Electronic Supplementary Material for Dalton Transactions

ESI_NMR

ELECTRONIC SUPPLEMENTARY INFORMATION

NMR MEASUREMENTS

Materials and reagents

DCl solution

The commercial solution of DCl 20% in D_2O was titrated with NaOH 1.00 M with methyl red as indicator. Once the titre (6.144 M) was known, the solution was also used to prepare a 60.3 mM solution by dilution with D_2O.

NaOD solution

A solution of NaOD ~1.00 M was prepared by diluting 0.34 mL of a concentrated solution of this reagent in 5 mL of D_2O. The titre of the solution (1M) was ascertained by titration with $HClO_4$ 0.996M, with methyl red as indicator. The solution was also used to prepare a 154 mM solution by dilution with D_2O.

Stock solution of H_2L_A in CD_3OD

The Schiff base is insoluble in water but very soluble in CD_3OD; consequently, stock solutions of the ligand were prepared in CD_3OD and then diluted in D_2O. In particular, a 40 mM solution was prepared by dissolving 66.20 mg of H_2L_A in 4 mL of CD_3OD.

Stock solution of H_2L_B in CD_3OD

The stock solution, 40mM in H_2L_B and 0.4M in DCl was prepared by dissolving 83.52 mg of the sample and 0.3255 mL of DCl 6.144M in a total volume of 5 mL of CD_3OD.

Stock solution of $Zn(ClO_4)_2 \cdot 6H_2O$ in D_2O

After determination of the correct water content in the commercial salt ($Zn(ClO_4)_2 \cdot 6.26H_2O$) a 20.2 mM stock solution of zinc perchlorate was prepared by dissolving 38.1 mg of the salt in 5 mL of D_2O.

Preparation of H_2L_A solutions for NMR spectroscopy

The solutions used for recording NMR spectra were prepared with the aid of a simulation program, which calculated the correct quantities of reagents which, when mixed, gave the highest relative percentage of the species in solution. Stock solutions of H_2L_A in CD_3OD was abundantly diluted to yeld a reaction environment as close as possible to an aqueous one. All solutions were prepared by adding D_2O to reach a volume of 5 mL. The exact quantities are reported in the table below.

Solution	pH	mL H_2L_A 40.0 mM	mL NaOD 154.0 mM	mL DCl 60.3 mM
1	~4	0.25	-----	0.35
2	~11	0.25	0.30	-----
3	~9	0.25	-----	-----

Study of H_2L_A-Zn^{2+} system in D_2O

On the basis of data obtained with the simulation program applied to the H_2L_A:Zn^{2+} =1:1 system, three solutions were prepared at pH= 6, 9 and 11, to verify the results of potentiometric measurements. The following table lists the quantities used to prepare 5 mL of each solution.

Solution	pH	mL H_2L_A 40.0 mM	mL Zn^{2+} 20.2 mM	mL NaOD 154 mM
1	~6	0.25	0.495	-----
2	~9	0.25	0.495	0.125
3	~11	0.25	0.495	0.250

For the solution at pH = 9, with the highest percentage of complex formation, bidimensional 2D COSY and NOESY spectra were also recorded.

Preparation of H_2L_B solutions for NMR spectroscopy

The quantities of NaOD needed to obtain various solutions with the highest percentage of a certain species were also calculated by the simulation program (Figure I).

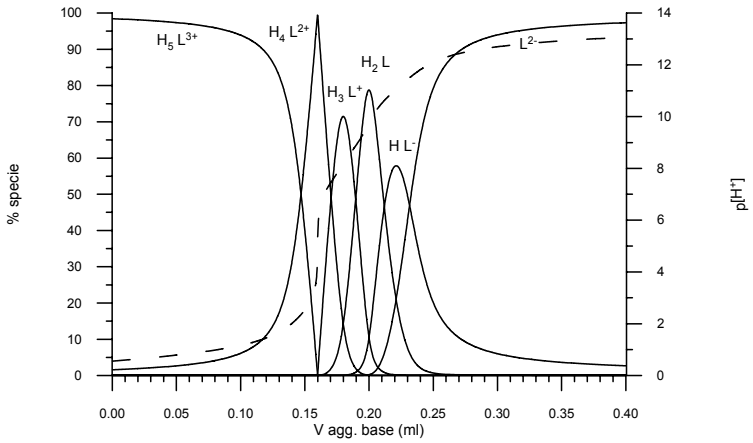

Figure I - Speciation of H_2L_B in aqueous solution and corresponding p[H^+] values.

Figure I shows variations in the relative concentrations of the differently protonated species of H_2L_B on changing the quantity of NaOD 154mM added to 0.5 mL of the ligand. The solutions for NMR experiments were prepared accordingly (see table below).

Solution	Species	%	mL H_2L_B 40mM	mL NaOD 154 mM	mL CD_3OD
1	$H_5L_B^{3+}$	100	0.5	0.00	0.5
2	$H_4L_B^{2+}$	100	0.5	0.16	0.34
3	$H_3L_B^{+}$	75	0.5	0.18	0.32
4	H_2L_B	80	0.5	0.20	0.30
5	HL_B^{-}	60	0.5	0.22	0.28
6	L_B^{2-}	100	0.5	0.35	0.15

To calculate the percent abundances of the various species, we did not take into account the fact that not all the solutions were the same: the water percentage varied from 0 to 35% V/V. In this treatment, it was presumed that the various solution media did not change the general picture of the protonation equilibria of the ligand. It should also be noted that the use of D_2O produces isotopic effects which may modify absolute values, particularly the constants of the protonation equilibria of basic species in solution. For instance, it was observed that the acidity constants of monoprotic acids may be reduced by 0.5-1 logarithmic unit, passing from water to deuterated water. In spite of this, the relative percent abundance of species in solution was not very affected by variations in R_L. For this reason, interpretation of NMR spectra refers to distribution diagrams obtained with protonation constants derived from potentiometric studies in water. In the case of H_2L_B, NMR spectra were recorded in a CD_3OD/D_2O mixture, due to its low solubility in water, assuming that the protonation equilibrium pattern remained substantially the same.

NMR RESULTS

DEPROTONATION OF H_2L_B.

The deprotonation sequence of the ligand was followed by NMR spectroscopy.

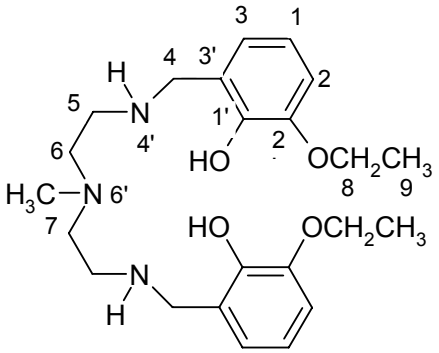

Figure II

The chemical shift values (ppm) assigned to each group of H_2L_B in the ^1H spectra, collected at varying values of R_L, are reported in the table below. The upper part of the table shows the prevailing species at the corresponding R_L values. Signal assignmentswere made referring to the numbering of Figure II.

R_L	<-2	1	2	3	~7	>8
Spectrum	1	2	3	4	5	6
Species / ^1H (ppm)	$H_5L_B^{3+}$	$H_4L_B^{3+}$	$H_3L_B^{+}$	H_2L_B	HL_B^{-}	L_B^{2-}
CH_3 (**9**) t	1.42	1.48	1.40	1.38	1.38	1.38
CH_2 (**8**) q	4.10	4.10	4.05	4.02	4.02	3.98
CH_2 (**4**) s	4.32	4.22	4.00	3.80	3.80	3.70
CH_2 (**5**) t	3.72	3.10	2.85	2.65	2.65	2.65
CH_2(**6**) t	3.65	2.75	2.55	2.45	2.45	2.45
CH_3 (**7**) s	3.05	2.20	2.12	2.12	2.12	2.12
CH (**1**) t	6.85	6.83	6.75	6.56	6.60	6.30
CH (**2-3**) dd	7.02	6.97	6.85	6.73	6.74	6.67

The NMR spectra show that, on going from solutions in which the predominant species is $H_5L_B^{3+}$ to those with prevailing $H_4L_B^{2+}$, the CH_3**(7)** signal shifts by 0.85 ppm, due to the

disappearance of the positive charge on the nitrogen **(6')** bound to the methyl group. This is supported by the position of the CH_3 **(7)** signal, which remains the same in all the subsequent spectra. Analogously, an upper field shift is observed for signals assigned to CH_2 groups **(4)**, **(5)** and **(6)**. The two triplets of **(5)** and **(6)** shift to lower ppm values on going from $H_5L_B^{3+}$ to H_2L_B, but do not change in a basic environment. The same behaviour is observed for the CH_2 **(4)** singlet, which shifts from 4.32 ppm in $H_5L_B^{3+}$ to 3.70 ppm in L_B^{2-}, with similar values (3.80 ppm) for H_2L_B and HL_B^-.

In conclusion, from the aliphatic signals it can be argued that it is plausible, in the deprotonation sequence of $H_5L_B^{3+}$, the tertiary amine group is involved first, and then the secondary ones.

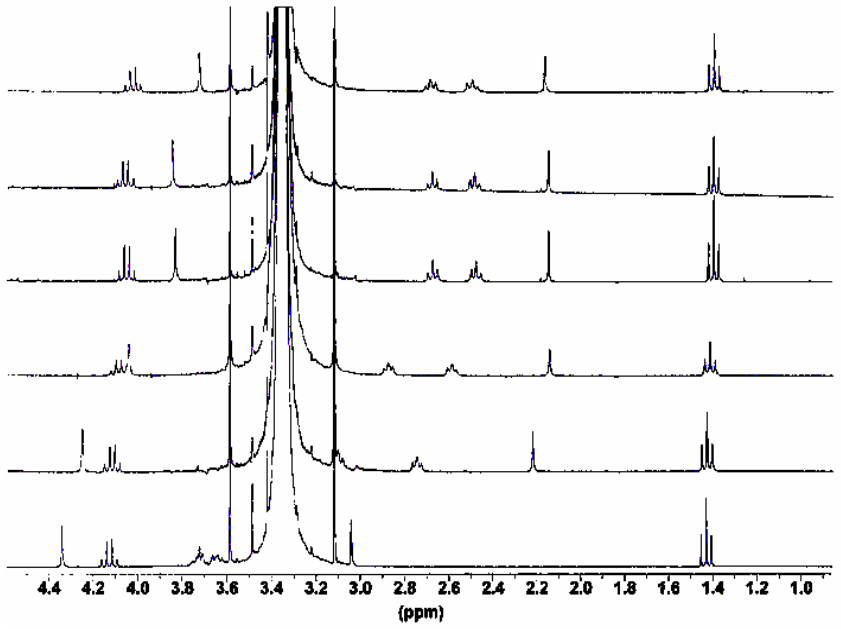

Figure III-Aliphatic region of ^{1}H-NMR spectra of H_2L_B in D_2O at different pH

Analysis of the aromatic region of the spectra is less clear. The signals of the aromatic protons of $H_5L_B^{3+}$ and $H_4L_B^{2+}$ remain unchanged, indicating that the aromatic moiety is not involved in deprotonation, whereas interactions between amine groups NH and phenol oxygens probably influence the chemical shift of aromatic protons **(1)**, **(2) and (3)**. With respect to the neutral molecule, In fact, their signals do shift to the lower field in $H_5L_B^{3+}$ and to the upper field (particularly **1**) in a basic environment (L_B^{2-}).

