Rearrangement and co-ordination of 1-[(4-methylphenyl)-sulfonamido]-2-[1-(2-pyridylmethylidene)amino]benzene

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Two different compounds, L^1 {3-[ethoxy(2-pyridyl)methyl]-1-[(4-methylphenyl)sulfonyl]-2-(2-pyridyl)-2,3-dihydro-1*H*-benzo[*d*]imidazole} and L^2 {1-[(4-methylphenyl)sulfonyl]-2-(2-pyridyl)-2,3-dihydro-1*H*-benzo[*d*]imidazole} have been synthesised by the reaction of 2-pyridinecarboxaldehyde with *N*-tosyl-1,2-diaminobenzene. L^1 was crystallographically characterised. The interaction of L^1 with a nickel centre was checked. Electrochemical interaction of Ni with L^1 and *N*-(2-hydroxyphenyl)salicylidenimine (H_2L^4) produces $NiL^1L^4 \cdot 2H_2O$ **1**. Its recrystallisation in dichloromethane leads to the isolation of single crystals of $NiL^3{}_2 \cdot 0.75H_2O$ **2** (HL^3 = 1-[(4-methylphenyl)sulfonamido]-2-[1-(2-pyridylmethylidene)amino]benzene), where L^1 underwent a rearrangement. In the reaction of L^1 with Ni and *p*-toluenesulfonic acid in an electrochemical cell, complex **2** is isolated as the bulk product. Nickel complexes have been characterised by elemental analysis, IR spectroscopy and magnetic measurements. The molecular structure of **2** has been determined by single X-ray diffraction studies.

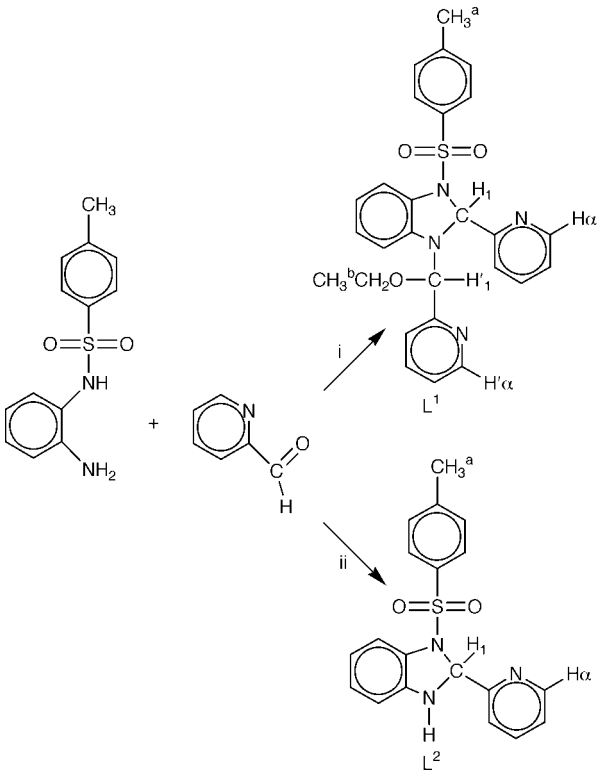
The co-ordination chemistry of Schiff base ligands has been widely investigated. The interest in these ligands arose not only from their versatility but also from their use for modelling the chemical environment in many metalloenzymes. The construction of models that can lead to a better understanding of their properties has attracted the attention of both biochemists and inorganic chemists. Many metallobiosites are formed by a metal atom surrounded by nitrogen atoms and some of them, such as cofactor F_{430}, involve a nickel centre. Thus, Schiff bases containing nitrogen donors could act as versatile models of the active centre of these enzymes. In addition, nickel complexes with nitrogen donor atoms often show interesting structural, electric and magnetic properties.[1–6]

Owing to our experience in the co-ordination chemistry of symmetrical and asymmetrical Schiff base ligands,[7,8] we extended our studies to the investigation of potentially tridentate asymmetrical Schiff bases containing *N*-donors. Herein we report our attempts to obtain the Schiff base 1-[(4-methylphenyl)sulfonamido]-2-[1-(2-pyridylmethylidene)-amino]benzene (HL^3) and its reorganisation in solution to yield two different ligands, L^1 and L^2. The interaction of L^1 with a nickel centre, under different reaction conditions, has also been investigated.

