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Equilibrium and structural studies of complexes with a hexadentate ligand containing amide, amine and pyridyl nitrogen donors. Crystal structures of copper(II), nickel(II) and cobalt(III) complexes †

Caroline Jubert,[a] Aminou Mohamadou,*[a] Christian Gérard,[a] Stéphane Brandes,[b] Alain Tabard[b] and Jean-Pierre Barbier[a]

[a] *GRECI, Groupe de Recherche en Chimie Inorganique, Faculté des Sciences, Université de Reims Champagne-Ardenne, Moulin de la Housse, BP 1039–51687 Reims cedex 2, France. E-mail: aminou.mohamadou@univ-reims.fr*

[b] *LIMSAG, Laboratoire d'Ingénierie Moléculaire pour la Séparation et les Applications des Gaz, UMR CNRS 5633, Faculté des Science "Gabriel", Université de Bourgogne, 6 Boulevard Gabriel, 21100 Dijon, France*

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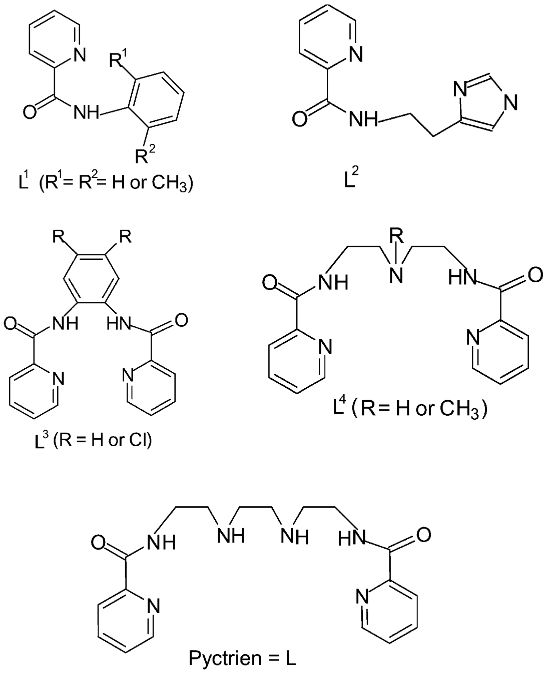
A novel potentially hexadentate ligand, 1,8-bis(2-pyridylcarbamoyl)-3,6-diazaoctane (pyctrien) has been synthesised as its tetrahydrochloride salt; its protonation constants and the stability constants of the copper(II) and nickel(II) chelates have been determined by potentiometry. Amide group deprotonation permits the formation of $[MLH_{-1}]^+$ and $[MLH_{-2}]$ species in all cases, whereas the detection of the neutral or the protonated species depends on the nature of the metal ions. The solid complexes of copper, nickel and cobalt with the neutral and the deprotonated ligand have been synthesised and characterised by IR and UV–VIS spectroscopy. The amidic groups are coordinated through the oxygen atoms in all solid complexes $[ML](ClO_4)_2$ ($M = Cu^{2+}$, Ni^{2+} and Co^{2+}). The complexes obtained with the deprotonated forms of the ligand imply the coordination through the nitrogen atoms of the amidic groups. In the cobalt compound, the coordination of the six nitrogen donor atoms leads to the spontaneous oxidation of Co(II) into Co(III); thus, NMR spectroscopic investigations show that this complex has an α-*cis* configuration. X-Ray crystal determination has shown that $[CuLH_{-1}(H_2O)](ClO_4)$ is square pyramidal with a water molecule fixed in the apical position, one picolinamide moiety remaining uncoordinated (in agreement with ESR studies), whereas $[NiLH_{-2}]$ and $[CoLH_{-2}](ClO_4)_{0.75}Cl_{0.25}$ are both octahedral with the two pyridine rings in *cis*-positions.

Introduction

The continuing interest in the study of amide complexes derives from their ability to model active sites present in some metalloproteins[1] and the search for a better understanding of the physicochemical properties of such complexes, especially the stereochemistry of the metallic center. In this case, linear ligand systems based upon 2-pyridine carboxamide are very useful to modulate the structural and electronic properties of first-row transition-metal centres. In this way, it was demonstrated that electronically or sterically demanding pyridine amide ligands can dictate the geometry and coordination number of such complexes. For example, the bidentate ligand L^1 with $R^1 = R^2 = H$ (Scheme 1) gives rise to a tetrahedral geometry with the Cu^{2+} ion,[2] whereas substitution on the two *ortho* positions of the phenyl ring leads to a trigonal bipyramidal geometry around copper(II) and cobalt(II) in $[M^{II}L^1_2(H_2O)]$ compounds. The tridentate ligand L^2 gives a centrosymetric diacetate bridge dimer, $[CuL^2(CH_3CO_2)]_2$ in which the geometry around each copper atom is distorted square-based pyramidal[3] as in $[ML^3(H_2O)]^{0 \text{ or } +}$ ($M = Cu^{II}$ and Co^{III}) compounds obtained[4] with the tetradendate ligand L^3. Nonoyama[5] and Mascharak and co-workers[6] have described the octahedral complexes obtained with the pentadentate ligand L^4; the sixth site is achieved by the fixation of a water molecule to the axial site. To our knowledge, no published data referring to the coordination of a linear hexadentate bis(picolinamide) ligand have been reported.



Scheme 1

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† Electronic supplementary information (ESI) available: COSY spectrum of the aliphatic chain in $[CoLH_{-2}](ClO_4)_{0.75}Cl_{0.25}$ in D_2O; molar absorption coefficients as a function of pH for the Cu^{2+}/pyctrien and Ni^{2+}/pyctrien systems. See http://www.rsc.org/suppdata/dt/b1/b111614b/

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In order to expand on the function of the metal ions in the biological systems, we are involved in a study of the impact of structural changes on the physicochemical properties of the model complexes of the first row transition metal. In previous papers we have described the complexation of different metal ions (Co^{2+}, Cu^{2+} and Zn^{2+}) with potentially hexadentate linear ligands involving two pyridyl groups and containing mixed heteroatom donors (N, O or S).[7,8] The structural and thermodynamic properties of these complexes depend on the nature of the two central heteroatom donors. It seemed worthwhile to us to extend this work by synthesising the same kind of ligands which possess carbamoyl groups in order to obtain a more complete picture of the factors influencing the stereochemical properties of these complexes. So, in this report, we describe the preparation of the new ligand pyctrien: 1,8-bis(2-picolinamide)-3,6-diazaoctane, abbreviated L (Scheme 1). This nucleating O_2N_6 type ligand is capable of donating six nitrogens (two aromatic, two amidic and two secondary amine) and also includes two carbonyl oxygens which can serve as potential donor atoms. Then, the equilibrium constants and structure in aqueous solution of the Ni(II) and Cu(II) complexes have been determined by the combined potentiometric and UV-VIS spectroscopic studies. In addition, solid complexes of cobalt, nickel and copper, with neutral and deprotonated forms of the ligand, have been synthesised and characterised by spectroscopic methods (UV-VIS, ESR and NMR). The crystal structure of $[CuLH_{-1}](ClO_4)$, $[NiLH_{-2}]$ and $[CoLH_{-2}](ClO_4)_{0.75}Cl_{0.25}$ compounds have been investigated.

Experimental

Reagents

All the solvents were purified by conventional procedures[9] and distilled prior to use. All the chemicals commercially available (Aldrich) were used as supplied without further purification.