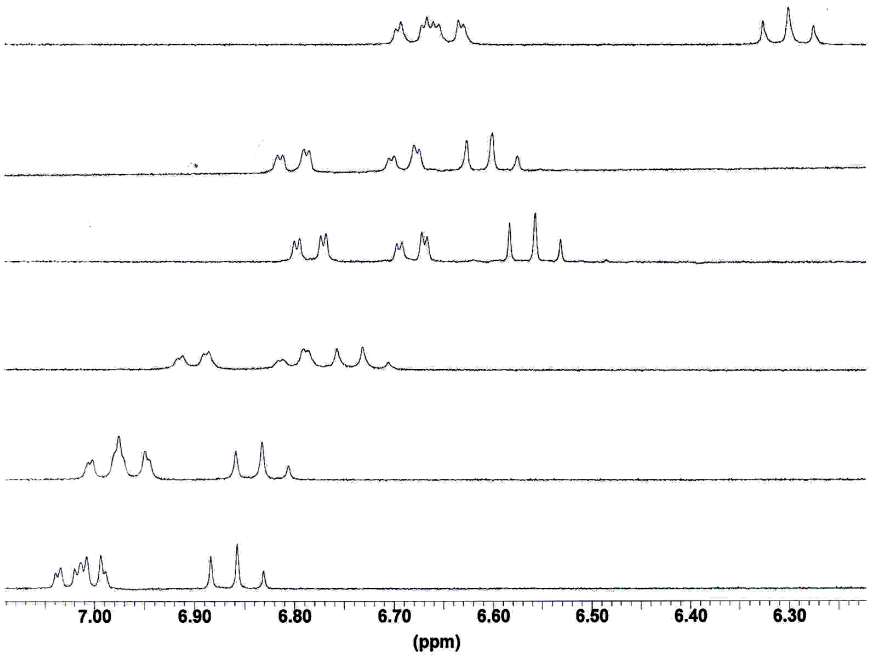

Figure IV-Aromatic region of ^{1}H-NMR spectra of H_2L_B in D_2O at varying pH values

The ^{13}C NMR spectra of H_2L_B confirm the data obtained from the proton spectra. The following table only shows the aliphatic signals, because it was difficult to assign the aromatic peaks. However, carbon C **(3')** is shifted 8 ppm downfield on going from the $H_5L_B^{3+}$ form to the neutral one; the others remain unchanged. When the basic environment caused deprotonation of both phenols, shifts of C **(1')** (5 ppm) and C **(3)** (4 ppm) in the L_B^{2-} form were observed with respect to the neutral one.

Species / ^{13}C(ppm)	$H_5L_B^{3+}$	$H_4L_B^{3+}$	$H_3L_B^{+}$	H_2L_B	HL_B^{-}	L_B^{2-}
C (**4**)	54.7	56.0	57.2	58.5	58.5	59.1
C (**5**)	48.5	49.2	51.0	52.5	52.5	53.0
C (**6**)	44.0	46.7	47.0	47.5	47.5	47.7
C (**7**)	42.7	42.2	43.0	43.5	43.5	43.8
C (**8**)	67.0	67.0	67.0	67.0	67.0	67.0
C (**9**)	16.2	16.2	16.2	16.2	16.2	16.2

Numbering refers to Figure II.

Although C **(9)** and C **(8)** signals (16.2 and 67.0 ppm respectively) are far from the protonation centre, and hence their chemical shift is unchanged in all forms of the ligand, C **(4)**, C **(5)** and C **(6)** show a change in chemical shift on going from a basic to an acid environment, due to

the protonation of the amine groups causing a lowering in the chemical shift of the nearby carbons. In fact, on going from the neutral specie to the completely protonated one, the $\underline{C}H_2$ **(4)** signal passes from 58.5 ppm to 54.7 ppm, that of $\underline{C}H_2$ **(5)** shifts by 4 ppm and that of $\underline{C}H_2$ **(6)** shifts from 47.5 ppm to 44.0 ppm.

Aliphatic signals $\underline{C}H_2$ **(4)**, $\underline{C}H_2$ **(5) and** $\underline{C}H_2$ **(6)** maintain their position in the spectra of H_2L_B, HL_B^- and L_B^{2-}. In conclusion, all the NMR results highlight the fact that deprotonation of the phenol groups of the ligand only occurs after deprotonation of the ammonium groups, according to the sequence of figure V.

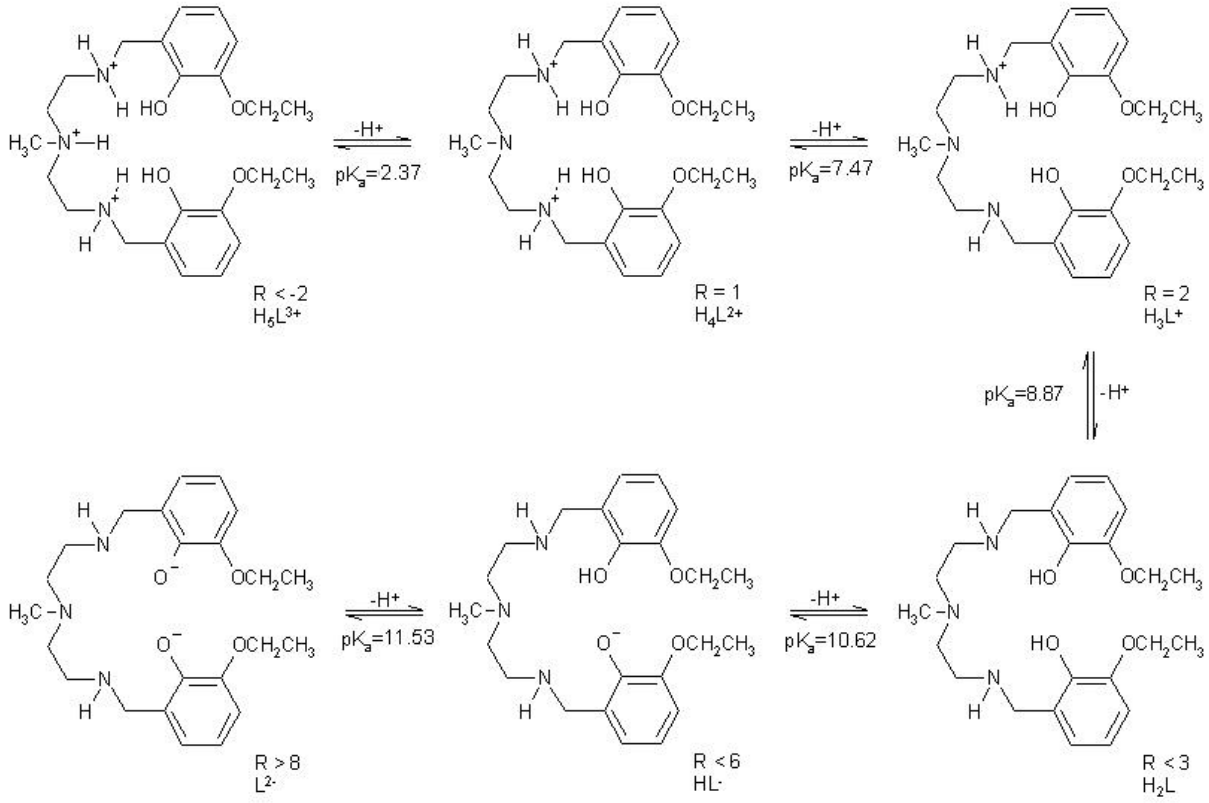

Figure V

NMR MEASUREMENTS ON H_2L_A SOLUTIONS

To evidence the effects of p[H^+] on the stability of the Schiff base H_2L_A, a series of NMR measurements in D_2O at three different p[D^+] values (~4, ~9, ~11) was performed.

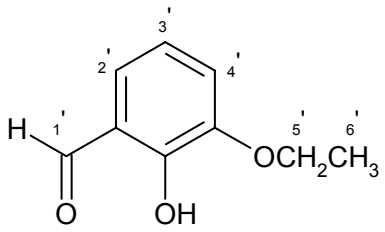

Figure VI

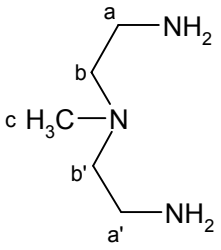

Figure VII

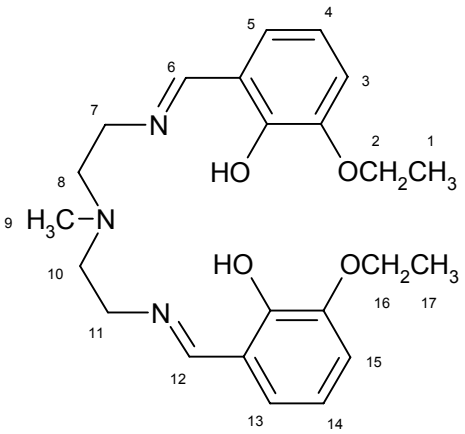

Figure VIII

In the ^{1}H NMR spectrum of the Schiff base at p[D^+]~4, only the signals of the amine and aldehyde precursors can be detected. In particular, the ^{1}H NMR spectrum (numbering refers to Figures VI, VII and VIII) shows a singlet at 9.97 ppm (aldehyde group proton **(1')**), a triplet at 7.05 ppm of proton **(3'),** and a multiplet at 7.35 ppm, attributed to protons **(2')** and **(4')**. The quartet at 4.20 ppm and the triplet at 1.40 ppm are due to the remaining signals of aldehyde, respectively CH_2 **(5')** and CH_3 **(6')**. The same spectra, also show the signals of the amine precursor: a singlet at 2.30 ppm (CH_3 **(c)**), and two triplets at 2.75 and 3.20 ppm for the protons of CH_2 **(a)**, **(a')** and **(b)**, **(b')**.