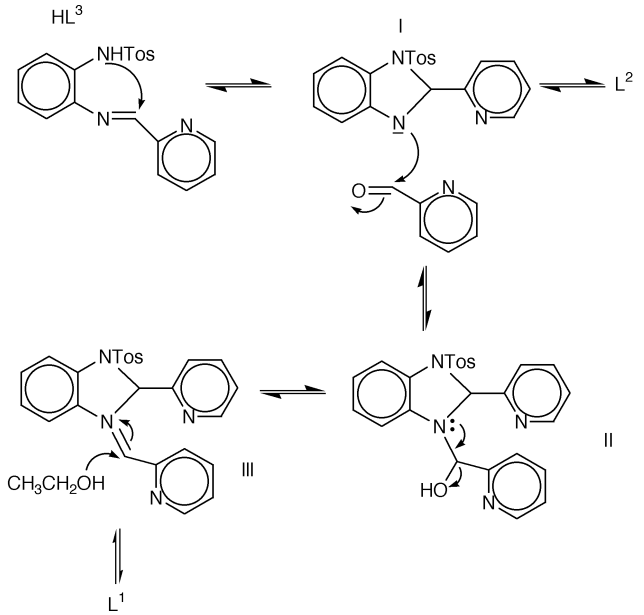
Results and discussion

N-Tosyl-1,2-diaminobenzene and 2-pyridinecarboxaldehyde were mixed in different ratios under various reaction conditions (room temperature, reflux, with or without traces of *p*-toluenesulfonic acid) in an attempt to obtain 1-[(4-methylphenyl)sulfonamido]-2-[1-(2-pyridylmethylidene)amino]benzene, HL^3. All efforts were unfruitful and treatment of *N*-tosyl-1,2-diaminobenzene with 2-pyridinecarboxaldehyde led always to the isolation of two different products (L^1 and L^2), depending on the reaction solvent (Scheme 1). The products can be formed through the reactions shown in Scheme 2.

The isolation of L^2 seems to indicate that the reaction begins with an intramolecular nucleophilic attack on the imine carbon atom by the tosyl protected amino group, followed by an intermolecular nucleophilic attack on the carbonyl carbon of 2-pyridinecarboxaldehyde. The elimination of the hydroxyl group would lead to the formation of water and an intermediate containing, again, an imine group. The final product L^1 could be obtained from **III**, by nucleophilic attack



Scheme 1 Reaction conditions (*i* absolute ethanol (99%), stir 5 h, room temperature, (*ii*) ethanol (96%), stir 5 h, room temperature or methanol, ethanol (96%) or chloroform, stir 3 h, reflux. Labels for the NMR spectra are also given.



Scheme 2 Proposed pathway for the formation of L^1 and L^2.

by the reaction solvent. Although all these products seem to be in a dynamic equilibrium in solution, the displacement of the reaction towards the formation of L^1 could be explained by the low solubility of the latter product in ethanol at room temperature. This proposed reaction pathway is also consistent with the isolation of L^2 in an undried solvent: the higher quantity of water would disfavour the formation of **III**, reverting the equilibrium and producing L^2 in yields high enough to precipitate.

The stability and reactivity induced in these compounds by the pyridine ring, directly bonded to the imine carbon atom, is quite surprising. The related Schiff bases *N*-[(2-pyrrolyl)methylidene]-*N*′-tosylbenzene-1,2-diamine and 2-tosylamino-(2-pyridyl)aniline have been previously reported.[7a,7c] Both were easily obtained by condensation of the corresponding amine and aldehyde; the bases seem to be stable in solution and no decomposition or rearrangement reactions were reported for either of them.

Characterisation of L^1 and L^2

The products L^1 and L^2 were characterised by elemental analyses, IR (Table 1) and ^{1}H NMR (Table 2) spectroscopies. A crystal structure determination on L^1 confirmed the nature of the compound.

Crystal structure of L^1. The nature of L^1 was determined by single X-ray diffraction studies (Fig. 1). The experimental details are given in Table 3 and main bond distances and angles in Table 4.

All the angles and distances are in the range of those expected for organic compounds containing a tosyl group[8,9] and do not deserve further consideration. However, it is noteworthy that the crystal structure shows that L^1 has two tertiary carbon atoms, the compound being optically active.