Synthesis

Synthesis of the ligand. *1,8-Bis(picolinamide)-3,6-diazaoctane tetrahydrochloride monohydrate (pyctrien·4HCl·H_2O).* The ligand was obtained from the coupling of the carboxylate moieties using 1,1′-carbonyldiimidazole (CDI).[10] To a mixture of picolinic acid (3.44 g, 28 mmol) in THF (200 mL) was added CDI (5.03 g, 31 mmol) in one portion. The resultant mixture was refluxed for 2 h whereupon triethylenetetraamine (2.0 g, 14 mmol) was added very slowly (over 3 h). Then, the mixture was refluxed for a further 15 h and the solvent was removed under reduced pressure. The dark yellow residue thus obtained was taken up in chloroform (200 mL), washed with an aqueous saturated ammonium chloride solution (2 × 100 mL) then with brine (2 × 100 mL). The organic layer was dried over $MgSO_4$ and filtered. The filtrate was rotoevaporated to give a yellowish oil which was taken up in methanol (30 mL). The solution was acidified with concentrated HCl (pH ≈ 1.5) and stirred at room temperature for about 2 h. The yellow crude crystalline product was filtered, washed with methanol and dried *in vacuo* (yield *ca.* 80%): mp 217 °C. Found: C, 41.6; H, 5.5; N, 15.8; Cl, 26.8. $C_{18}H_{30}N_6O_3Cl_4$ requires C, 41.6; H, 5.8; N, 16.1; Cl, 27.2%. IR (KBr disk, ν/cm^{-1}): 3520–3305 (s, $\nu_{N-H\ +\ OH}$); 3048–2750 (s or m, ν_{C-H}); 1677 (vs, $\nu_{C=O}$); 1606, 1441, (s, $\nu_{pyridine\ ring}$); 1525 (s, ν_{C-N} and δ_{N-H}).

Synthesis of metal complexes. CAUTION! Although we have experienced no problems while handling any of the substances described herein, readers are cautioned to handle these compounds as potentially explosive compounds.

$[M^{II}L](ClO_4)_2$. A mixture of sodium acetate trihydrate (0.54 g, 4 mmol) and ligand tetrahydrochloride monohydrate (0.52 g, 1 mmol), in absolute ethanol (30 mL) was stirred with boiling, 10 min on a water bath, cooled and the sodium chloride which precipitated was removed by filtration. Metal perchlorate hexahydrate (1 mmol) in absolute ethanol (20 mL) was added dropwise to the filtrate and the solution was stirred for 2 h at room temperature. The coloured powder formed was filtered off, washed with ethanol and recrystallized from water–acetone (1 : 1).

$[CuL](ClO_4)_2\cdot H_2O$ 1. Blue powder, (yield *ca.* 70%); mp 170 °C. Found: C, 34.2; H, 3.7; N, 13.1; Cu, 10.5. $C_{18}H_{26}N_6O_{11}Cl_2Cu$ requires C, 34.0; H, 4.1; N, 13.2; Cu, 10.06%. $\chi_M = 2020 \times 10^{-6}$ uem cgs, $\mu_{eff} = 2.18\ \mu_B$. λ_{max}/nm (solid state) 630, 730 sh; λ_{max}/nm (H_2O) 555 (ε/mol^{-1} L cm^{-1}, 106). IR (KBr disk, ν/cm^{-1}): 3450–3100, (s, $\nu_{N-H\ +\ OH}$); 2940–2850 (m, ν_{C-H}); 1639 (vs, $\nu_{C=O}$); 1600, 1442 (s, $\nu_{pyridine\ ring}$); 1565, 1310 (s, ν_{C-N} and δ_{N-H}). 1091 (vs, $\nu_{ClO_4^-}$).

$[NiL](ClO_4)_2$ 2. Grey–blue powder (yield *ca.* 75%); mp 230 °C. Found: C, 35.1; H, 3.9; N, 13.8; Ni, 10.0. $C_{18}H_{24}N_6O_{10}Cl_2Ni$ requires C, 35.2; H, 3.9; N, 13.7; Ni, 9.6%. $\chi_M = 5410 \times 10^{-6}$ uem cgs, $\mu_{eff} = 3.56\ \mu_B$. λ_{max}/nm (H_2O) 865 (ε/mol^{-1} L cm^{-1}, 15); 560 (ε/mol^{-1} L cm^{-1}, 10). IR (KBr disk, ν/cm^{-1}): 3450–3100, (s, $\nu_{N-H\ +\ OH}$); 2940–2850 (m, ν_{C-H}); 1636 (vs, $\nu_{C=O}$); 1599, 1443 (s, $\nu_{pyridine\ ring}$); 1567, 1306 (s, ν_{C-N} and δ_{N-H}). 1099 (vs, $\nu_{ClO_4^-}$).

$[CoL](ClO_4)_2$ 3. Orange powder, (yield *ca.* 70%); mp 245 °C. Found: C, 35.6; H, 3.5; N, 13.9; Co, 9.2. $C_{18}H_{24}N_6O_{10}Cl_2Co$ requires C, 35.2; H, 3.9; N, 13.7; Co, 9.6%. $\chi_M = 6240 \times 10^{-6}$ uem cgs, $\mu_{eff} = 3.82\ \mu_B$. λ_{max}/nm (solid state) 490, 400 sh; λ_{max}/nm (H_2O) 465 (ε/mol^{-1} L cm^{-1}, 270). IR (KBr disk, ν/cm^{-1}): 3360–3260 (s, ν_{N-H}); 2940–2850 (m, ν_{C-H}); 1629 (vs, $\nu_{C=O}$); 1599, 1444 (s, $\nu_{pyridine\ ring}$); 1567, 1298 (s, ν_{C-N} and δ_{N-H}). 1093 (vs, $\nu_{ClO_4^-}$).

Deprotonated complexes. These copper(II), nickel(II) and cobalt(III) compounds were obtained by the procedure described below. To a solution of the ligand tetrahydrochloride monohydrate (0.52 g, 1 mmol) dissolved in water (40 mL) was added dropwise with stirring the solution of metal(II) perchlorate hexahydrate (1 mmol) in water (10 mL). Solid sodium carbonate was added in small portions to the mixture with stirring until the pH reached 8.5. After stirring at room temperature for 1 h, the solvent was removed on a rotavapor and the crude crystalline product obtained was washed with ethanol. Recrystallization from water–acetone (1 : 1) gave crystals suitable for X-ray, after three months.

$[CuLH_{-1}(H_2O)](ClO_4)\cdot H_2O$ 4. Turquoise blue crystals (yield *ca.* 75%); mp 205 °C. Found: C, 38.9; H, 4.8; N, 14.7; Co, 11.1. $C_{18}H_{27}N_6O_8ClCu$ requires C, 39.0; H, 4.9; N, 15.2; Co, 11.5%. $\chi_M = 1730 \times 10^{-6}$ uem cgs, $\mu_{eff} = 2.01\ \mu_B$. λ_{max}/nm (H_2O) 550 (ε/mol^{-1} L cm^{-1}, 150). IR (KBr disk, ν/cm^{-1}): 3460–3260 (s, $\nu_{N-H\ +\ OH}$); 2940–2850 (m, ν_{C-H}); 1631 (vs, $\nu_{C=O}$); 1599, 1440 (s, $\nu_{pyridine\ ring}$); 1560, 1292 (s, ν_{C-N} and δ_{N-H}). 1091 (vs, $\nu_{ClO_4^-}$).

$[NiLH_{-2}]\cdot H_2O$ 5. Purple crystals (yield *ca.* 60%); mp 290 °C. Found: C, 50.7; H, 5.0; N, 19.3; Ni, 13.8. $C_{18}H_{24}N_6O_3Ni$ requires C, 50.2; H, 5.6; N, 19.5; Ni, 13.6%. $\chi_M = 4000 \times 10^{-6}$ uem cgs, $\mu_{eff} = 3.06\ \mu_B$. λ_{max}/nm (H_2O) 850 (ε/mol^{-1} L cm^{-1}, 29). IR (KBr disk, ν/cm^{-1}): 3470–3100 (s, $\nu_{N-H\ +\ OH}$); 2940–2850 (m, ν_{C-H}); 1629 (vs, $\nu_{C=O}$); 1601, 1445 (s, $\nu_{pyridine\ ring}$); 1566, 1291 (s, ν_{C-N} and δ_{N-H}).