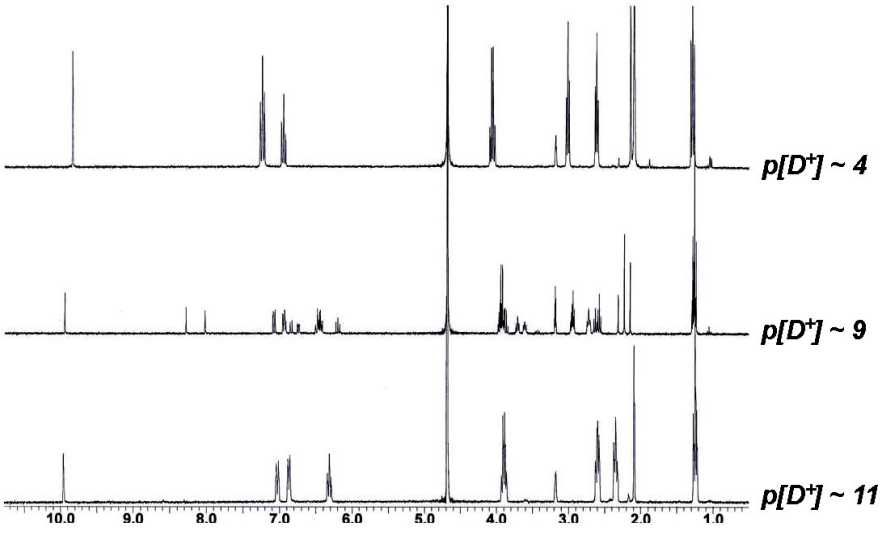

Figure IX –^{1}H-NMR spectra of H_2L_A at about p[D^+]= 4, 9 and 11

In the solution at p[D^+]~11, the Schiff base is also completely hydrolysed. The signal of the ^{1}H NMR spectrum can again be divided into two sets: the amine set of signals, with a singlet at 2.20 ppm (CH_3 ***c***), and two triplets of protons CH_2 at 2.45 and 2.70 ppm; and the aldehyde set of signals, with the singlet of CH **(1')** at 10.10 ppm, the triplet of proton **(3')** at 6.40 ppm, the doublet of doublets of aromatic protons **(2')** and **(4')** at 7.10 ppm, the quartet of CH_2 **(5')** at 4.00 ppm, and the triplet of CH_3 **(6')** at 1.40 ppm**.**

Proton	Multiplicity	ppm at pH 4	ppm at pH 11.5
CH (**1**)	s	9.97	10.10
CH (**2**)(**4**)	dd	7.35 (t)	7.10
CH (**3**)	t	7.05	6.40
CH_2 (**5**)	q	4.20	4.00
CH_3 (**6**)	t	1.40	1.40
CH_2 (**a**)(**a'**)	t	3.20	2.70
CH_2 (**b**)(**b'**)	t	2.75	2.45
CH_3 (**c**)	s	2.30	2.20

Behaviour at p[D^+]~9 is much more complex. In the ^{1}H NMR spectrum, the signals of the Schiff base, free aldehyde and amine with different degrees of protonation are present at the same time. There is a double set of amine peaks, because of the presence in solution of two species: monoprotonated and diprotonated amine. The following resonances were be attributed to these species: i) a singlet at 2.27 ppm, coupled (2D NOESY spectrum assignment) with the triplet at 2.57 ppm in the first species; ii) a second singlet at 2.45 ppm, coupled with the triplet at 2.95 of the second species; iii) triplets at 2.93 ppm (first species) and 2.95 ppm (second species), assigned by scalar correlation (2D COSY) to the adjacent CH_2 bound to the amine groups.

First species

Proton	Multiplicity	ppm
CH_2 (**a**)(**a'**)	t	2.95
CH_2 (**b**)(**b'**)	t	2.63
CH_3 (**c**)	s	2.45

Second species

Proton	Multiplicity	ppm
CH_2 (**a**)(**a'**)	t	2.93
CH_2 (**b**)(**b'**)	t	2.57
CH_3 (**c**)	s	2.27

The same spectrum at p[D^+]~9 reveals the signals of the Schiff base. Two signals, attributed to the imine group at 8.40 and 8.14 ppm, may be explained, as described below, by asymmetry in

the molecule, generated by the different distribution of the hydrogen bonds in the Schiff base. For correct assignment of all signals, bidimensional 2D COSY and NOESY spectra were recorded.

The moiety of the molecule in which the phenol proton interacts with the imine group is characterised by the singlet at 8.14 ppm of the imine proton, the doublets of doublets at 6.49 and 6.74 ppm of aromatic protons **(5)** and **(3)**, the triplet of CH **(4)** at 6.19 ppm, the triplet of CH_2 **(7)** at 3.60 ppm, a multiplet of CH_2 **(8)** at 2.72 ppm and, lastly, the triplet and quartet of the ethoxy group at 3.92 and 1.25 ppm, respectively. The coupling between the multiplet at 2.72 ppm (corresponding to CH_2 **(8)** and CH_2 **(10)**) and the two triplets at 3.60 and 3.71 ppm (corresponding to CH_2 **(7)** and CH_2 **(11)** protons), was evidenced by a bidimensional spectrum.

Proton	Multiplicity	ppm
CH_3 (**1**)	(t)m	3.92
CH_2 (**2**)	(q)m	1.25
CH (**3**)	dd	6.74
CH (**4**)	t	6.19
CH (**5**)	(dd)m	6.49
CH (**6**)	s	8.14
CH_2 (**7**)	t	3.60
CH_2 (**8**)	(t)m	2.72
CH_3 (**9**)	s	2.36
CH_2 (**10**)	(t)m	2.72
CH_2 (**11**)	t	3.71
CH (**12**)	s	8.40
CH (**13**)	dd	6.84
CH (**14**)	(t)m	6.45
CH (**15**)	(dd)m	6.92
CH_2 (**16**)	(q)m	1.25
CH_3 (**17**)	(t)m	3.92

The second moiety of the molecule shows the singlet of the imine group at 8.40 ppm, two doublets of doublets at 6.84 and 6.92 ppm for aromatic protons **(13)** and **(15)**, the triplet of proton **(14)** at 6.45 ppm, two triplets of CH_2 **(10)** and **(11)** at 2.72 and 3.71 ppm**,** and the peaks of the CH_3CH_2O group at 3.92 and 1.25 ppm. The singlet of CH_3**(9)** at 2.36 ppm integrates exactly for 3 protons belonging to a single molecule, and is correlated correctly to the two methylenes **(8)** and **(10).**

NMR measurements demonstrate that, at reagent concentrations higher than that employed for spectrophotometric analysis, the Schiff base is present in solutions at p[H^+]~9 at least.

Zn^{2+}/H_2L_A SYSTEM IN D_2O.

Some well-planned NMR experiments confirm, with an independent technique, the results regarding the nature of the species in solution obtained by potentiometric studies. Studies were run at three different p[D^+] values (~6, ~9, ~11.5). The value p[D^+]~9 was chosen, as the simulation program of solution equilibrium predicted the greatest concentration of neutral species ZnL_A in solution (90%).

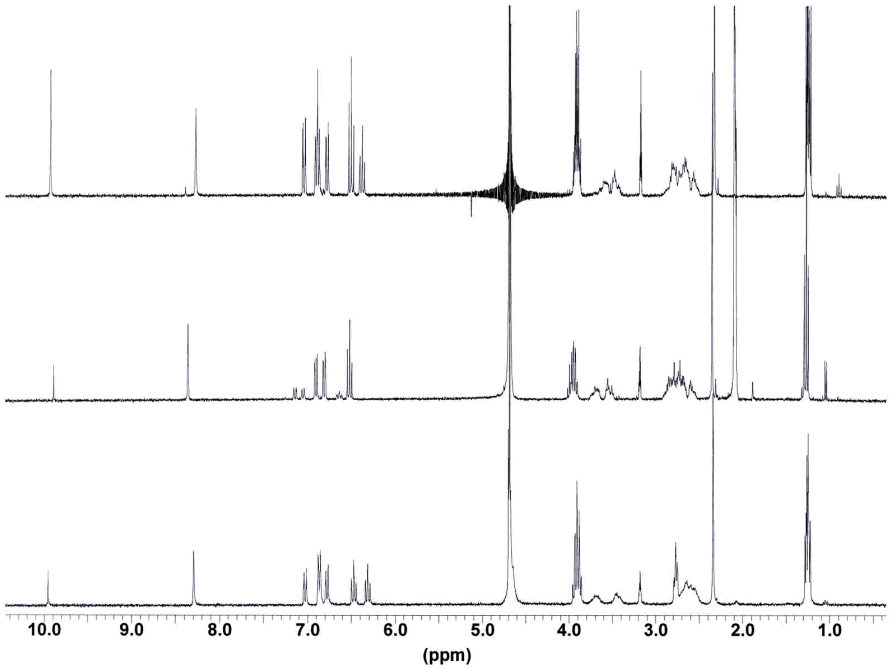

Figure X–^{1}H-NMR spectra of H_2L_A/Zn 1:1 system at about p[D^+] = 6, 9 and 11.5

The analysis of the ^{1}H spectrum and bidimensional spectra 2D COSY and 2D NOESY at 298 K at p[D^+]~9 determined the species in solution and their relative abundances, from integration of signals. The peaks of free aldehyde, the complexed amine and [Zn(L_A)] were present at the same time. The very broad signals related to the amine consist of a multiplet at 2.75 ppm and a singlet at 2.50 ppm, overlapping that of CH_3 **(9)** of the Schiff base. The NOESY spectrum shows dipolar coupling between the two signals, confirming that they belong to the same molecule. From the integration of aldehyde signals, it emerged that the quantity of this substance in solution is less than expected: this was due to the formation of a precipitate of formulation [Zn(aldehydate)(ClO_4)],

which reduced free aldehyde in solution. This was confirmed by potentiometric titrations of this system, in which a precipitate with the same formulation formed from p[H^+] 7.9.

Lastly, the presence of complex [Zn(L_A)] was confirmed by the singlet at 8.50 ppm of the imine proton. Bidimensional 2D COSY and NOESY spectra proved the coupling of this signal with the doublet of doublets at 6.95 ppm which was thus assigned to aromatic proton **(5)**, and the coupling of the doublet of doublets at 7.05 ppm with the multiplet at 4.10 ppm, attributed respectively to aromatic proton **(3)** and the CH_2 **(2)** protons. In addition, weak coupling was observed between the imine signal and the multiplets at 3.65 and 3.85 ppm which were therefore assigned to CH_2 **(7).** This group was also coupled with the multiplet at 2.90 ppm (CH_2 **(8)**), correlated with the singlet at 2.50 ppm (CH_3 **(9)**). **(**For numbering, see Figure VIII).

Protons	Multiplicity	ppm
CH_3 (**1**)	t	1.40
CH_2 (**2**)	(q)m	4.10
CH (**3**)	dd	7.05
CH (**4**)	t	6.65
CH (**5**)	dd	6.95
CH (**6**)	s	8.50
CH_2 (**7**)	m	3.85/3.65
CH_2 (**8**)	m	2.90
CH_3 (**9**)	s	2.50

Note that the coordinated Schiff base was still present at p[H^+] ~6 and ~11.5, unlike what was observed for the free ligand H_2L_A, which was completely hydrolysed at this p[H^+]. Coordination of Zn^{2+} partially inhibits this hydrolysis, confirming the templating and stabilizing effect of the metal ion.

ELECTRONIC SUPPLEMENTARY INFORMATION

POTENTIOMETRIC MEASUREMENTS

H_2L_B Systems

H_2L_B protonation reactions

TABLE 1SB - Experimental details of H_2L_B titrations.