IR spectroscopy. The IR spectra of L^1 and L^2 show a strong band at *ca.* 1595 cm^{-1}, assigned to $\nu(CN_{py})$. Besides, a broad and intense band at 3205 cm^{-1}, due to the NH stretching frequency,[7b] is observed for L^2. No bands above 2500 cm^{-1} were detected for L^1, indicating the absence of NH groups in the molecule, as the crystal structure shows. Very strong bands are observed at *ca.* 1340 and 1165 cm^{-1} for L^1 and L^2, due to $\nu(SO_2)_{as}$ and $\nu(SO_2)_s$, suggesting the presence of the tosyl group in both cases, in agreement with previous results.[10]

^{1}H NMR and mass spectroscopy. L^1 shows two doublets at 8.51 and 8.24 ppm, corresponding to two protons *ortho* to the nitrogen atom of the pyridine ring, indicating the presence of two pyridine moieties in the ligand. Two singlets at *ca.* 6 ppm are assigned to two protons attached to two different tertiary carbon atoms.[11] The spectrum shows a very complicated multiplet (15 H), assigned to the aromatic protons, at 6.5–8 ppm. The ethyl chain of the ethoxy moiety gives two signals: one at 0.58 ppm (t, 3H) and a second one at 2.38 ppm, which appears as a multiplet as it is overlapped by the peak corresponding to the methyl radical of the tosyl group.

The spectrum of L^2 shows just one signal assigned to an α-proton of the pyridine ring (8.56 ppm, d) and a multiplet for the aromatic hydrogen atoms. The hydrogen on the tertiary carbon atom occurs at 6.32 ppm and the methyl radical of the tosyl group at 2.34 ppm. The signal of the NH proton was not assigned because of overlap by the aromatic protons. No singlets at *ca.* 8.5 ppm were detected so no imine groups are present in L^1 or L^2.[12]

It is remarkable to note that the spectrum of L^1 changes with time: many new signals, most of them assigned to L^2, increase in intensity with time. This seems to indicate that L^1 is unstable in solution and that many species are present. The equilibrium between L^1 and L^2 is in agreement with the proposed reaction scheme.

The mass spectra of L^1 and L^2 were recorded by the electrospray technique. Peaks at 487 and 352 amu are assigned to the molecular ions of L^1 and L^2, respectively.

Table 1 Elemental analyses and some physical properties of the ligands

				Elemetal analysis[a]				IR spectroscopy[b]		
	Formula	Yield/%	Mp/°C	%C	%H	%N	%S	ν(NH)	$\nu(CN_{py})$	$\nu(SO_2)$
L^1	$C_{27}H_{26}N_4O_3S$	63.2	163–6	67.3 (66.7)	5.5 (5.3)	11.6 (11.5)	6.3 (6.6)	—	1593	1335, 1173
L^2	$C_{19}H_{17}N_3O_2S$	92.6	142–3	65.0 (65.0)	4.8 (4.8)	11.9 (12.0)	8.7 (9.1)	3205	1595	1349, 1165

[a] Found (calcd.). [b] In KBr, cm^{-1}.

Table 2 Most significant ^{1}H NMR peaks (ppm) and mass spectral data for the ligands

	$H_1 + H'_1$	$H_\alpha + H'_\alpha$	$H_{arom} + NH$	$-CH_2$	$-CH_3$[a]	$-CH_3$[b]	*m/z*
L^1	6.06 (s,1H), 5.85 (s,1H)	8.51 (d,1H), 8.24 (d,1H)	6.5–8 (m,15H)	2.38 (m,5H)[a]	2.39 (m,5H)[a]	0.58 (t,3H)	487
L^2	6.32 (s,1H), —	8.56 (d,1H)	6.4–7.8 (m,12H)	—	2.34 (s,3H)	—	352

[a] Overlapping peaks.

Table 3 Crystal data and structure refinement for L^1 and 2.

