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Electrochemical synthesis of adducts of 2-aminopyridine or methanol in metal chelates of a *N,N,N*-tridentate Schiff base ligand. X-ray crystal structures of the Ni(II) and Zn(II) derivatives

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Abstract

The electrochemical syntheses of series of novel adducts of 2-aminopyridine and methanol in Co(II), Ni(II), Cu(II) or Zn(II) chelates of the *N,N,N*-tridentate basic form of the Schiff base 2-*N*-tosylamino(2'-tosylaminobenzylidene)aniline (H_2L), $[M(L)L']$ ($M = Co, Ni, Zn, L' = 2\text{-aminopyridine}$; $M = Cu, L' = CH_3OH$), were performed by using the corresponding metal as a sacrificial anode. The compounds were characterized by elemental analysis, IR spectroscopy, FAB mass spectrometry, 1H NMR and magnetic measurements. The crystal structures of the Zn and Ni derivatives as well as of the Schiff base have been determined by X-ray diffraction. In the 2-aminopyridine complexes this ligand is bound to the metal through the endocyclic nitrogen whereas the aminogroup is involved in intramolecular $N-H \cdots O$ hydrogen bonds with one of the tosyl SO_2 groups.

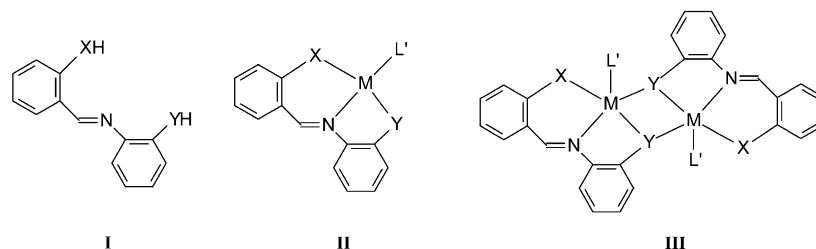
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Keywords: Electrochemical synthesis; 2-Aminopyridine; Methanol; Schiff base

1. Introduction

The deprotonated (basic) forms of the Schiff bases (I) that contain two proton donor groups (XH and YH =

TsNH, OH or SH; Ts = $-SO_2C_6H_4CH_3-p$) in *o*-positions of the phenyl rings can act as tridentate ligands in either mononuclear or dinuclear coordination compounds of the types II and III [1–5].



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Among the synthesized complexes of type II those with aminoheterocycles (L') are particularly interesting [6–8]. In fact, adducts of the aminoazoles and aminoa-

zines with different transition metals provide good models for natural purine base complexes [9,10]. Moreover, aminoheterocycles containing two or more potential donor centres play an important role in the study of competitive reactivity of ambidentate ligand systems [11–26]. In the present work we report the electro-synthesis of adducts (type **II**) of 2-aminopyridine and methanol in chelates of various first row transition metal ions with the tridentate basic form (L^{2-}) of 2-*N*-tosylamino(2'-tosylaminobenzylidene)aniline [27] [H_2L i.e. **I** ($X = Y = Ts$)]. The use of the electrochemical procedure with sacrificial electrodes allowed us to obtain adducts of type **II**, with 2-aminopyridine (L') for Ni(II), Zn(II) and Co(II) and with methanol (L') in the case of copper(II). The electrochemical reactions proceeded under mild conditions (room temperature) in contrast with the usual chemical syntheses [6–8] of type **II** complexes which require heating, namely in solvent refluxing conditions.