H_2L_B							
Symbols	*V°* *(mL)*	*$C°_{H2LB}$* *(mmol dm^{-3})*	*$C°_H$* *(mmol dm^{-3})*	*$p[H^+]_F$*	*$C_{OH,T}$* *(mmol dm^{-3})*	*Δt* *(s)*	**NP**
←	*35.0*	*0.25*	*2.985*	*11.22*	*104.4*	*90*	*49*
↔	*35.0*	*0.50*	*6.003*	*11.13*	*104.4*	*240*	*50*
♦	*35.0*	*1.01*	*12.00*	*11.15*	*105.3*	*90*	*86*
△	*20.0*	*4.97*	*25.23*	*11.85*	*101.5*	*60*	*58*
□	*21.0*	*2.37*	*11.90*	*12.02*	*101.5*	*60*	*86*
▽	*23.0*	*3.45*	*17.41*	*12.09*	*101.5*	*60*	*92*

Legend: V°: initial cell volume; $C°_{H2LB}$ and $C°_H$: initial concentrations of H_2L_B and mineral acid in cell solution; $p[H^+]_F$: $p[H^+]$ at the end of titration; $C_{OH,T}$: titrant standard base concentration; $C_{H,T}$: titrant standard acid concentration; Δt: waiting time imposed to the data collection criterion; NP: number of experimental points collected

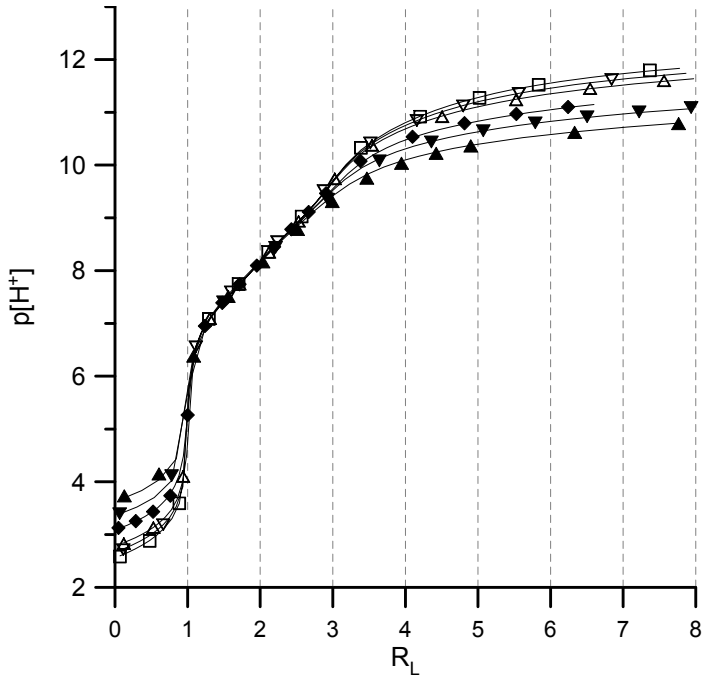

Figure 1SB – Potentiometric titration curves of H_2L_B. Symbol, $C^o_{H_2L_B}$ (initial concentration of ligand), $C_{H,exc}$, C_{OH} (titrant standard base concentration): ←, 0.25, 2.235, 104.4; ↔, 0.50, 4.503; 104.4; ♦, 1.01, 8.98, 105.3; □, 2.37, 4.790, 101.5; ▽, 3.45, 7.06, 101.5; △, 4.97, 10.32, 101.5 mmol dm^{-3}. Solid lines calculated with stability constants of Table 1

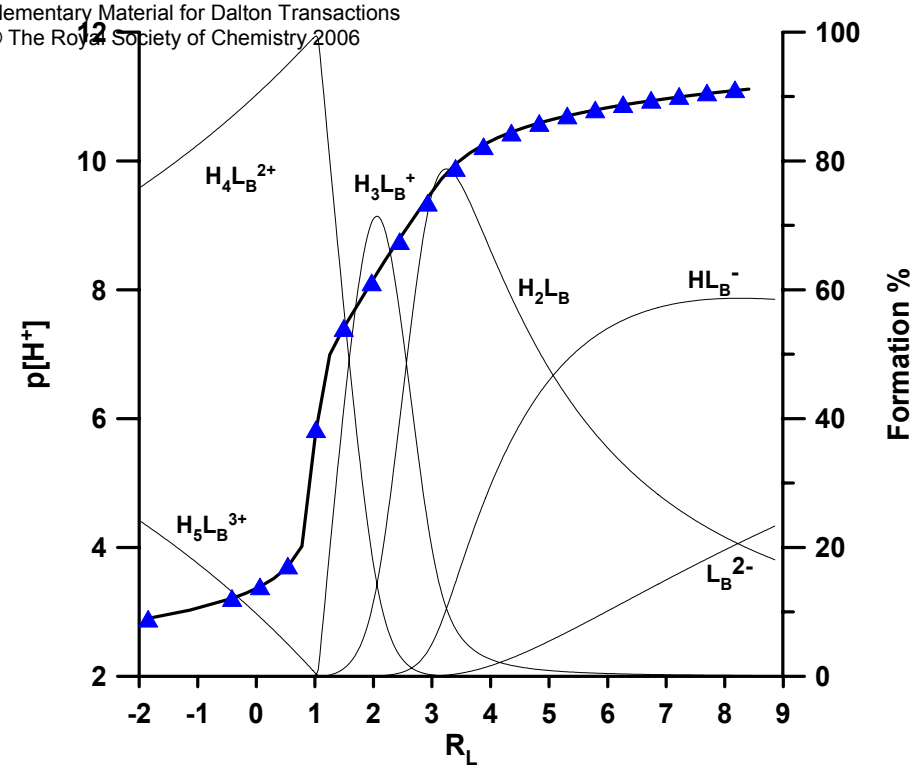

Figure 2SB – Species distribution diagram for a 0.5 mmol dm^{-3} H_2L_B solution. p[H^+] values (left y axis) reported as a function of R_L, moles of base added per mole of ligand; solid line calculated with stability constants on Table 1. % = percent of initial concentration of H_2L_B (right y axis).

H_2L_B Metal Complexes

System H_2L_B / Cu^{2+}

TABLE 2SB - Experimental details of H_2L_B/Cu^{2+} titrations.

H_2L_B									
Data set	Symbols	V° (mL)	$C°_{H2LB}$ (mmol dm^{-3})	$C°_{Cu2+}$ (mmol dm^{-3})	$C°_{H}$ (mmol dm^{-3})	$p[H^+]_F$	$C_{OH,T}$ (mmol dm^{-3})	Δt (s)	NP
1	▲	70.0	0.116	0.246	1.656	4.84	104.8	240	52
2	▲	70.0	0.270	0.246	3.209	11.20	104.8	240	81
3	▲	70.0	0.495	0.246	6.248	11.21	104.8	240	81
4	▲	70.0	0.995	0.246	12.248	11.33	104.8	240	80
5	▼	28.0	2.11	0.656	10.69	11.77	101.5	240	66
6	▼	28.0	2.11	1.752	10.69	11.76	101.5	240	78
7	▼	28.0	4.19	2.189	21.47	11.82	101.5	240	70

Legend: V°: initial cell volume; $C°_{H2LB}$, $C°_{Cu2+}$, $C°_{H}$ initial concentrations of H_2L_B, copper(II) and mineral acid in cell solution; $p[H^+]_F$: $p[H^+]$ at the end of titration; $C_{OH,T}$: titrant standard base concentration; Δt: waiting time imposed to the data collection criterion; NP: number of experimental points collected

TABLE 3SB	$\log \beta \pm 3\sigma$
Reaction	M = Cu
$Cu^{2+} + L_B^{=} + 2H^+ \leftrightarrows CuH_2L_B^{2+}$	34.43 ± 0.12
$Cu^{2+} + L_B^{=} + H^+ \leftrightarrows CuHL_B^{+}$	30.91 ± 0.05
$Cu^{2+} + L_B^{=} \leftrightarrows CuL_B$	23.22 ± 0.08
$Cu^{2+} + L_B^{=} + H_2O \leftrightarrows CuL_B(OH)^- + H^+$	-----[a]-----

[a] *Presence of this species uncertain. When data sets 1-4 were refined alone, minimisation program gave $\log\beta = 12.9 \pm 0.2$; however, presence of this species was excluded when all data sets were treated together.*

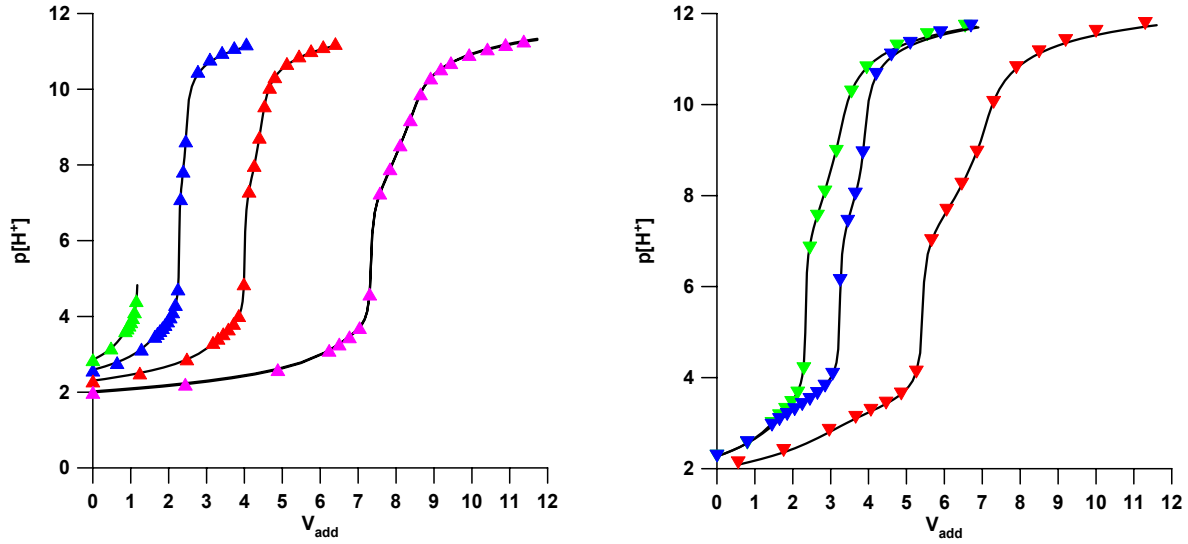

FIGURE 3SB – Experimental data and theoretical curves calculated with data on Table 2SB and stability constants on Table 1 and Table 2.

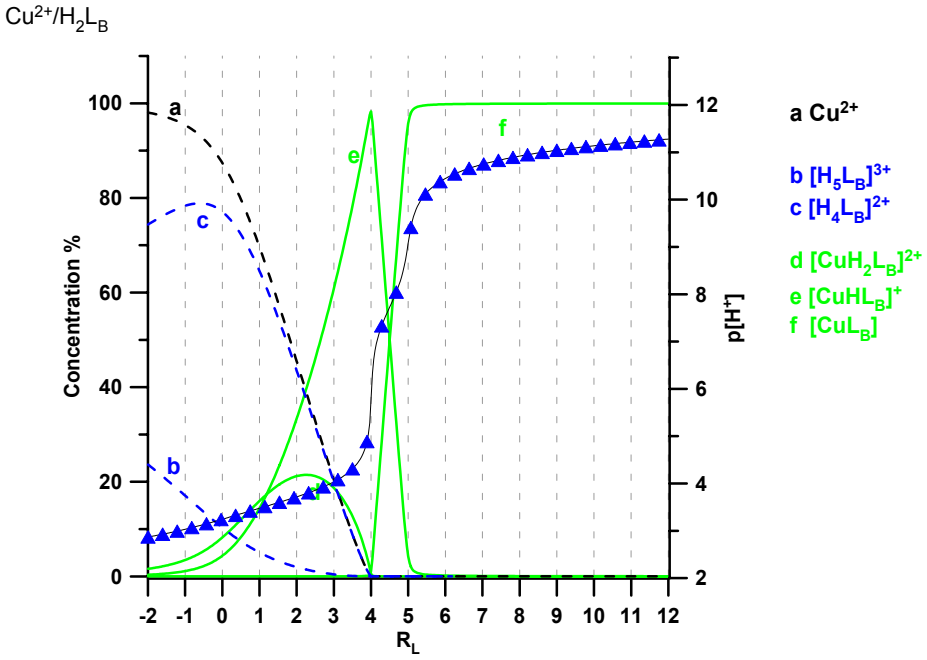

FIGURE 4SB – Species distribution diagram indicating species present in solution as a function of p[H$^+$]. Percent distribution calculated with respect to initial copper(II) concentration for a system initially containing H_2l_B:Cu(II) = 0.27:0.25 mmol dm^{-3}. p[H$^+$] values (left y axis) reported as a function of R_L, moles of base added per mole of ligand; solid line calculated with stability constants on Tables 1 and 2.