	L^1	**2**
Empirical formula	$C_{27}H_{26}N_4O_3S$	$C_{38}H_{33.5}N_6O_{4.75}NiS$
Formula weight	486.58	773.04
Crystal system	Monoclinic	Trigonal
Space group	*P*2/1	$R\bar{3}$
Z	2	18
Temperature/K	296(2)	296(1)
a/Å	8.7002(1)	27.512(4)
b/Å	10.0675(3)	—
c/Å	14.1389(4)	25.092(3)
α/°	90	90
β/°	91.217(1)	90
γ/°	90	120
U/Å^3	1238.14(5)	16447(4)
μ/mm^{-1}	0.167	2.257
Reflections collected	5226	7985
Independent reflections	2494 (R_{int} = 0.0537)	7557 (R_{int} = 0.04)
Final R_w indices [$I > 2\sigma(I)$]	0.0767	0.070
R_w indices (all data)	0.0884	0.049

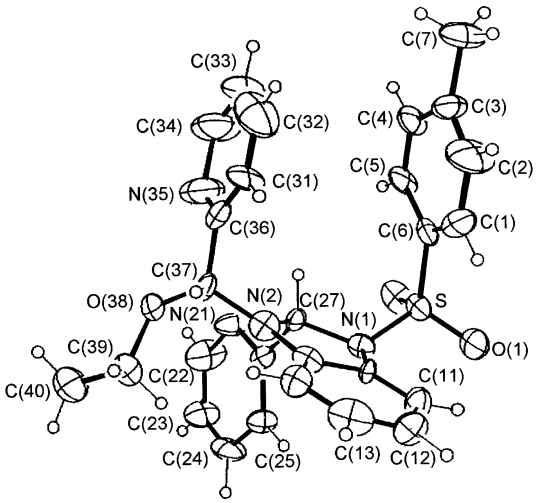


Fig. 1 An ORTEP view of the crystal structure of L^1.

Table 4 Selected bond distance (Å) and angles (°) for L^1

S–O1	1.422(8)	N2–C27	1.461(10)
S–O2	1.424(8)	N21–C26	1.306(11)
S–N1	1.648(6)	N21–C22	1.348(14)
S–C6	1.754(8)	C34–N35	1.45(2)
N1–C16	1.421(11)	N35–C36	1.41(2)
N1–C27	1.492(10)	C37–O38	1.396(11)
N2–C15	1.382(12)	O38–C39	1.418(12)
N2–C37	1.439(11)	C26–N21–C22	116.1(8)
O1–S–N1	105.7(4)	C23–C22–N21	125.2(11)
O2–S–N1	105.7(4)	N21–C26–C25	123.3(8)
O1–S–C6	108.8(5)	N21–C26–C27	115.7(7)
O2–S–C6	108.4(5)	N2–C27–N1	103.7(6)
N1–S–C6	107.7(3)	N2–C27–C26	112.8(6)
C16–N1–C27	107.8(6)	N1–C27–C26	110.8(6)
C16–N1–S	121.8(6)	C33–C34–N35	117(2)
C27–N1–S	118.0(5)	C34–N35–C36	116.1(13)
O1–S–O2	119.9(4)	C31–C36–N35	122.7(11)
C15–N2–C37	126.7(7)	N35–C36–C37	118.8(10)
C15–N2–C27	109.2(7)	O38–C37–N2	112.3(7)
C37–N2–C27	121.4(7)	O38–C37–C36	109.1(8)
C16–C15–N2	110.6(7)	N2–C37–C36	112.2(8)
C14–C15–N2	127.9(8)	C39–O38–C37	113.6(8)
C11–C16–N1	131.0(9)	O38–C39–C40	109.7(11)
C15–C16–N1	108.5(7)		

Characterisation of the nickel complexes

The unfruitful attempts to obtain HL^3, with the isolation of L^1 (or L^2), focussed our efforts on the isolation of a nickel complex containing L^1.

The electrochemical reaction of a nickel centre with L^1 does not seem to occur and the ligand L^1 could be identified as one of the species after evaporation of the solution. Thus, an alternative method was tried.