$[CoLH_{-2}](ClO_4)_{0.75}Cl_{0.25}\cdot 2.5H_2O$ 6. Orange crystals (yield *ca.* 75%); mp 325 °C. Found: C, 40.1; H, 4.9; N, 15.3; Cl, 1.3;Co, 11.3. $C_{18}H_{27}N_6O_{7.5}ClCo$ requires C, 39.9; H, 5.0; N, 15.5; Cl, 1.6;Co, 10.9%. λ_{max}/nm (H_2O) 480 (ε/mol^{-1} L cm^{-1}, 160). IR (KBr disk, ν/cm^{-1}): 3400–3100 (s, $\nu_{N-H\ +\ OH}$); 2940–2850 (m, ν_{C-H}); 1629 (vs, $\nu_{C=O}$); 1599, 1440 (s, $\nu_{pyridine\ ring}$); 1566, 1291 (s, ν_{C-N} and δ_{N-H}). 1089 (vs, $\nu_{ClO_4^-}$).

Measurements

Elemental analyses (C, H and N) were carried out on a Perkin-Elmer 2400 C, H, N element analyser in our University. The metal analyses were performed on an ICP AES Liberty Series II

Varian apparatus and chloride ions were determined potentiometrically using silver nitrate.

Protometric. Stock solutions of metal ion nitrates were prepared from commercially available reagents (Fluka) of the highest available purity (>99%) and were used without further purification. Their concentrations were determined by EDTA titration at pH = 10, by using murexide as an indicator for Co^{2+} and Ni^{2+}, and PAN [1-(2-pyridyl-azo)-2-naphthol] for Cu^{2+}. Ionic strength was kept constant (I = 1 mol dm^{-3}) by addition of potassium nitrate (Fluka) of the highest purity (>99 %). The solutions of carbonate-free titrating base KOH 0.1 mol L^{-1} were prepared from standardized 1 mol L^{-1} solutions (Prolabo).

Protometric titrations were performed with a Metrohm 665 Dosimat and a Metrohm 654 pH-meter. The combined glass electrode was standardized with nitric acid 10^{-2} mol L^{-1} (pH = 2.00) and the slope determined from a refinement of titration curves of acetic acid solutions. All measurements were performed at 20 °C under a nitrogen stream. Titration curves were fitted with the refining program PROTAF.[11,12] The concentrations of metal ions varied from 6.25×10^{-4} to 1.22×10^{-3} mol L^{-1}, the concentrations of the ligand from 9.33×10^{-4} to 2.43×10^{-3} mol L^{-1} and the ratios C_L/C_M from 1.06 to 3.84. The possible kinetic phenomena were tested by back titrations with 0.1 mol L^{-1} HNO_3. Study of the Co^{2+} complexes reveals such phenomena are probably due to oxidation of the metal ion during complex formation.

Spectroscopic. The electronic spectra in aqueous solutions were recorded in 1.00 cm quartz cells using a Shimadzu UV-2401-PC spectrophotometer equipped with a standard syringe sipper and a temperature-controlled cell holder TCC-240A. The solutions had the same concentrations in metal ions and ligand: 10^{-2} and 1.25×10^{-3} for Ni and Cu, respectively. In the solid state, visible spectra were obtained on a Beckman 5240 spectrophotometer by depositing the compound on Schleicher and Schul filter paper without ashes, and this paper was used as reference.

IR spectra were obtained in KBr pellets with a Nicolet Avatar 320. All NMR spectra were recorded in D_2O at room temperature with a Bruker AC 250 spectrometer. Chemical shifts (in ppm) for ^1H NMR spectra were referenced to residual protic solvent peaks. The ESR spectra in DMF or in acetonitrile were obtained in the X-band at 77 K and at room temperature with a Bruker ESP 300 spectrophotometer. The g values were measured relative to diphenylpicrylhydrazyl, dpph ($g = 2.0037$).

Crystal structure determination

In Table 1 are summarized the pertinent crystallographic data together with refinement details for $[Cu(LH_{-1})](ClO_4)\cdot 2H_2O$ **4**, $[NiLH_{-2}]\cdot H_2O$ **5** and $[CoLH_{-2}](ClO_4)_{0.75}Cl_{0.25}\cdot 2.5H_2O$ **6**.

The crystal data were collected at 173 K for complexes **4** and **5** and 294 K for **6** on a Kappa CCD diffractometer using monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å).

The structures were solved using direct methods. After refinement of the non hydrogen atoms, difference-Fourier maps revealed maxima of residual electron density close to positions expected for hydrogen atoms. Hydrogen atoms were introduced as fixed contributors at calculated positions (C–H = 0.95 Å, $B(H) = 1.3\ B_{eq}$). Final difference maps revealed no significant maxima. All calculations used the Nonius OpenMoleN package.[13] Neutral atom scattering factor coefficients and anomalous dispersion coefficients were taken from a standard source.[14]

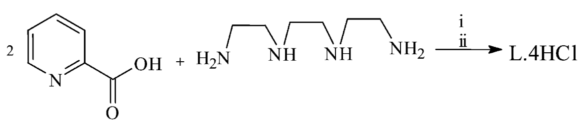
CCDC reference numbers 176982–176984.

See http://www.rsc.org/suppdata/dt/b1/b111614b/ for cystallographic data in CIF or other electronic format.

Results and discussion

Synthesis

The hexadentate ligand L (pyctrien) is obtained in a single-step synthesis from picolinic acid and triethylenetetraamine, activated by 1,1′-carbonyldiimidazole (Scheme 2). This new ligand has been characterized by IR, ^1H–^{13}C NMR and elemental analysis. The potentiometric titration of the ligand by silver nitrate confirmed that this compound was isolated as the tetrahydrochloride salt; two aliphatic amino groups and the aromatic nitrogen of the two pyridyl groups are likely to be protonated.



(i) = + CDI in THF; (ii) = + HCl conc. in MeOH

Scheme 2

New complexes with neutral ligand of general formulae, $[M^{II}L](ClO_4)_2$ (M = Cu^{2+} **1**, Ni^{2+} **2** or Co^{2+} **3**), were readily obtained by treating an ethanolic suspension of the ligand hydrochloride salt with four equivalents of sodium acetate and the appropriate metal(II) perchlorate hexahydrate. These three compounds were isolated as perchlorate salts, confirmed by the presence of a strong band at *ca.* 1090 cm^{-1} in the IR spectra. Complexes with deprotonated forms of the ligand, $[CuLH_{-1}(H_2O)](ClO_4)\cdot H_2O$ **4**, $[NiLH_{-2}]\cdot H_2O$ **5** and $[CoLH_{-2}](ClO_4)_{0.75}Cl_{0.25}\cdot 2.5H_2O$ **6** were synthesized in an aqueous medium in basic conditions (pH ≈ 8.5); the carbonate ion acts as a base to deprotonate the NH amido groups of the ligand. These six complexes were recrystallized from water–acetone (1 : 1) and only compounds **4**, **5** and **6** gave suitable crystals for X-ray structure determinations.

Major species in aqueous solution

The titration curve of the hydrochloride hydrated ligand with KOH (0.1 mol L^{-1}) shows two strong acidities due to the pyridinium groups and two weak acidities corresponding to the secondary amines. The plots $\bar{h}$ *vs.* pH ($\bar{h}$ = mean number of bound protons per mole of ligand) for C_L/C_M ratios varying from 1.06 to 3.84 were studied in order to determine the major complexes present as a function of pH:

$$\bar{h} = \frac{1}{C_L}(nC_L - [H^+] + [OH^-] - C_B + C_H)$$

(n = number of protons of the neutral species of the ligand; C_B = concentration of the strong base added; C_H = concentration of the strong acid initially present in the solution of the neutral form of the ligand). Spectrophotometric experiments were also carried out at different pH values ($R = C_L/C_M = 1$).

Plots of $\bar{h}$ *vs.* pH are given in Fig. 1 for the ratios slightly greater than 1 (1.06 for Cu and 1.14 for Ni). For the ligand alone, the $\bar{h}$ curve shows three plateaus at $\bar{h} = 2$ (LH_2), $\bar{h} = 1$ (LH) and $\bar{h} = 0$ (L). In the presence of Cu^{2+}, the values of $\bar{h}$ close to 2 from the beginning of the titration agree with the formation of the $CuLH_2$ species; the very large plateau in the pH range 5–8 ($\bar{h} = -0.9$) indicates that the ligand has lost three protons to form $CuLH_{-1}$. The minimum obtained at pH ≈ 11 involves the formation of the complex $CuLH_{-2}$. The $\bar{h}$ curve in the presence of Ni^{2+} reveals only the quantitative formation of $NiLH_{-2}$ from pH 7.5; the shift to lower values of $\bar{h}$ with regard to the ligand alone in the pH range 2.5–4 indicates the formation of protonated species $NiLH_2$.