System H_2L_B/Ni^{2+}

TABLE 4SB - Experimental details of H_2L_B/Ni^{2+} titrations.

H_2L_B									
Data set	**Symbols**	**V° (mL)**	**$C°_{H2LB}$ (mmol dm^{-3})**	**$C°_{Ni2+}$ (mmol dm^{-3})**	**$C°_{H}$ (mmol dm^{-3})**	**$p[H^+]_F$**	**$C_{OH,T}$ (mmol dm^{-3})**	**Δt (s)**	**NP**
1	▲	35.0	0.25	0.25	2.93	11.40	105.4	240	39
2	▲	35.0	0.50	0.25	5.94	11.20	105.4	240	27
3	▲	35.0	1.00	0.25	12.02	11.10	105.4	240	71
4	▼	28.5	3.39	1.36	16.94	5.51	101.5	240	72
5	▼	25.5	3.78	2.27	18.86	5.35	101.5	240	86

Legend: V°: initial cell volume; $C°_{H2LB}$, $C°_{Ni2+}$, $C°_{H}$ initial concentrations of H_2L_B, nickel(II) and mineral acid in cell solution; $p[H^+]_F$: $p[H^+]$ at the end of titration; $C_{OH,T}$: titrant standard base concentration; Δt: waiting time imposed to the data collection criterion; NP: number of experimental points collected

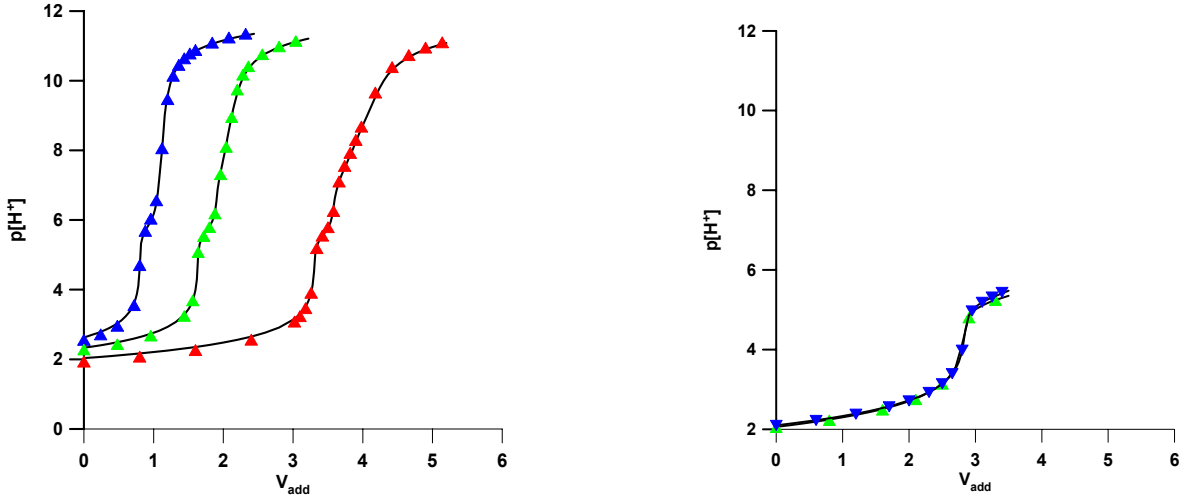

FIGURE 5SB – Experimental data and theoretical curves calculated with data on Table 4SB and stability constants on Table 1 and Table 2.

Ni^{2+}/H_2L_B

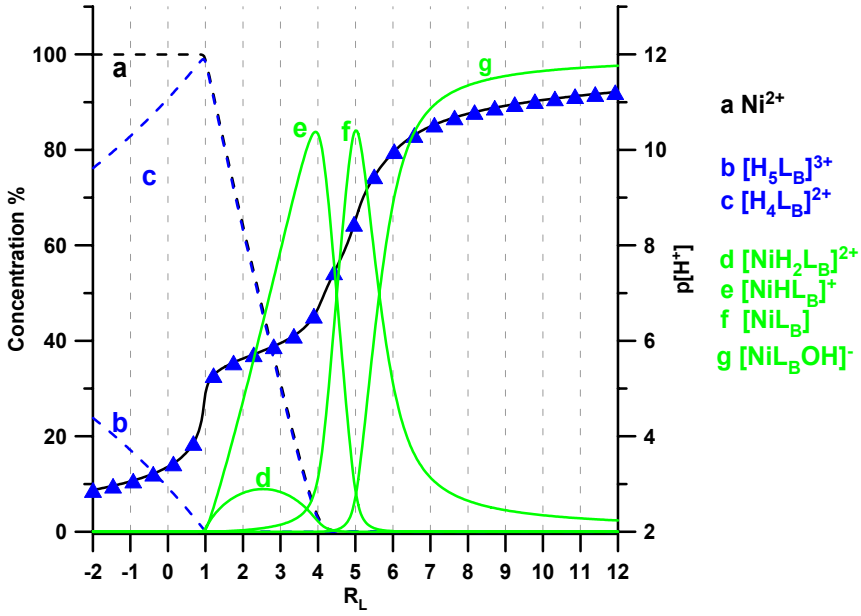

FIGURE 6SB – Species distribution diagram indicating species present in solution as a function of $p[H^+]$. Percent distribution calculated with respect to initial nickel(II) concentration for a system initially containing H_2l_B:Ni(II) = 0.25:0.25 mmol dm^{-3}. $p[H^+]$ values (left y axis) reported as a function of R_L, moles of base added per mole of ligand; solid line calculated with stability constants on Tables 1 and 2.

System H_2L_B/Zn^{2+}

TABLE 5SB - Experimental details of H_2L_B/Zn^{2+} titrations.

H_2L_B									
Data set	**Symbols**	**V° (mL)**	**$C°_{H2LB}$ (mmol dm^{-3})**	**$C°_{Zn2+}$ (mmol dm^{-3})**	**$C°_H$ (mmol dm^{-3})**	**$p[H^+]_F$**	**$C_{OH,T}$ (mmol dm^{-3})**	**Δt (s)**	**NP**
1	▲	*35.0*	*0.945*	*1.00*	*11.86*	*11.34*	*105.3*	*180*	*69*
2	▲	*35.0*	*0.945*	*0.50*	*11.86*	*11.39*	*105.3*	*180*	*69*
3	▲	*35.0*	*0.945*	*0.25*	*11.86*	*11.33*	*105.3*	*180*	*58*
4	▼	*25.5*	*3.784*	*1.08*	*18.83*	*11.83*	*101.5*	*60*	*68*
5	▼	*25.5*	*3.784*	*0.54*	*18.83*	*11.81*	*101.5*	*60*	*67*

Legend: V°: initial cell volume; $C°_{H2LB}$, $C°_{Zn2+}$, $C°_H$ initial concentrations of H_2L_B, zinc(II) and mineral acid in cell solution; $p[H^+]_F$: $p[H^+]$ at the end of titration; $C_{OH,T}$: titrant standard base concentration; Δt: waiting time imposed to the data collection criterion; NP: number of experimental points collected

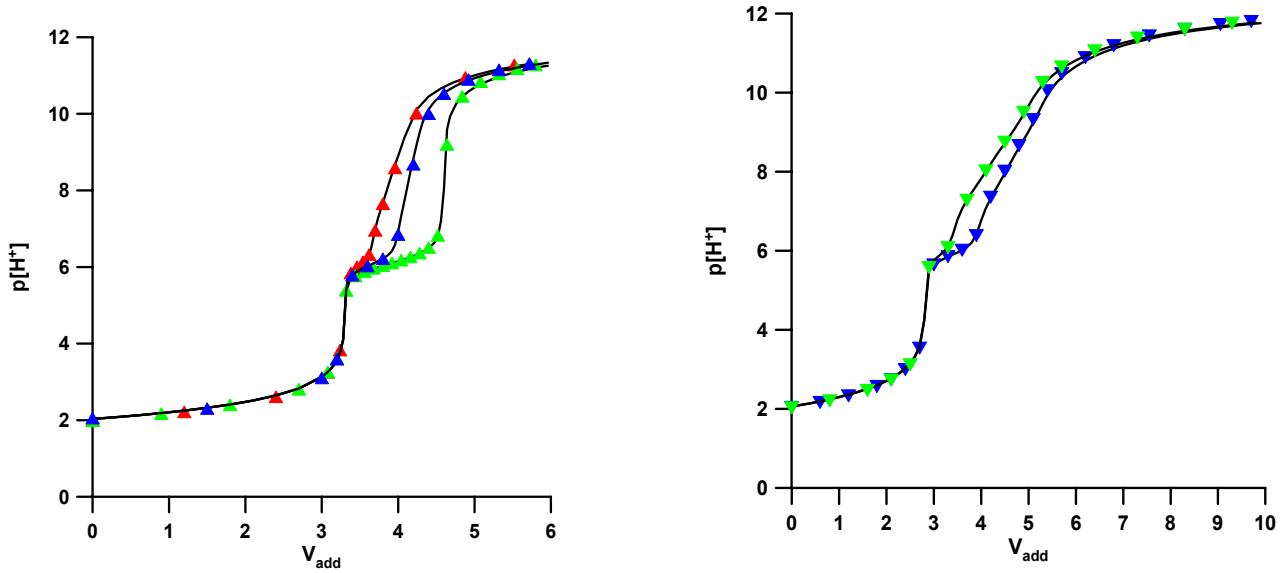

FIGURE 7SB – Experimental data and theoretical curves calculated with data on Table 5SB and stability constants on Table 1 and Table 2.

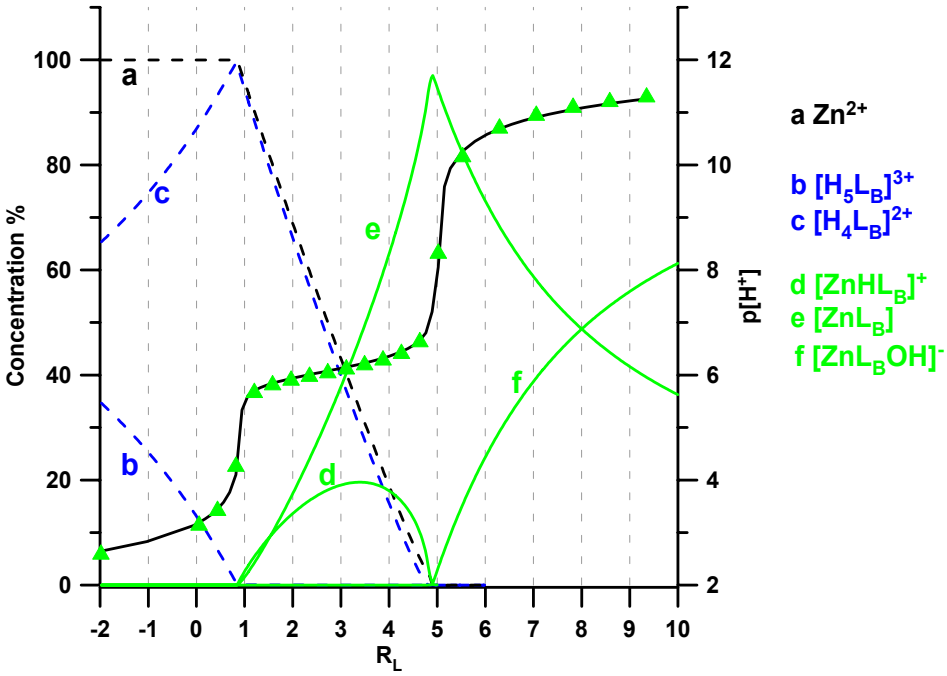

FIGURE 8SB – Species distribution diagram indicating species present in solution as a function of p[H⁺]. Percent distribution calculated with respect to initial zinc(II) concentration for a system initially containing H_5l_B:Zn(II) = 1.0:0.94 mmol dm^{-3}. p[H⁺] values (left y axis) reported as a function of R_L, moles of base added per mole of ligand; solid line calculated with stability constants on Tables 1 and 2.