2. Experimental

2.1. Analysis and physical measurements

Methanol, 2-aminopyridine, Et_4NClO_4 are commercially available products and were used as received. The sheets of metals (Zn, Ni, Co and Cu) were purchased from Aldrich, and 2-*N*-tosylamino(2'-tosylaminobenzylidene)aniline (H_2L) was prepared according to the published method [2]. C, H, N, S elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Melting points were determined on a Kofler table. Positive-ion FAB mass spectra were obtained on a Trio 2000 instrument by bombarding 3-nitrobenzyl alcohol matrixes of the samples with 8 keV ($\approx 1.28 \times 10^{15}$ J) Xe atoms. Mass calibration for data system acquisition was achieved using CsI. Infrared spectra (4000 – 400 cm^{-1}) were recorded on a Bio-Rad FTS 3000 MX instrument in KBr pellets. 1H NMR spectra were measured on a Varian Unity 300 spectrometer at ambient temperature. The electrolyses were carried out using an EG&G PAR/173 galvanostat. Magnetic susceptibilities of Ni(II), Co(II) and Cu(II) complexes have been determined using the Faraday's method on the equipment of the Rostov State University [28]. All the other instruments are at the Centro de Química Estrutural.

2.2. Electro-syntheses

The electro-syntheses of the complexes were performed in methanol solution using a Pt wire as the cathode and a metal (M) plate (M = Cu, Ni, Co, Zn) suspended on a platinum wire as the sacrificial anode, according to a standard electrochemical procedure [29]. The working

methanol solution (25 ml) contained 0.262 g (1.00 mmol) of the tosylamino-functionalized compound (H_2L), 2-aminopyridine (L') (0.095 g, 1.00 mmol) and 0.010 g of Et_4NClO_4 as the electrolyte. The electrolyses were carried out in a U-shaped glass tube at a current of 10 mA with initial voltage of 8 V for 2 h. After electrolyses the solid products were filtered off, washed three times with hot methanol and dried in vacuum. For complexes **IIc**, suitable crystals for X-ray diffraction analysis were obtained in this way. However, for **IIb** and H_2L , the crystals were obtained by dissolution of the electrolysis product in methanol/chloroform (1:1) followed by slow evaporation.

The electrochemical cell can be summarized as:
 $(-)\text{Pt} | \text{CH}_3\text{OH} + \text{H}_2\text{L} + \text{L}' | \text{M}(+)$.

2.2.1. [$Co(L)(L')$] ($L' = 2$ -aminopyridine) (**IIa**)

Under the electrochemical conditions, 22 mg of the Co sacrificial anode were dissolved ($E_f = 0.5$ mol F^{-1}). The yield is 76%. *Anal. Calc.* for $C_{32}H_{29}N_5O_4S_2Co$: C, 57.30; H, 4.36; N, 10.44; S, 9.56. Found: C, 57.16; H, 4.30; N, 10.44; S, 10.00. FAB⁺ MS, m/z : 599 [$M-L' + Na-H$]⁺, 422 [$M-L'-SO_2C_6H_4CH_3-p$]⁺. M.p. = 179–180 °C. IR spectrum (selected bands) in KBr, cm^{-1} : 3416 $\nu_{as}(NH_2)$, 3343 $\nu_s(NH_2)$, 3238 $\nu_s(NH_2)$, 1651 $\delta(NH_2)$, 1608 $\nu(C=N)$, 1262 $\nu_{as}(SO_2)$, 1138 $\nu_s(SO_2)$. $\mu_{eff} = 4.08$ B.M.

2.2.2. [$Ni(L)(L')$] ($L' = 2$ -aminopyridine) (**IIb**)

Twenty two milligram of the Ni sacrificial anode were dissolved during the electrolysis ($E_f = 0.5$ mol F^{-1}). The yield is 81%. *Anal. Calc.* for $C_{32}H_{29}N_5O_4S_2Ni$: C, 57.32; H, 4.36; N, 10.45; S, 9.57. Found: C, 57.14; H, 4.35; N, 10.45; S, 9.60. FAB⁺ MS, m/z : 670 [M]⁺, 598 [$M-L' + Na-H$]⁺, 421 [$M-L'-SO_2C_6H_4CH_3-p$]⁺. M.p. = 172–173 °C. IR spectrum (selected bands) in KBr, cm^{-1} : 3419 $\nu_{as}(NH_2)$, 3344 $\nu_s(NH_2)$, 3242 $\nu_s(NH_2)$, 1649 $\delta(NH_2)$, 1608 $\nu(C=N)$, 1258 $\nu_{as}(SO_2)$, 1138 $\nu_s(SO_2)$. $\mu_{eff} = 3.23$ B.M.