Spectrophotometric titrations for the complexes of the coloured metal ions are represented as curves of the mean

Table 1 X-Ray experimental data

	4	5	6
Formula	$C_{18}H_{27}ClN_6O_8Cu$	$C_{18}H_{24}N_6O_3Ni$	$C_{18}H_{27}N_6O_{7.5}ClCo$
M	554.44	431.14	1083.68
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	*Pbca*	$P2_1/c$	$P\bar{1}$
a/Å	7.4288(1)	10.1934(3)	11.6623(3)
b/Å	20.6531(4)	12.1481(3)	13.0775(3)
c/Å	30.1017(6)	15.4149(5)	16.7715(5)
α/°	90	90	75.898(5)
β/°	90	101.582(5)	71.629(5)
γ/°	90	90	71.844(5)
U/Å^3	4618.4(1)	1869.97(9)	2276.5(1)
T/K	173	173	294
Z	8	4	2
μ(Mo-Kα)/mm^{-1}	1.119	1.071	0.927
Reflections measured	9946	6969	10272
Unique reflections collected	2832	3105	5852
$wR(F^2)$	0.059	0.057	0.077
$R1\ [I > 2\sigma(I)]$	0.043	0.029	0.067
R_{int}	0.06	0.03	0.04

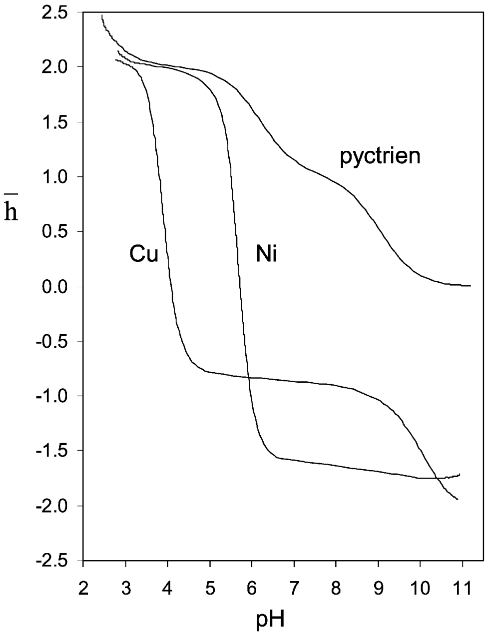


Fig. 1 Mean number of bound protons per mole of ligand, $\bar{h}$, for pyctrien alone and in the presence of Ni^{2+} (C_L = 9.43 × 10^{-4}–C_M = 8.24 × 10^{-4} mol L^{-1}) and Cu^{2+} (C_L = 9.33 × 10^{-4}–C_M = 8.80 × 10^{-4} mol L^{-1}).

molar absorption coefficients, ε, *vs.* pH (see ESI). The appearances of the spectra for pH < 4 confirm the presence of protonated species from the beginning of the titrations: ε_{max} = 6.1 L mol^{-1} cm^{-1} at 624 nm for the Ni^{2+}/L system at pH = 1.95 [$Ni(H_2O)_6^{2+}$: ε_{max} = 2.2 L mol^{-1} cm^{-1} around 725 nm] and ε_{max} = 58.2 L mol^{-1} cm^{-1} around 750 nm for the Cu^{2+}/L system [$Cu(H_2O)_6^{2+}$:ε_{max} = 11.7 L mol^{-1} cm^{-1} around 815 nm]. The different plateaus also confirm the quantitative formation of $CuLH_{-1}$ (5 < pH < 8), $NiLH_{-2}$ (pH > 6) and the formation of $CuLH_{-2}$ from pH = 8. The visible spectra of the Cu^{2+} complexes (Fig. 2) display an isosbestic point at 640 nm (ε = 154 L mol^{-1} cm^{-1}) in the pH range 7–11, indicating that only one equilibrium exists in this pH range between $CuLH_{-1}$ and the most deprotonated species $CuLH_{-2}$. The spectra were analysed by Schwarzenbach's method[15] using the equation:

$$\varepsilon = \varepsilon_{CuLH_{-2}} + \frac{[H^+](\varepsilon_{CuLH_{-1}} - \varepsilon)}{K}$$

$$\text{where } \varepsilon = \frac{\text{Absorbance}}{1\cdot[Cu^{2+}]_{tot}} \text{ and } K = \frac{[CuLH_{-2}][H^+]}{[CuLH_{-1}]}$$

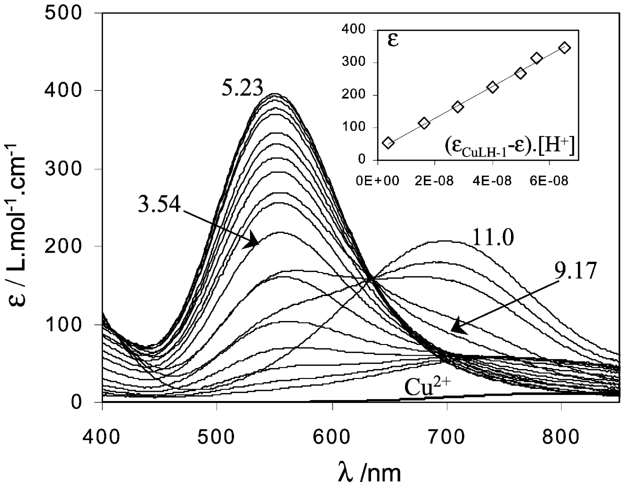


Fig. 2 Visible spectra for the Cu^{2+}/pyctrien system in the pH range 2.9–11.0; $C_L = C_{Cu} = 10^{-3}$ mol L^{-1} (four pH values are mentioned on the plot). The inset figure shows the Scharzenbach's curve at 550 nm for the pH range 8.9–11.0.

Plots of ε *vs.* ($\varepsilon_{CuLH_{-1}} - \varepsilon$)[$H^+$] for the pH range 8.9–11.0 (Fig. 2, inset figure) are linear, in agreement with the equilibrium:

$$CuLH_{-1} \rightleftharpoons CuLH_{-2} + H^+$$

The value of log $K = -9.7$ was determined from the slope. On the other hand, the Schwarzenbach's method failed in the pH range 2.8–4.5 indicating that at least three species exist in this pH range; this method also failed in the study of the system of Ni complexes.

Equilibrium constants

In ligands containing amide groups, several authors[16] have shown that protonation of the amidic nitrogen is not possible ($pK_a \approx -8$) and the deprotonation of this amidic nitrogen is not observed in water ($pK_a \geq 15$). Then, only the relatively strong acidity of pyridinium groups and the weak acidities of the protonated secondary amino nitrogen atoms can be obtained from the protometric titration curves.

The $\bar{h}$ *vs.* pH curves as well as the spectrophotometric titrations show that complexation of the Cu^{2+} and Ni^{2+} ions as MLH_2 complexes occurs as soon as the metal is added to the ligand solution below pH 3. As can be assumed from Schwarzenbach's method applied in UV/Visible spectroscopy, intermediate species exist in addition to those described above:

Table 2 Logarithms of equilibrium constants of pyctrien alone and Ni(II) and Cu(II) complexes; $I = 1$ mol dm^{-3} (KNO$_3$); 20 °C

	pyctrien	Ni^{2+}	Cu^{2+}
$\log \beta_{011}$	9.06(1)		
$\log \beta_{012}$	15.30(1)		
$\log \beta_{013}$	17.49(2)		
$\log \beta_{014}$	19.09(2)		
$\log \beta_{112}$		18.55(2)	19.41(7)
$\log \beta_{111}$		13.19(3)	
$\log \beta_{110}$		6.8(2)	11.36(7)
$\log \beta_{11-1}$		1.55(7)	7.71(5)
$\log \beta_{11-2}$		−3.63(2)	−2.17(6)

Values in parentheses refer to estimated standard deviations.

the best fitting of the titration curves with the program PROTAF requires that these minority species are taken into account. Constants referring to the following equilibria:

$$m\mathrm{M} + l\mathrm{L} + h\mathrm{H} \rightleftharpoons \mathrm{M}_m\mathrm{L}_l\mathrm{H}_h \qquad \beta_{mlh} = \frac{[\mathrm{M}_m\mathrm{L}_l\mathrm{H}_h]}{[\mathrm{M}]^m[\mathrm{L}]^l[\mathrm{H}]^h}$$

are given in Table 2.

