11)–C(15)–C(14)	124.1(6)
N(12)–C(15)–C(14)	130.0(7)	N(22)–S(2)–C(26)	107.1(4)
C(21)–N(21)–C(25)	116.7(7)	C(25)–N(22)–S(2)	124.1(5)
N(22)–C(25)–N(21)	107.2(6)	N(22)–C(25)–C(24)	132.7(7)
N(21)–C(25)–C(24)	120.0(7)	C(35)–N(31)–C(31)	116.0(6)
C(36)–N(32)–C(310)	117.0(6)		

The Ni–$\mathrm{N_{amide}}$ bond distances [2.104(6), 2.101(7) Å] in **4** and [2.095(6), 2.096(6) Å] in **5** are very similar, but, as expected, significantly longer than those found in tetrahedral [1.916(3) [15], 1.839(6) [16] Å] or square planar [1.904(3) Å] [17] nickel(II) amide complexes, in keeping with the lower co-ordination number in these compounds. The Ni–$\mathrm{N_{py}}$ bond distances in **4** and **5** differ slightly, one [2.089(5) in **4** and 2.063(5) Å in **5**] being shorter than other [2.142(6) in 4 and 2.110(6) Å in 5]. These values are larger than that of 1.905(4) Å found in square planar bis-μ-{2-2[2-(pyridylethyl) amino]ethylthiolato] dinickel(II) perchlorate [18] and 1.897(3) Å in bis{4-methyl-N-(2-pyridin-2-yl-ethyl) benzenesulfonamide} nickel(II) [17], but shorter than those in other pyridine complexes of six-coordinate nickel(II); e.g. 2.175(3) Å in bis{N-[2[2-(2-pyridyl)ethyl] salicylideneiminato} nickel(II) [19] and 2.209(4) Å in bis{1,1,1,-trifluoromethyl)-2-pentanolato} nickel(II) [20], probably as a result of the anionic character of the nitrogen donor atom.

The Ni–$\mathrm{N_{bipy}}$ bond distances of **4** are only slightly different from those reported for Ni–$\mathrm{N_{bipy}}$ in *cis*-bis-(benzenethiolato)bis(2,2′-bipyridine) nickel(II), 2.089 Å [21] and for other hexacoordinated nickel(II) complexes, such as (2,2′-bipyridine)bis(pyridine-2-thiolato)nickel(II), 2.074(2) and 2.067(3) Å [22]. Similarly, the Ni–$\mathrm{N_{phen}}$ bond distances in **5** are shorter than those found in other mixed hexacoordinated nickel(II) complexes containing 1,10-phenanthroline, e.g 2.121(5), 2.136(5) Å in 1,10-phenanthroline bis{[2-(2-pyrrole)-methylimino-4-methyl phenolato}nickel(II) [23].

The two pyridine portions of the bipyridine ligand are planar, with no atom deviating from the least-squares plane by more than 0.014 Å. The interplanar angle between these two pyridine rings is 9.27°, similar to that found in [Ni(bipy)$_3$]SO$_4$ [24] and in [Ni(bipy)$_3$](ClO$_4$)$_3$ [25]. The phenanthroline ligand is also essentially planar, with maximum carbon and nitrogen displacements of 0.032(7) Å and 0.045(6) Å, respectively. The bond lengths and angles within the bipyridine and phenanthroline are similar to those found in other bipyridine and phenanthroline complexes. The pyridine portion of the ligand is planar, with the largest deviation being 0.015(6) Å from the least-squares plane. The deviation of the exocyclic nitrogen amide atom is 0.036(5) Å, so that these nitrogen atoms are practically in the plane of the pyridine ring to which they are bound. The nickel atom is also practically in the plane of the pyridine group of one of the ligands, with deviations of only 0.055(12) Å for [NiL$_2$bipy] and 0.070(10) Å for [NiL$_2$phen], but lies 0.124(13) and 0.269(10) Å out of the plane of the pyridine portion of the other ligand.

The average N–C distance in the ligands, 1.398(8) Å, is longer than that found in the free ligand, whose value of 1.350(5) Å can be considered as indicating some double bond character.

The solvent acetone molecule in [NiL$_2$bipy] does not interact with the complex in any significant manner and there are no noteworthy intermolecular contacts.

3.1.2. Spectroscopic and magnetic studies

The IR spectra of the complexes do not show the band attributable to ν(N–H), which in the free ligand appears at 3230 cm^{-1}, confirming that the hydrogen atom of the amide group is lost during the electrolysis. The IR spectra of the mixed complexes show IR absorptions typical of co-ordinated pyridine (662 and 437 cm^{-1}) [26,27], 1,10-phenanthroline (1520, 844 and 728 cm^{-1}) and 2,2′-bipyridine (773 and 735 cm^{-1}) [28,29].

The magnetic moment of [NiL$_2$], 3.04 B.M., and its solid reflectance spectrum is in accordance with a tetrahedral geometry for the complex. The bands observed at ca. 8800, 15,800 and 26,300 cm^{-1} are assigned to the three expected spin-allowed transitions, $^3A_2 \rightarrow {}^3T_1$ (ν_1), $^3A_2 \rightarrow {}^3T_1$(F) ($\nu_2$), and $^3A_2 \rightarrow {}^3T_2$($\nu_3$), respectively.

The electronic reflectance spectra of the mixed complexes are all very similar and show bands in the 9500–10,000 and 17,000–17,900 cm^{-1} regions and a shoulder at ca. 12200 cm^{-1}, consistent with an octahedral environment around the nickel(II) atom and assigned to transitions $^3A_{2g} \rightarrow {}^3T_{2g}$ (ν_1) and $^3A_{2g} \rightarrow {}^3T_{1g}$(F) ($\nu_2$). The shoulder is presumably due to the splitting of the ν_1 band as a consequence of the low symmetry of the ligand field, and clearly indicates the distorted octahedral environment of these complexes. The third expected spin-allowed transition has not been observed, presumably due to the presence of a strong charge-transfer band in the region [30]. The room temperature effective magnetic moment of these complexes, 2.92–3.13 B.M., is also within the range for octahedral complexes. These conclusions are in keeping with the X-ray diffraction results.

Supplementary data

Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition numbers 111587, 111588, and 111589.

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