2.2.3. [$Zn(L)(L')$] ($L' = 2$ -aminopyridine) (**IIc**)

Over the period of electrolysis the Zn sacrificial anode lost 24.0 mg ($E_f = 0.49$ mol F^{-1}). The yield is 74%. *Anal. Calc.* for $C_{32}H_{29}N_5O_4S_2Zn$: C, 56.76; H, 4.32; N, 10.34; S, 9.47. Found: C, 56.91; H, 4.28; N, 10.07; S, 9.90. FAB⁺ MS, m/z : 608 [$M-L' + Na + 2H$]⁺, 605 [$M-L' + Na-H$]⁺. M.p. = 187–188 °C. IR spectrum (selected bands) in KBr, cm^{-1} : 3414 $\nu_{as}(NH_2)$, 3349 $\nu_s(NH_2)$, 3239 $\nu_s(NH_2)$, 1655 $\delta(NH_2)$, 1608 $\nu(C=N)$, 1259 $\nu_{as}(SO_2)$, 1142 $\nu_s(SO_2)$.

2.2.4. [$Cu(L)(CH_3OH)$] (**IIId**)

The weight of the Cu sacrificial anode reduced by 22 mg ($E_f = 0.5$ mol F^{-1}). The yield is 63%. *Anal. Calc.* for $C_{28}H_{27}N_3O_5S_2Cu$: C, 54.90; H, 4.40; N, 6.85; S, 10.44. Found: C, 55.01; H, 4.27; N, 7.09; S, 10.46. FAB⁺ MS,

m/z : 582 $[M-CH_3OH]^+$, 581 $[M-CH_3OH-H]^+$, 426 $[M-CH_3OH-H-SO_2C_6H_4CH_3-p]^+$, 271 $[M-CH_3OH-H-2SO_2C_6H_4CH_3-p]^+$. M.p. = 174–175 °C. IR spectrum (selected bands) in KBr, cm^{-1} : 1602 $\nu(C=N)$, 1273 $\nu_{as}(SO_2)$, 1142 $\nu_s(SO_2)$. $\mu_{eff} = 1.92$ B.M.

2.3. Crystal structure determinations

Diffraction measurements were carried out at room temperature on an Enraf–Nonius CAD4 diffractometer, equipped with a graphite monochromator and Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). Cell dimensions were obtained from centered reflections with θ between 2 and 25° (**H₂L**, **IIc**), 1.6 and 24° (**IIb**). Range of hkl : $h = 0$ to 20, $k = -24$ to 24, $l = 0$ to 8 (**H₂L**); $h = -20$ to 20, $k = 0$ to 14, $l = 0$ to 29 (**IIb**); $h = -12$ to 11, $k = -13$ to 13, $l = 0$ to 17 (**IIc**). The intensities of 4534 (**H₂L**), 9600 (**IIb**) or 5576 (**IIc**) reflections were observed and a total of 2311 (**H₂L**), 9368 (**IIb**) or 5354 (**IIc**) ($R_{int} = 0.0791$, 0.0531 and 0.0598, respectively) unique reflections were used for structures solution and refinement. Structures were solved by direct methods, by using the SHELXS-97 package [30]. The structure refinements were carried out with SHELXL-97 [31]. Crystallographic data are summarised in Table 1. Molecular structures with their respective numbering schemes are shown in Figs. 1–3 and selected bond lengths and angles in Tables 2–4. In **IIb** the single crystal X-ray diffraction analysis shows the presence of two molecules, A and B, in the asymmetric unit cell (Fig. 2). In **IIc** the molecule has two possible orientations in the crystal and therefore the N=CH group is split in two positions as shown in Fig. 3. As a consequence, the bond lengths involved in this group are not perfect, especially N4A–C11 which is very long. Least square refinements with anisotropic thermal motion parameters for all the non-hydrogen atoms (except for N4A and N4B atoms in **IIc** which could not be refined anisotropically) and isotropic for the