In order to make these equilibrium constants more explicit, the distribution curves of the various species were plotted as a function of pH for 10^{-3} mol L^{-1} 1 : 1 solutions (Fig. 3). These curves confirm the different behaviour of pyctrien in the presence of Cu^{2+}. While NiLH$_{-1}$ remains a minority species over a small pH range, CuLH$_{-1}$ is present over a large pH range from pH = 3. MLH$_{-2}$ complexes appear from pH = 5–6 for Ni, and pH = 8–9 for Cu. So amidic nitrogen atoms are deprotonated from very low pH values. In an acidic medium, the plateaus observed for the curve of NiLH$_2$, and to a lesser extent CuLH$_2$, indicate that the nitrogen atoms involved in these complexes are only those of the pyridines which are fully deprotonated.

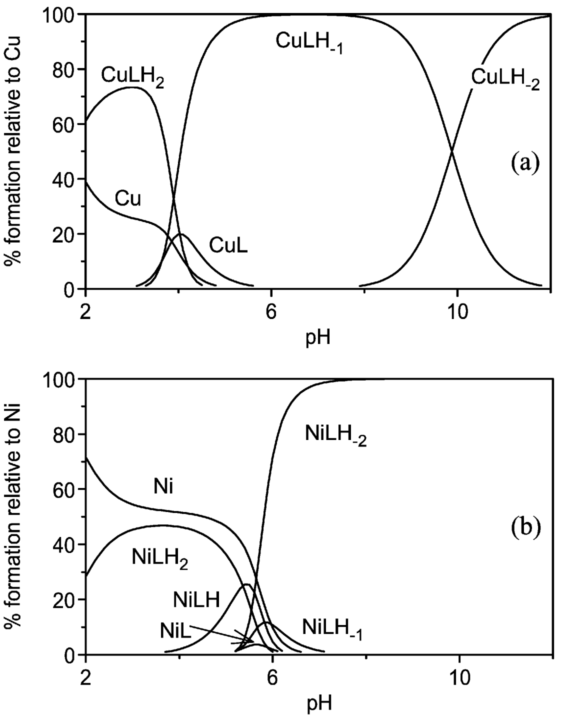


Fig. 3 Distribution curves; C_L = C_M = 10^{-3} mol L^{-1}; (a) Cu(II) complexes; (b) Ni(II) complexes.

Metal complex structures in aqueous solution

Variable pH UV/VIS studies are compared with the speciation behaviour in order to probe the solution structures of these complexes. The position of d–d transitions gives information on the ligand field and the coordination geometry around the metal ion. For a square pyramidal coordination geometry, the energy of the d–d transition depends on the nature of the four donor atoms lying in the equatorial sites: the ligand field of a nitrogen atom is considerably higher that of an oxygen atom. However, an axial donor atom (eventually H$_2$O) has a slight effect on $\lambda_{\max}$. Fig. 4 shows the electronic spectra for the different copper(II) complexes with pyctrien. The spectrum of [CuLH$_2$]$^{4+}$ species indicates an octahedral geometry characterised by the high value of $\lambda_{\max}$ (756 nm), the ligand being coordinated through the two pyridyl nitrogen atoms and probably the two carbonyl oxygen atoms of the amidic group. The hexacoordination is achieved by two water molecules (Scheme 3a). The shape of the band and $\lambda_{\max}$ value (560 nm) for [CuLH$_{-1}$]$^+$ are similar to those obtained by Vagg and coworkers[17] for analogous CuN$_4$O chromophores, characteristic of a square pyramidal geometry with four equatorial nitrogen donors (N$_\mathrm{pyridyl}$, N$_\mathrm{amido}$, N$_\mathrm{amino}$, N$_\mathrm{amino}$) and a water molecule in the apical position (Scheme 3b). The dissymetric large band around 700 nm obtained for [CuLH$_{-2}$] is characteristic of an octahedral geometry involving six nitrogen atoms[18] (Scheme 3c or 3d).

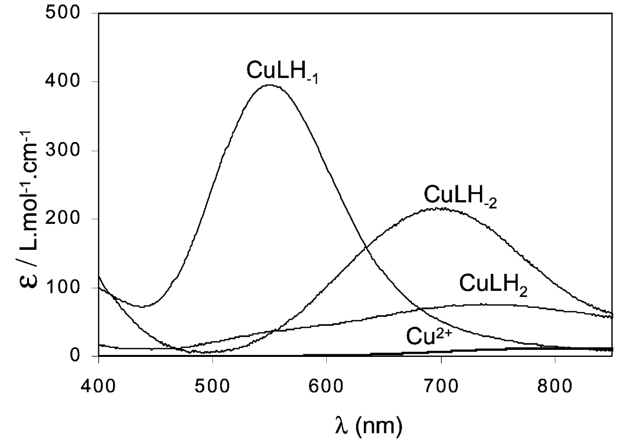
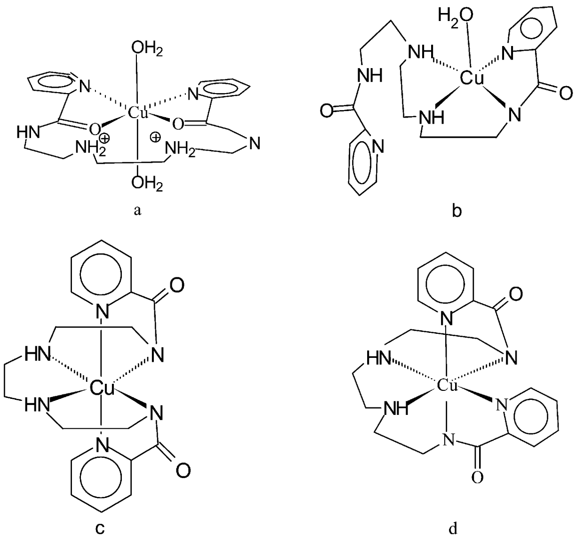


Fig. 4 Calculated visible spectra for the Cu(II) complexes of pyctrien.

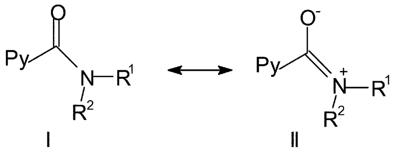


Scheme 3

In the case of nickel compounds, the curves $\bar{h}$ *vs.* pH have shown the existence of two major species, [NiLH$_2$]$^{4+}$ and [NiLH$_{-2}$]. Variable pH UV/VIS studies indicate that each complex exhibits two bands at 620 and 1000 nm for the first and 550 and 860 nm for the second; the third band is obscured by the ligand charge transfer band. These values are consistent with an octahedral geometry[19] around Ni, in agreement with NiN_2O_4 and NiN_6 chromophores for $[NiLH_2]^{4+}$ and $[NiLH_{-2}]$ species, respectively.