Once the structure of L^1 was known, it was thought that its size would prevent the co-ordination of more than one ligand to the same metal centre. Besides, L^1 has no acidic protons. Thus, it should be necessary to react L^1 with a nickel centre in the presence of a ligand containing easily deprotonable groups, which could balance the charge of the central atom, in order to obtain a Ni(II) complex containing L^1. A simple potentially tridentate and dianionic Schiff base, such as H_2L^4 [*N*-(2-hydroxyphenyl)salicylidenimine], was chosen for this purpose. The electrolysis of an acetonitrile solution containing L^1 and H_2L^4, as described below, was done. Elemental analysis of the orange insoluble product isolated (Table 5) seems to indicate that the compound obtained is $NiL^1L^4 \cdot 2H_2O$ **1**, although the evaporation of the mother waters of the electrochemical synthesis yields $NiL^3{}_2 \cdot 0.75H_2O$ **2**, crystallographically characterised. Attempts were made to determine the structure of $NiL^1L^4 \cdot 2H_2O$. However, its recrystallisation in dichloromethane led, again, to the isolation of complex **2**.

As a consequence of this unexpected result, we tried to substitute for ligand H_2L^4 a weakly co-ordinating acid, which could be easily deprotonated and balance the charge of the nickel(II) cation, maybe by acting as a counter ion. The acid used in this case was *p*-toluenesulfonic acid (*p*-TosH). Electrolysis of an acetonitrile solution containing L^1 and *p*-TosH in a

Table 5 Elemental analyses and some physical properties for the nickel complexes

			Elemental analysis[a]				IR spectroscopy[b]		
	Yield/%	Mp/°C	%C	%H	%N	%S	$\nu(CN_{imine}) + \nu(CN_{py})$	ν(OH)	μ/BM
1	37.6	>300	60.4 (60.3)	5.3 (5.4)	8.7 (8.8)	4.0 (3.4)	1609, 1596	3417	3.1
2	30.5	>300	58.8 (59.0)	4.1 (4.3)	10.8 (10.9)	8.1 (8.3)	1592	3477	3.1

[a] Found (calcd.). [b] In KBr, cm^{-1}.

1 : 2 ratio was performed in the presence of a nickel anode. Complex **2** was obtained after slow evaporation of the mother waters. Thus, this seems to indicate that L^1 is unstable in solution, as previously observed, and that the presence of a metal centre accelerates the reorganisation process. Therefore, the experimental findings indicate that the best results that can be achieved are the isolation of complexes containing $[L^3]^-$ as a ligand.

With these considerations in mind, it was thought that, it might be enough to catalyse the interaction of Ni and L^1 with a weak acid, in order to obtain complex **2**. The electrochemical interaction of Ni and L^1, using traces of *p*-TosH, was checked. It was observed that quick evaporation of the solution produces a copious product of unknown nature. When the solution is left to stand and slowly evaporates, the isolated product is compound **2**. These data show that L^1 rearranges to HL^3 in solution. However, the reorganisation is not instantaneous and thus, a quick precipitation leads to a mixture of products, perhaps containing simultaneously derivatives of L^1 and HL^3, as well as other fragments of the reorganisation process, which does not allow us to characterise the copious material isolated. On the contrary a slow evaporation of the solution allows L^1 to rearrange in higher quantity. The most insoluble product, in this case the nickel complex **2**, precipitates as a crystalline product and can be isolated with high purity.

Crystal structure of $NiL^3_2 \cdot 0.75H_2O$ 2. The X-ray structure of **2** is shown in Fig. 2. Experimental details are given in Table 3 and significant bond lengths and angles are listed in Table 6. The unit cell contains 18 asymmetric units, accounting for the large volume. The asymmetric unit contains, in addition to the nickel complex, three disordered water fragments, with partial occupancies.

The structure of the Ni compound consists of a metal centre surrounded by six nitrogen atoms corresponding to two Schiff bases, which act as tridentate and monoanionic. The ligands adopt a *mer* configuration in the distorted octahedral complex. It is remarkable, in spite of the adopted configuration, that both ligands are not equivalent. This is clearly shown by a comparison of the Ni–N distances: while the