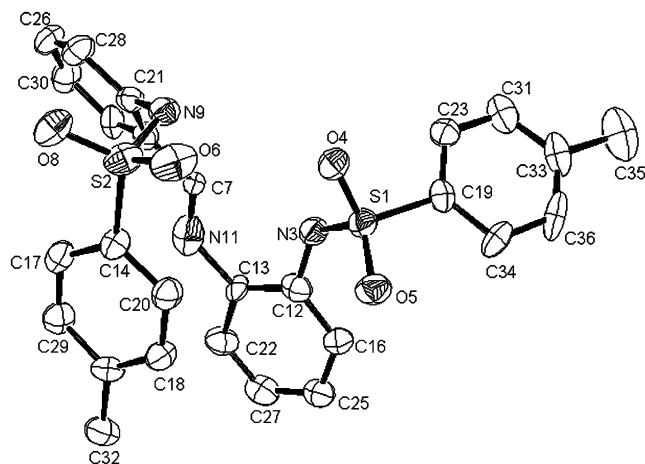


Fig. 1. Molecular structure of compound **H₂L**.

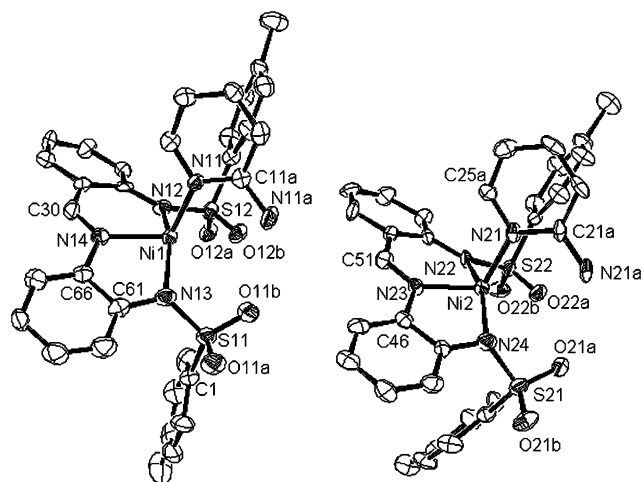


Fig. 2. Molecular structure of $[Ni\{N(SO_2C_6H_4CH_3-p)(C_6H_4)\}_2(CH=N)(NC_5H_4NH_2)]$ (**IIb**).

remaining atoms gave $R_1 = 0.0588$ (**H₂L**), 0.0757 (**IIb**) or 0.0673 (**IIc**) [$I > 2\sigma(I)$]; $R_1 = 0.1422$ (**H₂L**), 0.1708 (**IIb**) or 0.1131 (**IIc**) (all data)].

Table 1
Crystallographic data for compound **H₂L** and for the complexes **IIb** and **IIc**

	$C_{27}H_{25}N_3O_4S_2$ (H₂L)	$C_{32}H_{29}N_5O_4S_2Ni$ (IIb)	$C_{32}H_{29}N_5O_4S_2Zn$ (IIc)
Empirical formula	$C_{27}H_{25}N_3O_4S_2$ (H₂L)	$C_{32}H_{29}N_5O_4S_2Ni$ (IIb)	$C_{32}H_{29}N_5O_4S_2Zn$ (IIc)
Formula weight	519.64	670.43	677.13
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	$P2_1ab$	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a (Å)	17.5080(50)	18.280(3)	10.1500 (8)
b (Å)	20.3660(50)	13.080(3)	11.1514 (5)
c (Å)	7.1180(50)	25.381(7)	15.0913 (6)
α (°)	90	90	99.250 (3)
β (°)	90	98.708(16)	102.242 (3)
γ (°)	90	90	109.426 (4)
V (Å ³)	2538.05(20)	5999(2)	1523.89 (16)
Z	4	8	2
ρ_{calc} (g cm ⁻³)	1.360	1.485	1.476
μ (Mo $K\alpha$) (mm ⁻¹)	0.249	0.833	0.989
R	0.0588	0.0757	0.0673
wR	0.1396 $w = 1/[\sigma^2(F_o^2) + (0.0555P)^2]$, $P = (F_o^2 + 2F_c^2)/3$	0.1954 $w = 1/[\sigma^2(F_o^2) + (0.0438P)^2 +$ $32.3043P]$, $P = (F_o^2 + 2F_c^2)/3$	0.1729 $w = 1/[\sigma^2(F_o^2) + (0.0676P)^2 +$ $2.3370P]$, $P = (F_o^2 + 2F_c^2)/3$