Spectroscopic studies

IR spectra. IR spectra of these complexes are similar to that of the ligand. For all six compounds, small shifts to lower energies are observed for the characteristic secondary amine bands at *ca.* 3400–3060 cm^{-1}, with decreasing intensity. ClO_4^- anions in the compounds **1**, **2**, **3**, **4** and **6** have been characterised by a large band at *ca.* 1090 cm^{-1}. The ligand pyctrien has two amido groups and each group has the following resonance structures[20] (Scheme 4) with predominant formula I. Coordination through the oxygen atom increases the contribution of formula II. If coordination occurs through the nitrogen atom, its hybridisation will be sp^3 and the C=O bond will become a complete double bond with loss of the resonance energy.[21]



Scheme 4

The amide I band consists mainly of $\nu_{C=O}$, and the amide II and III bands arise from ν_{C-N} as well as from δ_{N-H}, although these modes are coupled to one another.[22] Consequently for an amide group coordinated through the oxygen atom, the amide I band will shift to lower and the amide II and III bands to higher frequencies. On the other hand, if the amide-nitrogen atom coordinates, the amide I, II, III bands should shift to opposite directions. Our experimental data (see Experimental section) reveal that the amide bands of complexes **1**, **2** and **3** shifted towards the direction expected for amide-oxygen coordination, whereas in compounds **5** and **6** these amide bands shifted towards amide-nitrogen coordination; the coordination of the amide-nitrogen leads to its deprotonation.[23]

Absorption spectra. The electronic spectra of the six complexes, were obtained both in the solid state and in aqueous solution (see Experimental). The absorption spectra for these compounds exhibit essentially similar patterns in the 250–500 nm region, with two strong bands possibly due to intraligand[24] and charge transfer transitions.

In the visible region, it is to be noted that the spectra of compounds $[CuL](ClO_4)_2 \cdot H_2O$ **1** and $[CoL](ClO_4)_2$ **3** in the solid state display a band at 630 nm with a shoulder at 730 nm for **1** and 490 nm with a shoulder at 400 nm for **3**. For both complexes, the stereochemistry in the solid state is expected to be tetrahedral and octahedral, respectively. According to IR data, we can conclude that both compounds have CuN_2O_2 and CoN_4O_2 chromophores. The main absorption band is considerably blue-shifted (by 85 and 25 nm, respectively) and the shoulder disappears completely in going from the solid state to aqueous solution, which is probably due to solvent-induced structural changes.

For the remaining four complexes (**2**, **4**, **5** and **6**) the spectra in the solid state are not different from those in aqueous solution. Thus $[CuLH_{-1}(H_2O)](ClO_4) \cdot H_2O$ **4**, exhibits a dissymetric band at 550 nm; this feature is characteristic of a square-based pyramidal geometry around the Cu^{2+} ion.[25] Complexes $[NiL](ClO_4)_2$ **2**, and $[NiLH_{-2}] \cdot H_2O$ **5**, have similar spectra, each one displaying two bands. We note that the higher energy band for compound **5** is obscured by charge-transfer and appears only as a shoulder. These bands arise from $^3A_{2g} \longrightarrow {}^3T_{2g}$ and $^3A_{2g} \longrightarrow {}^3T_{1g}(^3P)$ transitions. The third band at higher energy is completely obscured by metal–ligand charge-transfer. These observations are consistent with an octahedral geometry around the Ni^{2+} ion, and data obtained from IR spectra lead us to suppose that the chromophores of these two compounds are NiN_4O_2 and NiN_6, respectively.

Table 3 ESR data for compounds **1** and **4**, and other copper(II) complexes

Entry	Complex	$g_{//}$	$g_\perp$	$10^{-4}A_{//}$/cm^{-1}	Ref.
1	**1**	2.19	2.06	189	This work
2	**4**	2.19	2.05	195	This work
3	Cu(II)(BLM)[a]	2.21	2.05	189	30
4	Cu(II)(KIM1)[b]	2.20	2.05	184	34
5	Cu(II)(KIM2)[b]	2.21	2.06	185	34
6	Cu(II)(PMA)[c]	2.21	2.05	190	33
7	Cu(II)(Py$_3$P)[d]	2.20	2.04	158	6, 35
8	Cu(II)(APPy)[d]	2.21	2.05	142	6, 35

[a] BLM = Bleomycin. [b] KIM1 = 2-[((2-(4-Imidazolyl)ethyl)amino)-carbonyl]-6-[*N*-(2-aminoethyl)aminoethyl]pyridine. [c] KIM2 = 2-[((2-(4-Imidazolyl)ethyl)amino)carbonyl]-6-[((2-amino-2-carbamoylethyl)-amino)methyl]pyridine. [d] PMA = 2-[[(2-aminoethyl)amino]methyl]-5-bromo-*N*-[2-(1*H*-imidazol-4-yl)ethyl]-4-pyrimidinecarboxamide. [e] Py$_3$P = *N*,*N*′-bis(2-(2-pyridyl)ethyl)pyridine-2,6-dicarboxamide; APPy = bis[3-(2-pyridinecarboxamido)ethyl]methylamine.

The d–d absorption band occurs at 480 nm for $[Co^{III}LH_{-2}](ClO_4)_{0.75}Cl_{0.25} \cdot 2.5H_2O$ **6**. Comparison between compound **6**, $[Co^{III}(2,2',2''\text{-trioxosenH}_{-3})]$[26] and $[Co^{III}sen]^{3+}$ [27] [where sen is 1,1,1-tris(4-amino-2-azabutyl)ethane] shows that the band intensities increase with the number of amide groups in the ligand (ε = 160, 163 and 113 mol^{-1} L cm^{-1}, respectively). This characteristic absorption band may arise from a Laporte forbidden transition $^1A_{1g} \longrightarrow {}^1T_{1g}$ for low spin Co^{III}.

ESR studies. The ESR spectra of **1** and **4** in frozen DMF–toluene (1 : 1 v/v) or water–ethylene glycol (5 : 1 v/v) are shown in Fig. 5 and the data are summarised in Table 3. The ESR spectra are anisotropic and typical of axially symmetric monomeric copper(II) complexes exhibiting a tetragonal geometry, with $g_{//} > g_\perp$ and a $d_{x^2-y^2}$ ground state.[26] A small anisotropy is also observed in the perpendicular part of the spectrum. Although pyctrien has at least six coordination sites, no intra- or inter-molecular dimeric complex is formed which should lead to a more complicated spectrum typical for a triplet spin state.[28] The hyperfine coupling constant and g values are very close to those found for the copper-bleomycin complex[29]

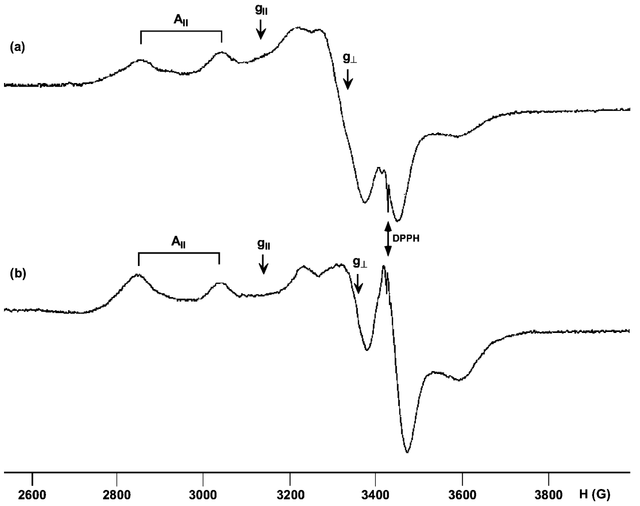
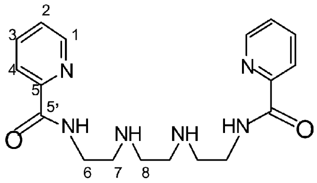


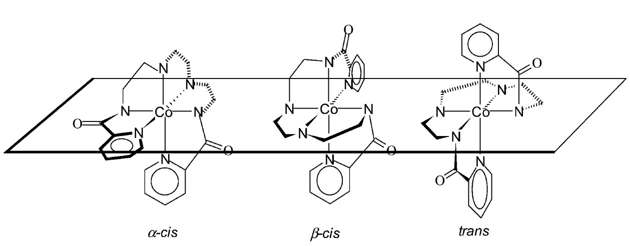
Fig. 5 ESR spectra at 100 K for (a) **1** in DMF–toluene (1 : 1 v/v), and (b) **4** in water–ethylene glycol (5 : 1 v/v).