H_2L_A PRECURSORS

Protonation and complexation reactions of 1,2-ethanediamine,N-(2-aminoethyl)-N-methyl (MeDIEN)

TABLE 1SA - Experimental details for MeDIEN and M^{2+}/MeDIEN systems.

MeDIEN								
V° (mL)	$C°_{MeDIEN}$ (mmol dm^{-3})	$C°_{M2+}$ (mmol dm^{-3})	$C°_{H}$ (mmol dm^{-3})	$p[H^+]_F$	$C_{OH,T}$ (mmol dm^{-3})	$C_{H,T}$ (mmol dm^{-3})	Δt (s)	NP
70	5.12		-----	2.40	-----	99.45	120	98
72	4.98		20.51	10.00	102.3	-----	120	81
70	0.510		5.98	11.30	102.3	-----	120	91
70	0.50	M=Cu 0.50	6.24	11.30	102.3		120	100
70	0.50	M=Cu 0.25	6.06	11.40	102.3		120	100
70	0.50	M=Ni 0.50	5.94	11.00	102.3		240	87
70	0.50	M=Zn 0.50	6.20	10.90	102.3		120	91
70	0.50	M=Zn 0.25	6.08	9.60	102.3		120	70

Legend: V°: initial cell volume; $C°_{MeDIEN}$, $C°_{M2+}$, $C°_{H}$: initial concentrations of MeDIEN, metal(II) and mineral acid in cell solution; $p[H^+]_F$: $p[H^+]$ at the end of titration; $C_{OH,T}$: titrant standard base concentration; $C_{H,T}$: titrant standard acid concentration; Δt: waiting time imposed to the data collection criterion; NP: number of experimental points collected

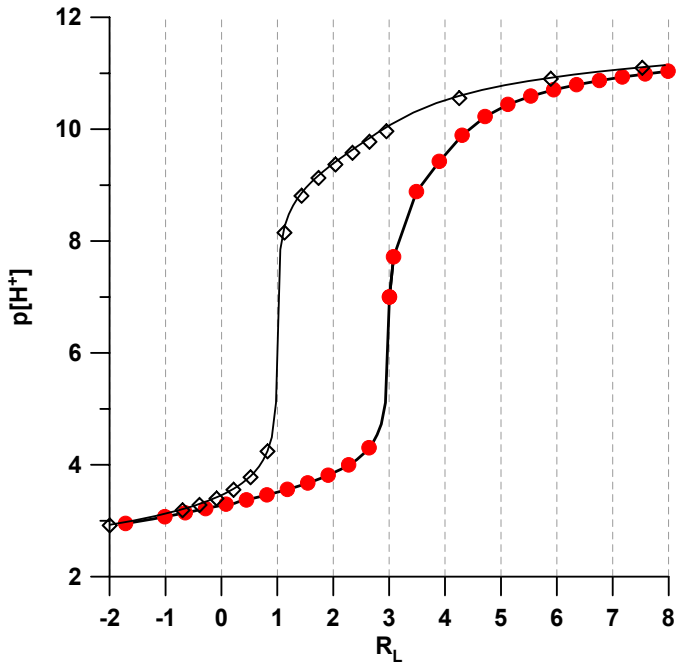

FIGURE 1SA –Potentiometric titration curve of Cu(II)/MeDIEN = 0.50/0.50 mmol dm^{-3} as a function of R_L.(●). Empty symbols: titration of MeDien alone. Solid lines calculated with stability constants of Tables 3 and 5.

Protonation and complexation reactions of 3-ethoxy-2-hydroxybenzaldehyde (HAld)

TABLE 2SA - Experimental details for HAld and Me2+/HAld systems.

HAld							
V° *(mL)*	*$C°_{HAld}$* *(mmol dm^{-3})*	*$C°_{M2+}$* *(mmol dm^{-3})*	*$C°_{H}$* *(mmol dm^{-3})*	*$p[H^+]_F$*	*$C_{OH,T}$* *(mmol dm^{-3})*	**Δt** *(s)*	**NP**
70	*0.50*		*6.47*	*11.31*	*102.3*	*60*	*100*
70	*1.00*		*12.97*	*11.72*	*102.3*	*60*	*100*
70	*0.50*	*M=Cu 0.50*	*6.74*	*5.60*	*102.3*	*120*	*37*
70	*0.50*	*M=Cu 0.25*	*6.55*	*5.30*	*102.3*	*120*	*46*
70	*0.50*	*M=Ni 0.50*	*6.46*	*7.26*	*102.3*	*240*	*32*
70	*0.50*	*M=Zn 0.50*	*6.29*	*7.90*	*102.3*	*120*	*38*

Legend: V°: initial cell volume; $C°_{HAld}$, $C°_{M2+}$, $C°_{H}$: initial concentrations of Ald^-, metal(II) and mineral acid in cell solution; $p[H^+]_F$: $p[H^+]$ at the end of titration; $C_{OH,T}$: titrant standard base concentration; $C_{H,T}$: titrant standard acid concentration; Δt: waiting time imposed to the data collection criterion; NP: number of experimental points collected

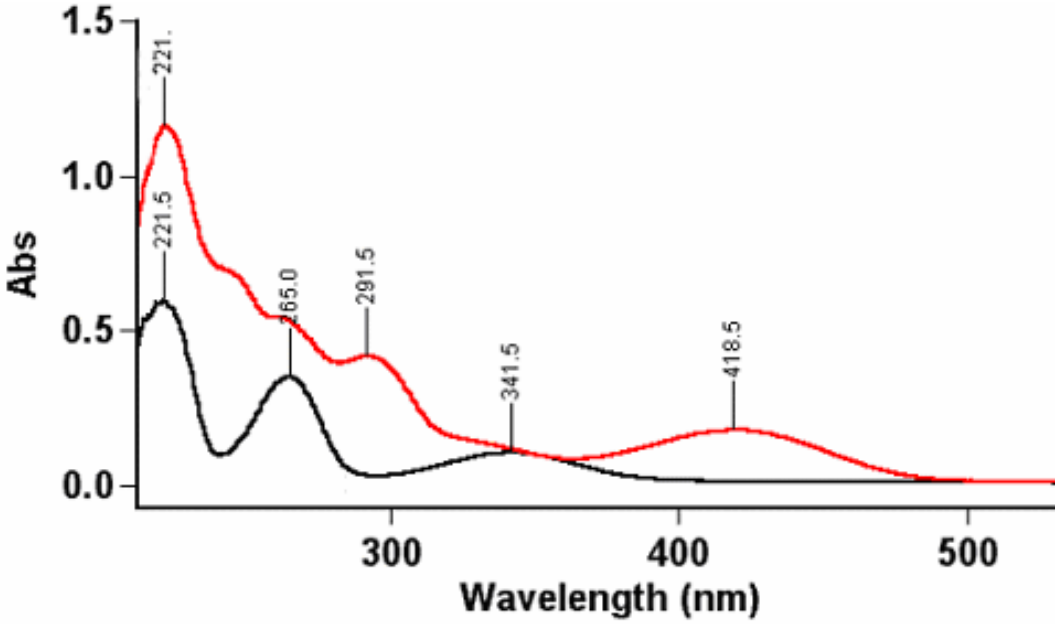

Figure 2SA – UV-Vis spectra of H_2L_A (red) and of HAld (black) in methanol.

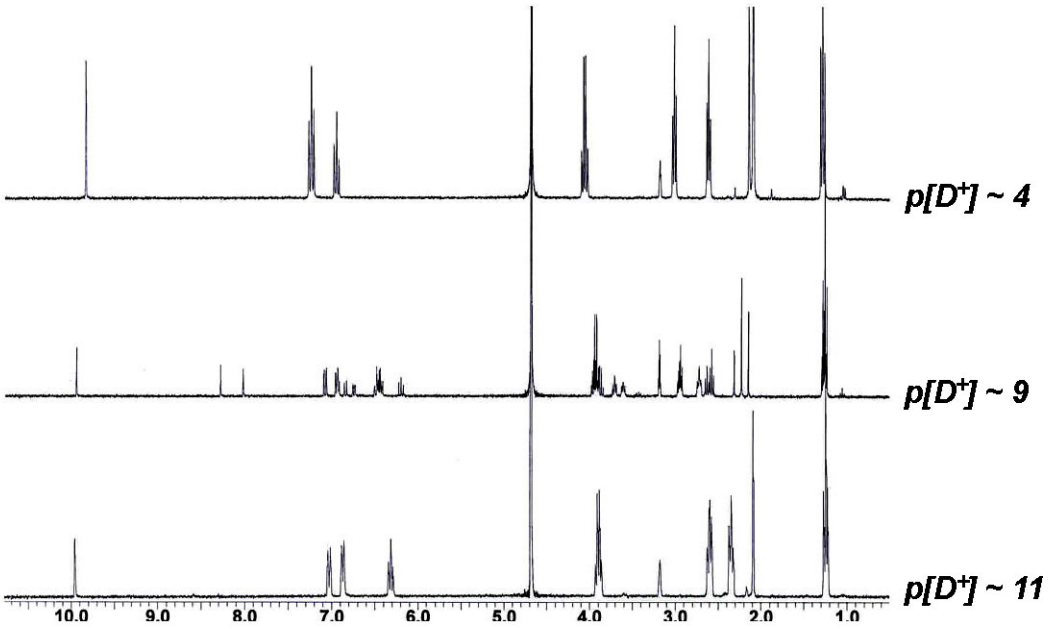

Figure 3SA – NMR spectra of H_2L_A solutions in D_2O at p[D^+] ~4, ~9, ~11.

H_2L_A FORMATION AND PROTONATION REACTIONS

TABLE 3SA - H_2L_A formation: experimental details.

H_2L_A							
Symbols	$V°$ *(mL)*	$C°_{H2LA}$ *(mmol dm^{-3})*	$C°_H$ *(mmol dm^{-3})*	$p[H^+]_F$	$C_{OH,T}$ *(mmol dm^{-3})*	Δt *(s)*	NP
●	70.0	0.260	2.99	10.99	100.0	120	81
◆	70.0	0.520	5.99	11.34	100.0	120	91
▲	72.8	0.990	3.92	10.98	100.0	120	90

Legend: $V°$: initial cell volume; $C°_{H2LA}$: initial concentration of H_2L_A, $C°_H$: mineral acid in the cell solution; $p[H^+]_F$: $p[H^+]$ at the end of titration; $C_{OH,T}$: titrant standard base concentration; $C_{H,T}$: titrant standard acid concentration; Δt: waiting time imposed to the data collection criterion; NP: number of experimental points.