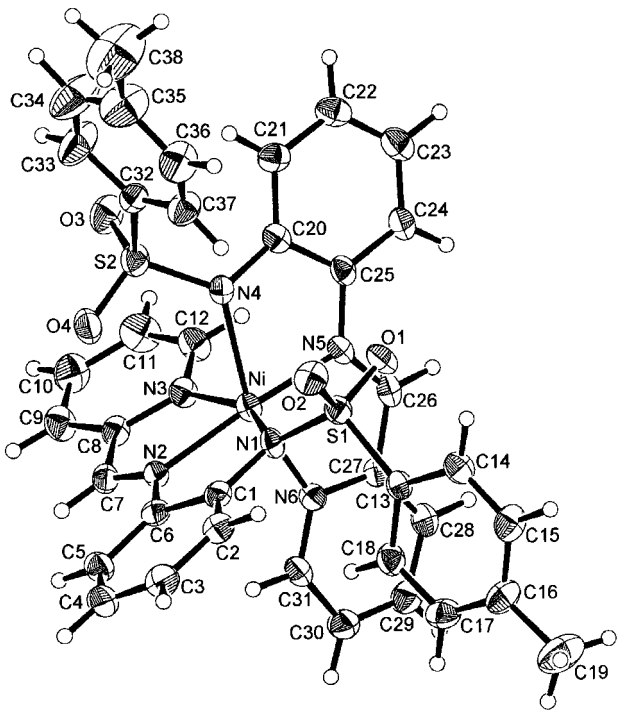


Fig. 2 An ORTEP view of the crystal structure of $NiL^3_2 \cdot 0.75H_2O$ 2. Water solvent molecules have been omitted for clarity.

Table 6 Selected bond distances (Å) and angles (°) for 2

Ni–N1	2.090(5)	Ni–N2	2.030(5)
Ni–N3	2.105(5)	Ni–N4	2.146(5)
Ni–N5	2.025(5)	Ni–N6	2.125(6)
S1–O1	1.443(4)	S1–O2	1.444(4)
S1–N1	1.584(5)	S1–C13	1.780(7)
S2–O3	1.454(5)	S2–O4	1.456(5)
S2–N4	1.597(5)	S2–C32	1.783(7)
N1–C1	1.409(8)	N2–C6	1.401(8)
N2–C7	1.271(8)	N3–C8	1.347(8)
N3–C12	1.323(8)	N4–C20	1.398(8)
N5–C25	1.383(8)	N5–C26	1.283(8)
N6–C27	1.345(8)	N6–C31	1.317(8)
N1–Ni–N2	78.6(2)	N1–Ni–N3	156.7(2)
N1–Ni–N4	97.7(2)	N1–Ni–N5	108.5(2)
N1–Ni–N6	92.7(2)	N2–Ni–N3	78.5(2)
N2–Ni–N4	109.4(2)	N2–Ni–N5	169.5(2)
N2–Ni–N6	93.7(2)	N3–Ni–N4	86.5(2)
N3–Ni–N5	94.8(2)	N3–Ni–N6	92.3(2)
N4–Ni–N5	77.9(2)	N4–Ni–N6	156.1(2)
N5–Ni–N6	78.4(2)	O1–S1–O2	116.1(3)
O1–S1–N1	106.7(3)	O3–S2–O4	115.7(3)
O2–S1–N1	113.1(3)	N1–S1–C13	109.1(3)

$Ni–N_{imine}$ bond lengths are identical for both ligands [Ni–N2 = 2.030(5) and Ni–N5 = 2.025(5) Å] remarkable differences are observed in the $Ni–N_{amide}$ and $Ni–N_{pyridine}$ bond lengths. These distances are significantly shorter for one of the ligands [Ni–N1 = 2.090(5) and Ni–N3 = 2.105(5) Å, respectively] than for the second one [Ni–N4 = 2.146(5) and Ni–N6 = 2.125(5) Å, respectively]. In addition, the distance $Ni–N_{amide}$ is shorter than the distance $Ni–N_{pyridine}$ for one of the ligands while is longer for the other one. Thus, the geometry of the complex can be considered as an octahedron with a tetragonal distortion due to the elongation of the apical bonds, with no interchangeable positions between both ligands. In this polyhedron, one of the Schiff base ligands uses its three donor atoms, N1, N2 and N3, to bind the Ni atom in the equatorial plane and the second one uses the imine nitrogen atom, N5, to link the Ni centre in the equatorial plane and the amide and pyridine nitrogen atoms, N4 and N6, to fill the apical positions.

The Ni–N distances in the equatorial plane are quite similar and shorter than those of the apical positions. All these distances are in the range of those expected for octahedral Ni complexes containing N-donor ligands[13,14] but are longer than those found for tetrahedral[15–17] and square planar[7b,18] Ni compounds. This is a reflection of the lower co-ordination number in the related complexes.