Table 4 ^1H and ^{13}C NMR chemical shifts (ppm) and coupling constants (Hz) of L·4HCl and $[CoLH_{-2}](ClO_4)_{0.75}Cl_{0.25}·2.5H_2O$ **6** in D_2O



	pyctrien		Co(III) complex	
	^1H	^{13}C	^1H	^{13}C
1	8.60 d	148.12	8.15 d, $J = 5.5$	150.2
2	7.70 t	131.94	7.50 t, $J = 7.7$	128.4
3	8.20 t	147.22	8.07 t, $J = 6.3$	141.2
4	8.10 d	127.1	7.89 d, $J = 7.9$	124.8
5	—	153.2	—	157.1
5′	—	167.3	—	169.6
6	3.80 t	39.35	a: 4.19 dd, $^2J = 14.9$, $^3J = 7.7$ b: 3.89 dt, $^2J = 14.1$, $^3J = 6.1$	448
7	3.40 t	46.18	a: 3.21 dt, $^2J = 13.2$, $^3J = 7.8$ b: 2.88 m	57.3
8	3.50 s	50.58	a: 3.31 d, $J = 8.8$ b: 2.84 m, $J = 9.1$	55.8

[a] Values in ppm relative to residual solvent. [b] s = singlet, t = triplet, m = multiplet.



Scheme 5

([Cu^{II}BLM]) and are in agreement with a regular square pyramidal coordination geometry[30] for both **1** and **4**. It has been demonstrated[31] that larger $A_{//}$ values are consistent with stronger in-plane ligand strength in square pyramidal copper(II) complexes due to a better overlap between the magnetic orbital ($d_{x^2-y^2}$) and the ligand orbitals for a square pyramidal geometry. The high value of $A_{//}$ is thus indicative of a minimally-distorted square pyramidal geometry (X-ray of **4**: $\tau = 0.13$; see below) and the strong in-plane ligand strength shown by UV-visible analysis of **1** and **4** in water ($\lambda_{max} = 555$ nm and 550 nm, respectively) is corroborated by the large $A_{//}$ values. These facts are in full agreement with the X-ray structure of **4** and show that the structural arrangement is maintained in solution. Similar data between **1**, **4** and other copper-bleomycin models[32,33] (Table 3 entries 4 to 6) show that the coordination structure of these complexes are rather similar, and the smaller $A_{//}$ values for the dicarboxamido complexes[6,34] (Table 3 entries 7 and 8) arise from weaker in-plane crystal field due to axial elongation and in-plane distortion. Moreover, it is to be noted that the ESR spectrum of **4** in frozen DMF–toluene (1 : 1 v/v) is more complicated due to the presence of two species, probably a penta- and hexa-coordinated with a DMF molecule in the axial position.

NMR spectra. In order to examine chelate ring proton interaction and to better confirm isomeric geometries for coordination compounds derived from polydentate ligands, NMR experimental techniques have been investigated. The ^1H and ^{13}C NMR spectra of the ligand pyctrien and its deprotonated Co(III) complex, **6**, are presented and general regions of the proton and carbon spectra are assigned (Table 4). The proton resonance signals for both compounds indicate that the ligand is symmetrical in each. For an octahedral complex with this linear hexadentate ligand, three configurations α-*cis*, β-*cis* or *trans* (Scheme 5) can be considered with one, two or three ethylene groups in the same plane, respectively. Only an α-*cis* configuration can preserve the symmetry of the ligand in the complex.

The combination of COSY (see ESI) and decoupling methods allows the assignment of all the proton resonance signals. The complete ^1H assignment is extended to the ^{13}C resonance signals by reference to the ^1H–^{13}C HMBC and HMQC data.[35] The ^1H NMR spectrum reveals four well-resolved signals for the pyridine moiety with typical values of coupling constants[36] (Table 4). The spectrum of the complex shows a shielding for all the four pyridine protons. This shielding, which is more important for proton 1 (−0.45 ppm), can be explained by the presence of these protons in the interatomic anisotropic contributions of the second pyridine. In the cobalt(III) complex, two signals are always obtained for the protons of each methylene group (Fig. 6). The non-equivalence of these two protons is probably due to the shielding effect of the neighbouring five-membered ring anisotropic bond contributions.[8] Moreover, no splitting is observed for any proton or carbon signal indicating the presence of only one isomer. All these results are in agreement with an α-*cis* configuration, confirmed by an X-ray analysis (see below).

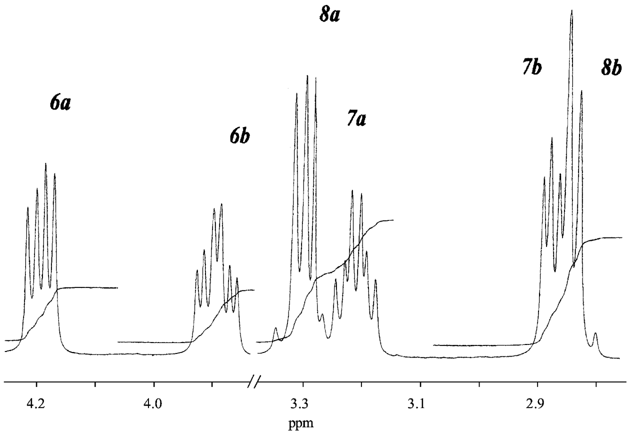


Fig. 6 Proton spectrum of the aliphatic chain in $[CoLH_{-2}](ClO_4)_{0.75}Cl_{0.25}$ in D_2O.

Crystal structures

The crystal structure of complexes $[CuLH_{-1}(H_2O)](ClO_4)·H_2O$ **4**, $[NiLH_{-2}]·H_2O$ **5** and $[CoLH_{-2}](ClO_4)_{0.75}Cl_{0.25}·2.5H_2O$ **6** were determined by single crystal X-ray diffraction.

$[CuLH_{-1}(H_2O)](ClO_4)·H_2O$ 4. The crystal structure determination revealed that crystals of **4** consist of $[CuLH_{-1}(H_2O)]^+$ cations which are well separated from ordered and well behaved perchlorate anions. The Cl–O bond lengths and the O–Cl–O angles are consistent with those reported earlier.[8] A view of the cation with the labelling scheme is shown in Fig. 7. Principal bond distances and angles are listed in Table 5.

Although pyctrien is a potentially hexadentate ligand, the copper(II) complex has a distorted square pyramidal geometry. Four nitrogen atoms from the pyridine-2-caboxamido moiety [N(1) and N(2)] and the two central secondary amines [N(3) and N(4)] form the base of a square pyramid with the oxygen donor atom of one water molecule occupying the apical position. Thus, one of the two pyridine-2-carbamoyl groups remains uncoordinated. The Cu–N$_{pyridyl}$ bond length [Cu–N(1) = 2.011(3) Å] is comparable to those observed in other five coordinate complexes where Cu^{2+} ion is bound to the pyridine-2-carboxamido moiety.[34,37] The Cu–N$_{amido}$ bond

Table 5 Selected bond lengths (Å) and angles (°) for complexes **4**, **5** and **6**