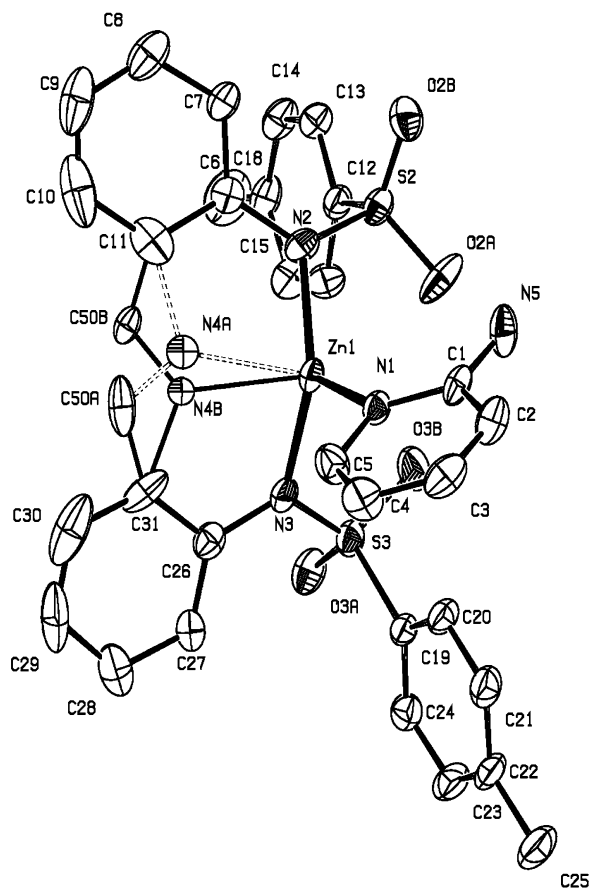


Fig. 3. Molecular structure of $[Zn\{N(SO_2C_6H_4CH_3-p)(C_6H_4)\}_2(CH=N)(NC_5H_4NH_2)]$ (**IIc**).

Table 2
Selected bond lengths (Å) and angles (°) for compound H_2L

S1–O4	1.437(7)	S2–O6	1.427(7)
S1–O5	1.433(7)	S2–O8	1.415(7)
S1–N3	1.593(9)	S2–N9	1.652(8)
S1–C19	1.775(9)	S2–C14	1.732(9)
N3–C12	1.414(13)	N9–C21	1.425(11)
N11–C7	1.245(13)	N11–C13	1.506(13)
O4–S1–O5	120.3(4)	O6–S2–O8	119.5(4)
O4–S1–N3	103.6(5)	O6–S2–N9	104.9(4)
O5–S1–N3	110.8(5)	O8–S2–N9	107.1(4)
N3–S1–C19	105.7(5)	N9–S2–C14	107.0(4)
S1–N3–C12	130.2(8)	S2–N9–C21	118.7(6)
C7–N11–C13	125.1(9)		

3. Results and discussion

The electrochemical oxidation of cobalt, nickel or zinc metals, used as sacrificial anodes, in the presence of the potential tridentate species 2-*N*-tosylamino(2'-tosylaminobenzylidene)aniline (H_2L) and 2-aminopyridine (L'), in methanol, led to the complexes of general formula $[M(L)(L')]$ ($M = Co$ **IIa**, Ni **IIb**, Zn **IIc**) where L stands