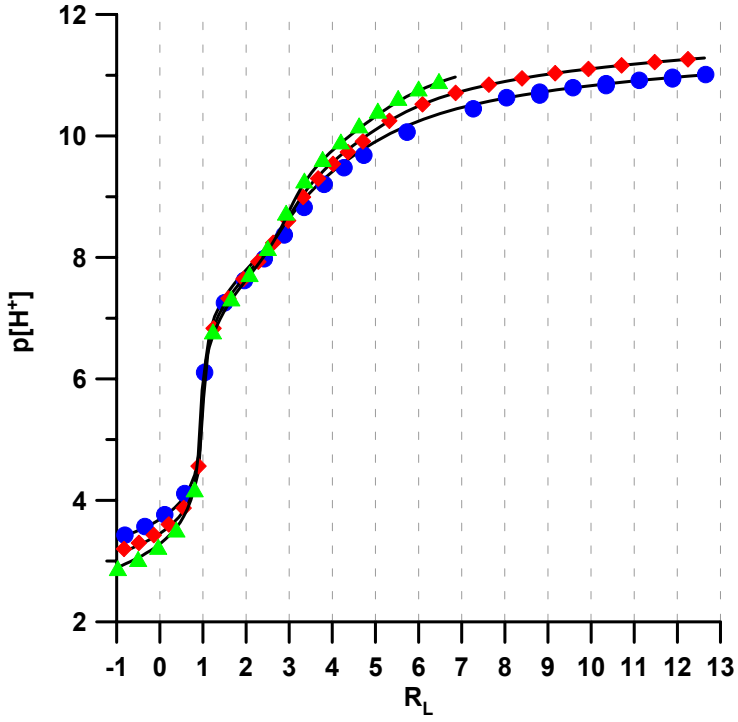

Figure 4SA. ***Potentiometric titration curves of H_2L_A. Symbol, $C^o_{H_2L_A}$ (initial concentration of ligand), $C_{H,exc}$, C_{OH} (titrant standard base concentration): ℓ, 0.263, 2.205, 100.0; ⎯, 0.522, 4.430; 100.0; ⎯, 0.990, 0.950, 100.0 mmol dm^{-3}. Solid lines calculated with stability constants of Table 6***

H_2L_A Metal Complexes

System H_2L_A / Cu^{2+}

TABLE 4SA - Experimental details of H_2L_A/Cu^{2+} titrations.

Symbols	V° (mL)	$C°_{H2LA}$ (mmol dm^{-3})	$C°_{Cu2+}$ (mmol dm^{-3})	$C°_H$ (mmol dm^{-3})	$p[H^+]_F$	$C_{OH,T}$ (mmol dm^{-3})	Δt (s)	NP
△	70.0	0.52		5.99	11.00	100.0	120	81
◆	70.0	0.51	0.50	5.97	11.20	100.0	240	101
●	70.0	0.51	1.00	6.22	4.60	100.0	240	60
▲	70.0	0.48	0.25	5.79	11.30	100.0	240	86

Legend: V°: initial cell volume; $C°_{H2LA}$, $C°_{Cu2+}$, $C°_H$ initial concentrations of H_2L_A, copper(II) and mineral acid in cell solution; $p[H^+]_F$: $p[H^+]$ at the end of titration; $C_{OH,T}$: titrant standard base concentration; Δt: waiting time imposed to the data collection criterion; NP: number of experimental points.

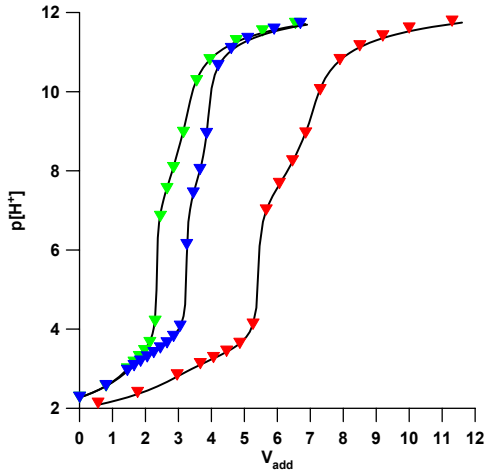

FIGURE 5SA – Experimental data and theoretical curves calculated with the data on Table 4SA and the stability constants of Tables 4, 5 and 6.

TABLE 5SA – Stability constants for H_2L_A/Cu^{2+} system.

TABLE 5SA	
Reaction	**log β ± 3σ**
$Cu^{2+} + MeDIEN + 2A^- + H^+ \leftrightarrows CuHL_A^+$	36.26 ± 0.15
$Cu^{2+} + MeDIEN + 2A^- \leftrightarrows CuL_A$	28.43 ± 0.16
$Cu^{2+} + MeDIEN + 2A^- + H_2O \leftrightarrows CuL_A(OH)^- + H^+$	note [a]

[a] *Presence of this species uncertain. Throughout minimisation process, a value of* $\log\beta = 17.2$ *for its formation constant was calculated; however, presence of this species was excluded in the following minimisation step, due to high standard deviation of* $\log\beta$.

TABLE 6SA - Experimental details of H_2L_A/Ni^{2+} titrations.

Symbols	*V°* *(mL)*	*$C°_{H2LA}$* *(mmol dm^{-3})*	*$C°_{Ni2+}$* *(mmol dm^{-3})*	*$C°_{H}$* *(mmol dm^{-3})*	*$p[H^+]_F$*	*$C_{OH,T}$* *(mmol dm^{-3})*	*Δt* *(s)*	*NP*
△	*70.0*	*0.52*		*5.99*	*11.00*	*100.0*	*120*	*81*
◆	*70.0*	*0.50*	*0.50*	*5.96*	*11.19*	*102.3*	*240*	*91*
●	*70.0*	*0.51*	*1.00*	*5.59*	*6.16*	*102.3*	*240*	*39*
▲	*70.0*	*0.51*	*0.27*	*5.79*	*11.22*	*102.3*	*240*	*90*

Legend: V°: initial cell volume; $C°_{H2LA}$, $C°_{Ni2+}$, $C°_{H}$ initial concentrations of H_2L_A, nickel(II) and mineral acid in cell solution; $p[H^+]_F$: $p[H^+]$ at the end of titration; $C_{OH,T}$: titrant standard base concentration; Δt: waiting time imposed to the data collection criterion; NP: number of experimental points collected

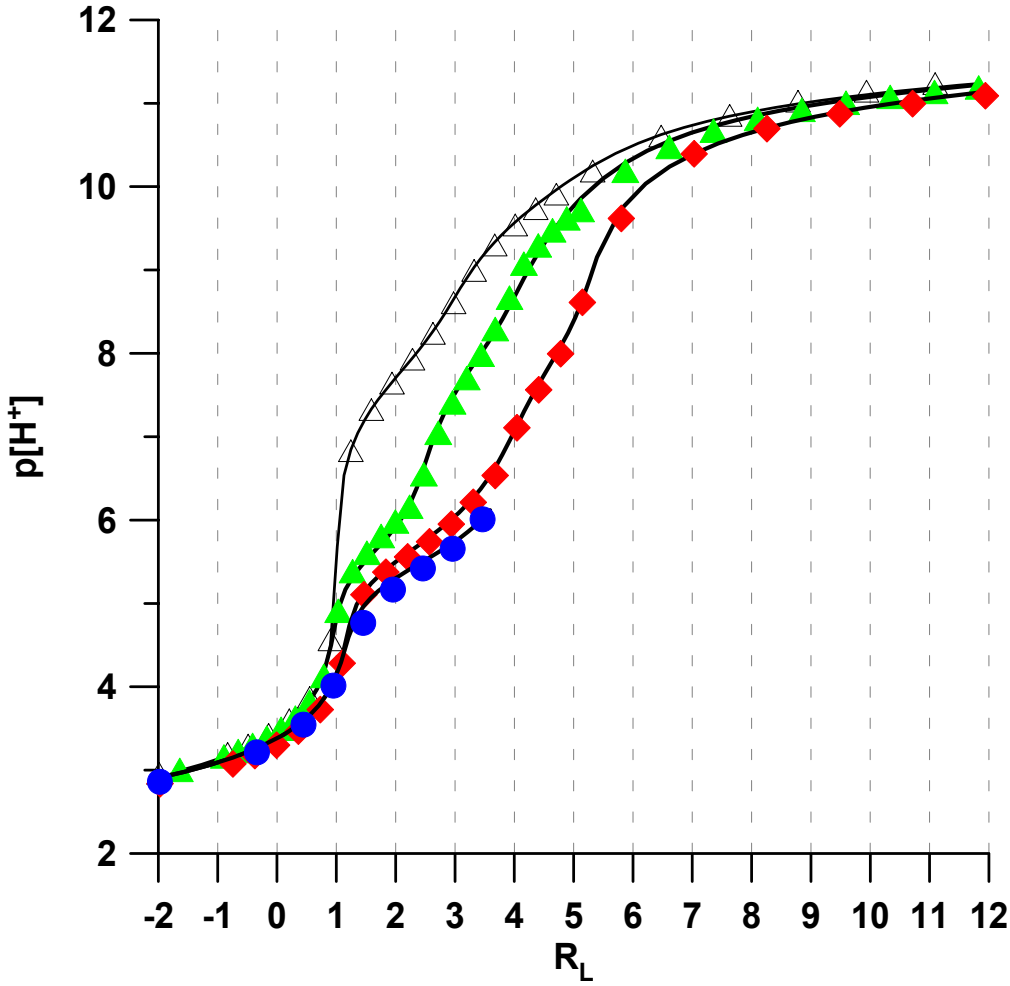

FIGURE 6SA – Experimental data and theoretical curves calculated with the data on Table 6SA and the stability constants on Tables 4, 5 and 6.

System H_2L_A/Zn^{2+}

TABLE 7SA - Experimental details of H_2L_A/Zn^{2+} titrations.