The equatorial angles around the Ni atom in the distorted octahedron vary from 77.9° to 108.5° and are quite different from the ideal value of 90°. The interaxial angle N4–Ni–N6 of 156.1(2)° further reinforces the distortion from the ideal geometry, which can be mainly attributed to the small bite angles of the tridentate ligand. This observation is in agreement with previous results, where chelate ligands induce a distortion from the ideal octahedral geometry.[14,15,19]

IR spectroscopy and magnetic measurements. The IR spectrum of complex **2** shows a strong and broad band at 1592 cm^{-1}, assigned to $\nu(CN_{pyridine}) + \nu(CN_{imine})$.[13,14] A broad band at 3477 cm^{-1} is assigned to ν(OH) from the water of crystallisation. A comparison of the spectra of complexes **1** and **2** shows a clear difference. Complex **1** shows two strong bands in the range 1590–1620 cm^{-1}: a sharp and strong band at 1596 cm^{-1} that can be assigned to $\nu(CN_{pyridine})$ of L^1, present in the free ligand; a second strong band at 1609 cm^{-1}, assigned to $\nu(CN_{imine})$ of $[L^4]^{2-}$.

The room temperature magnetic moments for the complexes are 3.1 BM and are very close to the ideal value of 2.9 for magnetically diluted Ni(II) ions. The magnetic moment value for **2** is in good agreement with the octahedral geometry

of the compounds, deduced from the X-ray results. However, this value does not allow one to draw any unambiguous conclusions concerning the geometry of the chelate core in complex **1**.[3] This only allows one to reject the square planar geometry for the complex.

Conclusion

The reaction of *N*-Tosyl-1,2-diaminobenzene and 2-pyridinecarboxaldehyde yields two different optically active organic compounds, L^1 and L^2, depending on the reaction medium. However, the expected Schiff base, product of the condensation of the amine and carbonyl reactants, could not be isolated.

The electrochemical interaction of L^1 with nickel always leads to the isolation of $NiL^3{}_2 \cdot 0.75H_2O$, obtained by reorganisation of the ligand to the Schiff base (HL^3) in solution.

Experimental

General

All solvents and 2-pyridinecarboxaldehyde are commercially available and were used without further purification. Nickel (Ega Chemie) was used as *ca.* 2 × 2 cm^2 plate. *N*-tosyl-1,2-diaminobenzene was obtained as previously reported by Malik and Sharma.[20]

Elemental analyses were performed on a Carlo Erba EA 1108 analyser. NMR spectra were recorded on a Bruker AC-300 spectrometer using DMSO-d_6 as solvent. Infrared spectra were recorded as KBr pellets on a Bio-Rad FTS 135 spectrophotometer in the range 4000–600 cm^{-1}. Electrospray mass spectra were obtained on a Hewlett–Packard LC/MS spectrometer, in methanol as solvent. Room temperature magnetic measurements were performed using a Digital Measurement system MSB-MKI, calibrated using tetrakis(isothiocyanato)cobaltate(II).

Syntheses

L^1. To an absolute ethanol (99%) solution (75 mL) of *N*-tosyl-1,2-diaminobenzene (0.524 g, 2 mmol) was added 2-pyridinecarboxaldehyde (0.2 mL, 2.1 mmol). The mixture was stirred for 5 h at room temperature until a white solid precipitated. The solid was collected by filtration, washed with diethyl ether (10 mL) and dried in air.

When the amine and aldehyde are mixed in a 1 : 2 molar ratio in absolute ethanol, the same ligand is obtained. Crystals of L^1, suitable for X-ray diffraction studies, were obtained by recrystallisation of the white powder in hot ethanol.

L^2. L^2 could be synthesised by two different methods.

Method A: To an ethanol (96%) solution (75 mL) of *N*-tosyl-1,2-diaminobenzene (0.524 g, 2 mmol) was added 2-pyridinecarboxaldehyde (0.2 mL, 2.1 mmol). The mixture was stirred for 5 h at room temperature until a white solid precipitated. The solid was filtered, washed with diethyl ether (10 mL) and dried in air.