Table 3
Selected bond lengths (Å) and angles (°) for $[Ni\{N(SO_2C_6H_4CH_3-p)(C_6H_4)\}_2(CH=N)(NC_5H_4NH_2)]$, **IIb**

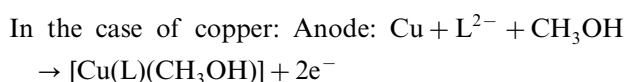
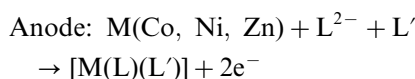
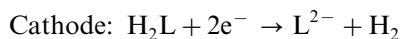
Ni1–O12B	2.459(7)	Ni2–N22	1.972(8)
Ni1–N11	2.033(8)	Ni2–N23	1.960(8)
Ni1–N12	1.964(7)	Ni2–N24	2.001(8)
Ni1–N13	1.989(8)	Ni2–O22A	2.385(6)
Ni1–N14	1.971(8)	Ni2–N21	2.031(7)
S11–N13	1.578(9)	S21–N24	1.600(8)
S12–N12	1.594(8)	S22–N22	1.587(8)
N14–C30	1.245(12)	N23–C51	1.292(11)
N14–C66	1.483(13)	N23–C46	1.450(11)
N11–Ni1–N12	101.8(3)	N21–Ni2–N22	100.9(3)
N11–Ni1–N13	111.1(3)	N21–Ni2–N24	104.0(3)
N12–Ni1–N14	90.1(3)	N22–Ni2–N23	90.2(3)
N13–Ni1–N14	83.2(3)	N23–Ni2–N24	84.2(3)
N12–Ni1–N13	147.0(3)	N22–Ni2–N24	155.1(3)
N11–Ni1–N14	106.0(3)	N21–Ni2–N23	106.0(3)
C46–N23–C51	121.3(8)	C30–N14–C66	121.5(8)

Table 4
Selected bond lengths (Å) and angles (°) for $[Zn\{N(SO_2C_6H_4CH_3-p)(C_6H_4)\}_2(CH=N)(NC_5H_4NH_2)]$, **IIc**

Zn1–N1	2.053(5)	S2–N2	1.599(6)
Zn1–N2	1.983(6)	S3–N3	1.608(6)
Zn1–N3	2.000(6)	N4A–C50A	1.24(2)
Zn1–N4A	2.059(13)	N4B–C50B	1.29(2)
Zn1–N4B	2.064(13)		
N(1)–Zn(1)–N(2)	116.0(2)	N(2)–Zn(1)–N(3)	140.3(2)
N(1)–Zn(1)–N(3)	103.5(2)	N(2)–Zn(1)–N(4A)	78.3(6)
N(1)–Zn(1)–N(4A)	112.4(4)	N(2)–Zn(1)–N(4B)	94.3(5)
N(1)–Zn(1)–N(4B)	108.4(4)	N(3)–Zn(1)–N(4A)	90.6(5)
		N(3)–Zn(1)–N(4B)	75.9(5)
		N(4A)–Zn(1)–N(4B)	16.4(7)

for the basic dianionic form of the tridentate Schiff base. The oxidation of copper in the same conditions resulted in the formation of the methanol adduct $[Cu(L)(CH_3OH)]$ (**IIId**).

The value (see Section 2) of the electrochemical efficiency, E_f (defined as the number of moles of metal dissolved per Faraday of charge), close to 0.5 mol F^{-1} , and the liberation of hydrogen at the cathode are in accord with the following process:



3.1. X-ray molecular structures

The molecular structures of the sulfonylamino-functionalized imine (H_2L) and of its nickel (**IIb**) and zinc

(IIc) complexes were unambiguously established by X-ray diffraction analyses.

In the H₂L molecule the bond distances and angles lie within normal values [32], with the *p*-tolyl moieties being bent due to the steric control induced by the SO₂ fragment.