Symbols	*V°* *(mL)*	*$C°_{H2LA}$* *(mmol dm^{-3})*	*$C°_{Zn2+}$* *(mmol dm^{-3})*	*$C°_H$* *(mmol dm^{-3})*	*$p[H^+]_F$*	*$C_{OH,T}$* *(mmol dm^{-3})*	*Δt* *(s)*	*NP*
△	*70.0*	*0.52*		*5.99*	*11.00*	*100.0*	*120*	*81*
▲	*70.0*	*0.51*	*0.25*	*5.78*	*11.13*	*100.0*	*240*	*90*
◆	*70.0*	*0.51*	*0.50*	*5.96*	*11.25*	*100.0*	*240*	*91*
●	*70.0*	*0.51*	*1.00*	*6.31*	*11.09*	*100.0*	*240*	*91*

Legend: V°: initial cell volume; $C°_{H2LA}$, $C°_{Zn2+}$, $C°_H$ initial concentrations of H_2L_A, zinc(II) and mineral acid in cell solution; $p[H^+]_F$: $p[H^+]$ at the end of titration; $C_{OH,T}$: titrant standard base concentration; Δt: waiting time imposed to the data collection criterion; NP: number of experimental points collected

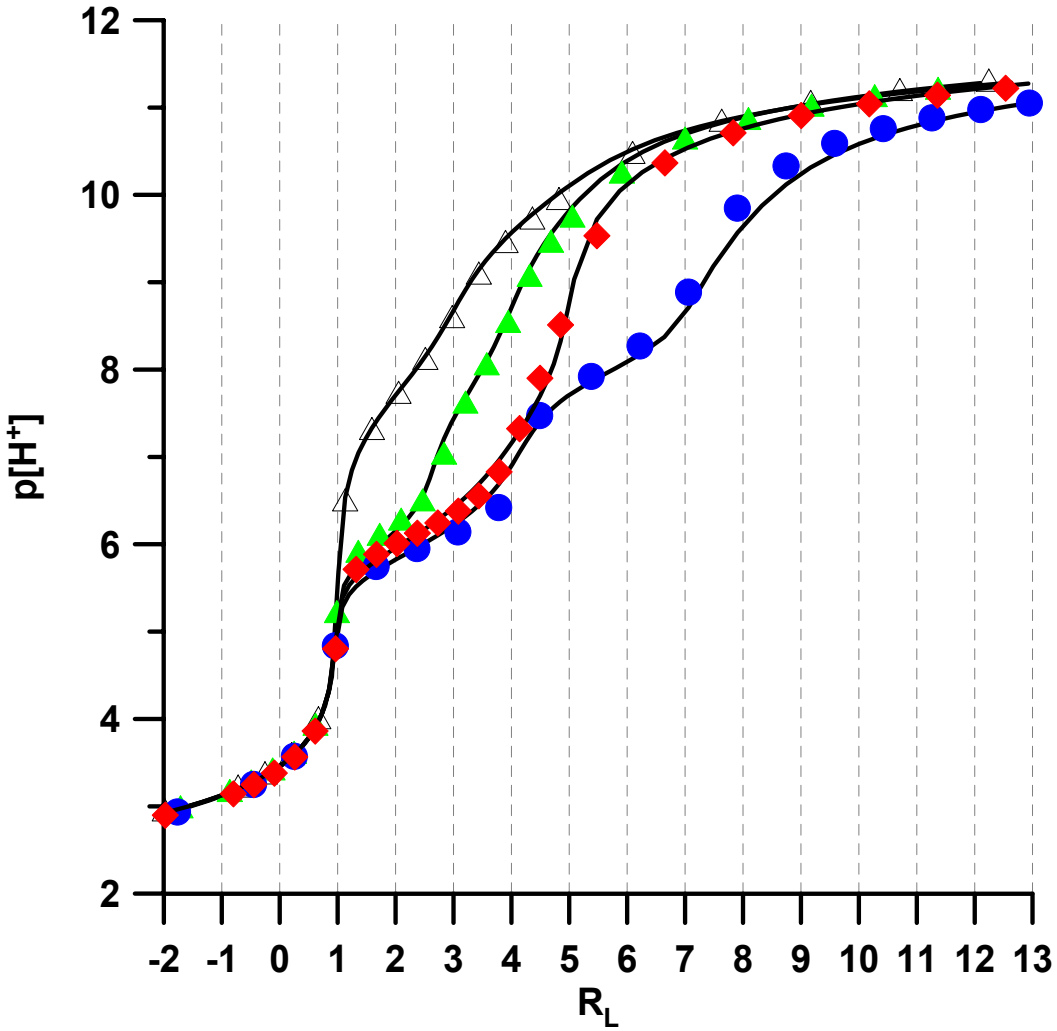

FIGURE 7SA – Experimental data and theoretical curves calculated with the data on Table 7SA and stability constants on Tables 4, 5 and 6.

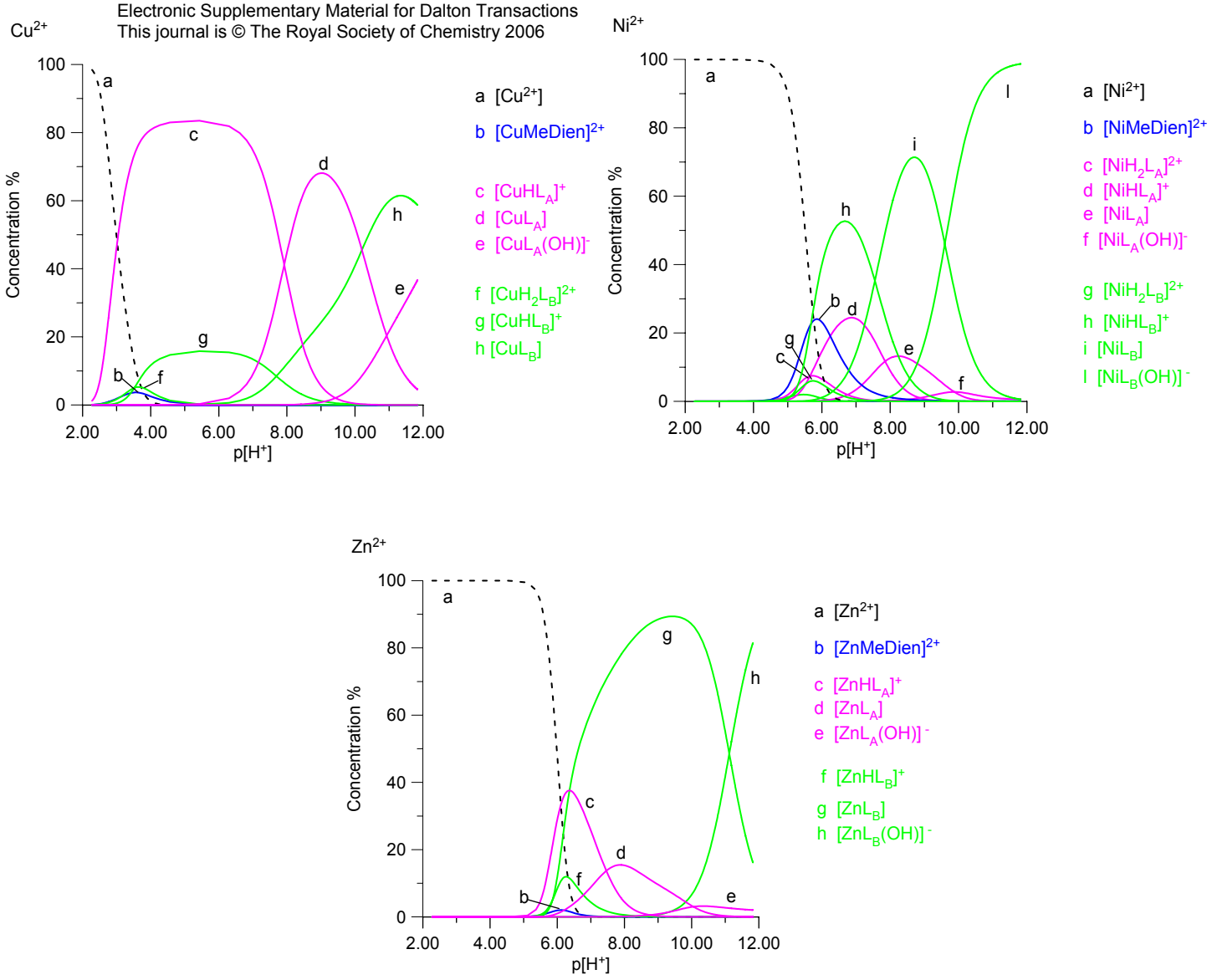

Figure 8SA. Species distribution plots for copper(II)-, nickel(II)- and zinc(II)-H_2L_A/H_2L_B systems. Percent distributions, where calculated, with respect to initial M(II) concentration, for systems containing M(II):H_2L_A:H_2L_B =0.5:0.5:0.5 mmol dm^{-3}, with stability constants of Tables 4, 5 and 6.

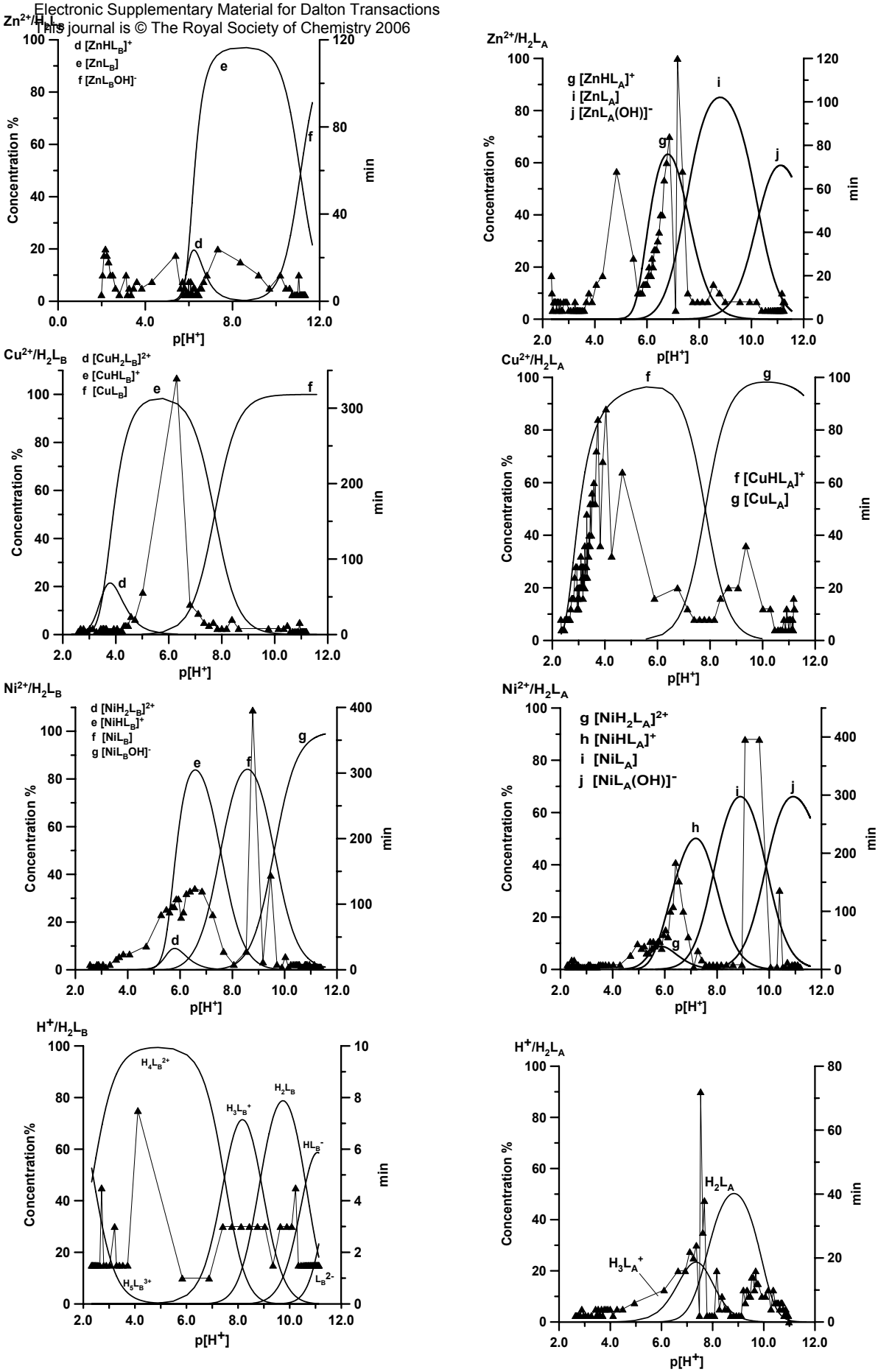

Figure 9SA. Equilibration time and formation of H_2L_B (left) and H_2L_A (right) complexes for the titrations of Figures 2 and 4, respectively. Right axis: time needed to reach equilibrium after any addition during titration.