Method B: To an ethanol (96%), chloroform or methanol solution (100 mL) of *N*-tosyl-1,2-diaminobenzene (0.524 g, 2 mmol) was added 2-pyridinecarboxaldehyde (0.2 mL, 2.1 mmol). The resultant yellow solution was refluxed for 3 h, removing the water with a Dean Stark. The solution was reduced in volume (25 mL) and the solid collected by filtration and dried in air.

$NiL^1L^4 \cdot 2H_2O$ 1. The compound was obtained using an electrochemical procedure. The cell can be summarised as: $Pt_{(-)} \mid L^1 + H_2L^4 + MeCN \mid Ni_{(+)}$. A platinum wire was used as the cathode and a nickel plate as the anode.

An acetonitrile solution (70 mL) of L^1 (0.2 g, 0.41 mmol) and H_2L^4 (0.09 g, 0.41 mmol), containing about 10 mg of tetramethylammonium perchlorate, as supporting electrolyte, was electrolysed for 2 h and 12 min with a current of 10 mA. A small quantity of an insoluble orange solid of unknown nature was isolated (*ca.* 0.06 mg). The mother waters were reduced in volume (20 mL) and a second orange solid precipitated. The product was filtered, washed with diethyl ether and dried in air; the elemental analysis is in agreement with the formulation $NiL^1L^4 \cdot 2H_2O$ **1** for the latter compound.

Recrystallisation of **1** in dichloromethane yielded small crystals of $NiL^3{}_2 2 \cdot 0.75H_2O$ **2**.

$NiL^3{}_2 \cdot 0.75H_2O$ 2. Complex **2** could be synthesized by two other methods.

Method A: An acetonitrile solution (70 mL) of L^1 (0.2 g, 0.41 mmol) and *p*-TosH (0.14 g, 0.82 mmol), containing about 10 mg of tetramethylammonium perchlorate as supporting electrolyte, was electrolysed for 2 h and 12 min with a current of 10 mA, as for 1. A small quantity (*ca.* 0.05 g) of an insoluble product of unknown nature was filtered. The mother waters were left to stand for one week. Slow evaporation of the solution yields small crystals, suitable for X-ray diffraction, of $NiL^3{}_2 : 0.75H_2O$ 2.

Method B: An acetonitrile solution (70 mL) of L^1 (0.2 g, 0.41 mmol) containing about 10 mg of tetramethylammonium perchlorate, as supporting electrolyte, and 10 mg of *p*-toluenesulfonic acid as catalyst, was electrolysed for 2 h and 12 min with a current of 10 mA, as for 1. The resultant garnet-coloured solution was slowly evaporated and, after one week, small crystals of $NiL^3{}_2 \cdot 0.75H_2O$ 2 were recovered and dried in air.

Crystallographic measurements

L_1. White crystals, suitable for single-crystal X-ray studies, were obtained as previously described. Data were collected at 296 K with a CAD-4 diffractometer, employing graphite-monochromated Mo-Kα ($\lambda = 0.710\,73$ Å) radiation. The structure was solved by direct methods[21] and refined by full-matrix least squares on F^2. A semiempirical correction from psi scans was applied. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculation in idealised positions. The aromatic ring of the tosyl group (C1–C6) is disordered over two sites, with partial occupancies of 0.5.

$NiL^3{}_2 \cdot 0.75H_2O$ 2. Red needle crystals of **2** were obtained as previously described and mounted on a glass fiber. All measurements were made at 296 K on a Rigaku AFC5R diffractometer, employing Cu-Kα ($\lambda = 1.541\,78$ Å) radiation and a rotating anode generator, using the $\omega - 2\theta$ scan technique ($2\theta_{max} = 159.4°$). The structure was solved by direct methods,[21] expanded using Fourier techniques[22] and refined by full-matrix least squares on F^2. An absorption correction was applied. Data were corrected for Lorentz and polarisation effects. Non-hydrogen atoms were refined anisotropically, except oxygen atoms of the disordered water fragment, which were refined isotropically. Hydrogen atoms were included in the structure factor calculation in idealised positions but not refined. All calculations were performed using the TEXSAN crystallographic software package.[23]

CCDC reference 440/155. See http://www.rsc.org/suppdata/nj/a9/a907731f// for crystallographic files of complex **2** in .cif format.

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