For both molecules II, the ligand L acts as a tridentate chelating species by means of the two amino- and the imino-nitrogen atoms. The fourth coordination position is occupied by the aminopyridine which is bound in a monodentate fashion through the endocyclic N atom, as found in other complexes with Lewis acids [11]. The coordination polyhedra of the metal atoms in both structures are highly distorted tetrahedrons. In fact, the angles around the metal ion are in the range 83.0(3)–110.8(3)° (IIb) and 75.9(5)–116.0(2)° (IIc) except for the N–M–N angle involving the nitrogen atoms of the two sulfonylamino groups which is 147.2(4) or 155.2(3)° (IIb) or 140.3(2)° (IIc). The metal–N distances are not unusual and are similar to those reported for other Ni or Zn complexes [33–37]. In the Zn complex IIc, these distances are slightly longer than in the Ni analogue as observed in other cases [33]. In addition, in each structure the M–N_{pyr} bond distances are slightly longer than the other metal–nitrogen bonds, although in IIc it is of the same order of magnitude as the Zn–N(4A) [or N(4B)] bond length. In both structures the nitrogen atom of the NH₂ group of the 2-aminopyridine ligand is oriented towards the oxygen atoms of one of the SO₂ groups in such a manner that the N···O distances in the range from 2.907(9) to 3.193(11) Å allow us to assume that the intramolecular hydrogen bonds N–H···O have distances of 2.0551–2.2938 Å and NHO angles of 164.65–170.32°.

3.2. Spectroscopic properties

The IR spectra of the coordination compounds IIa–IIc are in agreement with the X-ray data discussed above. In comparison with the IR spectrum of the free ligand (H₂L) they do not exhibit the band at 3297 cm⁻¹ attributable to $\nu(\text{N–H})$ of the tosylated amino group and show a lower frequency shift (10 cm⁻¹) of the stretching vibration band of the imino group (1618 cm⁻¹ in the ligand). These features can be interpreted as a result of the participation of both deprotonated nitrogens of the tosylated fragments and of the imine nitrogen in coordination to the metal with formation of a chelate ring. Moreover, the stretching vibration bands of the amino group of the coordinated 2-aminopyridine appear at 3500–3200 cm⁻¹, i.e. at lower frequencies than in the case of the uncoordinated 2-aminopyridine. Taking into account our previous results [11], this shift is indicative of an intramolecular hydrogen bond between an hydrogen atom of the amino group of 2-

aminopyridine and an oxygen atom of a tosylated fragment of the Schiff base ligand.

The ¹H NMR of the Zn(II) complex (IIc) confirms the 4-N environment of the metal centre. In fact, the spectrum (run in *d*⁶-dmsO) does not display any resonance assigned to the tosylated amino protons (which in the free ligand, H₂L, appear as two singlets at δ 9.6 and 11.4), whereas that of the azomethinic proton occurs at δ 9.0, i.e. shifted to lower field in comparison with that (at δ 8.2) of the free ligand. These observations testify in favour of the basic form (L²⁻) of the ligand and its tridentate chelation via both the amido-*N* atoms and the imino-*N* atom. In addition, the appearance of a broad singlet at δ 5.9, assigned to the amino protons of 2-aminopyridine, confirms the presence of this ligand (L'). Thus, both IR and NMR data favour a {MN₄} coordination for the complexes IIa–c with participation of two (deprotonated) amide nitrogen atoms, the nitrogen of the imine group and the endocyclic nitrogen of 2-aminopyridine.

The FAB⁺ mass spectra of the complexes (IIa–c) show the peaks due to the fragment [M–L' + Na–H]⁺ and the molecular ion is also observed for the Ni(II) complex IIb. The peak at *m/z* 582 [M–CH₃OH]⁺ is detected in the fragmentation of the methanol complex IIc. The values of the magnetic moments (μ_{eff}) at room temperature 4.08, 3.23 and 1.92 B.M. for the Co(II), Ni(II) and Cu(II) complexes, respectively, support the mononuclear structure of these compounds [38].

4. Supplementary material

Crystallographic data have been deposited to the Cambridge Crystallographic Data Center as supplementary publications No. CCDC-197531 (H₂L), CCDC-197532 (IIb), CCDC-197533 (IIc). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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