$[CuLH_{-1}(H_2O)](ClO_4)\cdot H_2O$ **4**			
Cu–N(1)	2.011(3)	Cu–N(4)	2.010(3)
Cu–N(2)	1.907(3)	Cu–O(7)	2.375(3)
Cu–N(3)	2.014(4)		
N(1)–Cu–N(2)	82.7(1)	N(2)–Cu–N(4)	159.0(1)
N(1)–Cu–N(3)	167.2(1)	N(2)–Cu–O(7)	105.6(1)
N(1)–Cu–N(4)	104.0(1)	N(3)–Cu–N(4)	87.4(1)
N(1)–Cu–O(7)	91.7(1)	N(3)–Cu–O(7)	93.3(1)
N(2)–Cu–N(3)	84.6(6)	N(4)–Cu–O(7)	94.2(1)
$[NiLH_{-2}]\cdot H_2O$ **5**			
Ni–N(1)	2.139(2)	Ni–N(4)	2.138(2)
Ni–N(2)	2.001(1)	Ni–N(5)	2.009(1)
Ni–N(3)	2.144(2)	Ni–N(6)	2.152(2)
N(1)–Ni–N(2)	78.15(6)	N(2)–Ni–N(6)	96.82(6)
N(1)–Ni–N(3)	157.64(6)	N(3)–Ni–N(4)	82.62(6)
N(1)–Ni–N(4)	99.71(6)	N(3)–Ni–N(5)	105.99(6)
N(1)–Ni–N(5)	96.27(6)	N(3)–Ni–N(6)	97.87(6)
N(1)–Ni–N(6)	88.97(6)	N(4)–Ni–N(5)	79.46(6)
N(2)–Ni–N(3)	79.91(6)	N(4)–Ni–N(6)	155.89(6)
N(2)–Ni–N(4)	106.94(6)	N(5)–Ni–N(6)	77.24(6)
N(2)–Ni–N(5)	172.02(7)		
$[CoLH_{-2}](ClO_4)_{0.75}Cl_{0.25}\cdot 2.5H_2O$ **6**			
Co–N(1)	1.937(5)	Co–N(4)	1.953(5)
Co–N(2)	1.879(5)	Co–N(5)	1.884(5)
Co–N(3)	1.958(5)	Co–N(6)	1.938(5)
N(1)–Co–N(2)	82.6(2)	N(2)–Co–N(6)	98.1(2)
N(1)–Co–N(3)	167.5(2)	N(3)–Co–N(4)	87.8(2)
N(1)–Co–N(4)	92.6(2)	N(3)–Co–N(5)	94.4(2)
N(1)–Co–N(5)	98.0(2)	N(3)–Co–N(6)	92.2(2)
N(1)–Co–N(6)	90.1(2)	N(4)–Co–N(5)	85.3(2)
N(2)–Co–N(3)	85.0(2)	N(4)–Co–N(6)	167.5(2)
N(2)–Co–N(4)	94.3(2)	N(5)–Co–N(6)	82.2(2)
N(2)–Co–N(5)	179.3(2)		

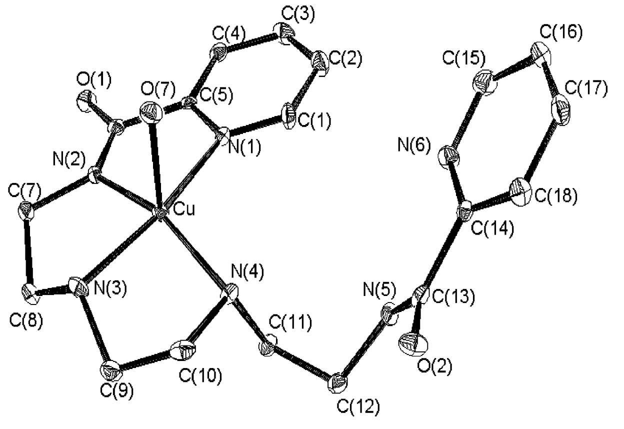


Fig. 7 ORTEP[42] drawing of the $[CuLH_{-1}(H_2O)]^+$ cation showing 50% probability ellipsoids and the atom labelling scheme; hydrogen atoms are omitted for clarity.

length [Cu–N(2) = 1.907(3) Å] is shorter than the $Cu–N_{amine}$ (average 2.012 Å), which is consistent with the stronger donor ability of the deprotonated amido nitrogen compared to the amine nitrogen.[38] This amido bond length is well within the range of $Cu–N_{amido}$ distances noted in similar complexes.[39] The long apical bond $Cu–O_{water}$ distance [Cu–O(7) = 2.375(3) Å] reflects a weak axial interaction as expected for Jahn–Teller sensitive copper(II) complexes. The angle between the *trans* basal nitrogens [N(1)–Cu–N(3) = 167.2(1)°], although less than the expected 180°, is in the range for *SPY* Cu(II) complexes (160–170°) in which the Cu(II) center lies slightly above the basal plane.[31] So the geometry around the copper(II) ion is best described as distorted square pyramidal with the structural index $\tau = 0.13$ [$\tau = (\beta - \alpha)/60$, where β = N(1)–Cu–N(3) 167.3(2)° and α = N(2)–Cu–N(4) 159.6(2)°]; for perfect square pyramidal and trigonal bipyramidal geometries the value of τ is zero and unity, respectively.[39]

In the crystalline structure, the complex **4** has a superstructure based on two C=O ··· HO hydrogen interactions between the amidic groups and the water molecules. In the lattice, two complex units interact *via* OH ··· O hydrogen bonds between the oxygen atom of the coordinated picolinamide group [O(1)] and the coordinated water molecule of the neighbouring molecule; the distance C=O ··· HO being 1.560 Å. The second hydrogen bond is between the oxygen atom of the uncoordinated picolinamide group and the water molecule of crystallisation [O(2) ··· H(07) = 1.863 Å].

The structure of complex **4** is different from the hexacoordinated N_6 $[Cupytrien]^{2+}$ compound,[9] containing a ligand similar to pyctrien, but possessing pyridylmethyl groups instead of picolinamide groups. This latter complex exhibits coordination of the two pyridyl nitrogen atoms to the copper center; this difference could be explained by an extended π electron delocalisation in the picolinamide group which induces the rigidity of the moiety.

$[NiLH_{-2}]\cdot H_2O$ 5 and $[CoLH_{-2}](ClO_4)_{0.75}Cl_{0.25}\cdot 2.5H_2O$ 6. The unit cell of complex **5** consists of the $[NiLH_{-2}]$ molecule and one water molecule of crystallisation. The asymmetric unit of complex **6** is composed of two $[CoLH_{-2}]^+$ cations, two ClO_4^- anions (with a site occupancy of 0.5 and 1, respectively), one Cl^- anion (with a site occupancy of 0.5) and five water molecules leading to the given molecular formula. In the crystal lattice, one of the two ClO_4^- anions is disordered and this kind of perchlorate disorder has been observed in several other structures.[8,9,40] The values of the bond lengths and angles found for both $[CoLH_{-2}]^+$ cations are identical within the standard limits.

The complex species **5** and **6** have the same geometry around the metal ion and can be discussed together. A view of the cobalt complex is given in Fig. 8. Principal bond distances and angles are listed in Table 5 for the $[NiLH_{-2}]$ and $[CoLH_{-2}]^+$ complexes, respectively.

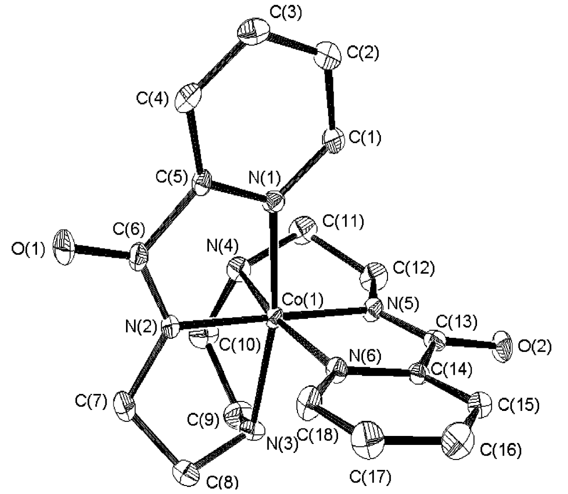


Fig. 8 ORTEP drawing of the $[CoLH_{-2}]^+$ cation. Details as in Fig. 7.

The $[MLH_{-2}]^{n+}$ (M = Ni^{II}, $n = 0$ and M = Co^{III}, $n = 1$) have an octahedral coordination geometry. The ligand encapsulates the metal atom through the six ligating nitrogen atoms: two pyridyl [N(1) and N(6)], two amido [N(2) and N(5)] and two secondary amine [N(3) and N(4)] nitrogen atoms. Though several isomers can be isolated with a linear hexadentate ligand, the one observed here has the pyridine nitrogen atoms in the *cis* position and the amido nitrogen atoms in the *trans* position. In both structures, the bond lengths involving pyridine nitrogen atoms are not significantly different from those involving secondary amine nitrogen atoms; all metal–nitrogen bond lengths in the nickel complex are longer than those in the cobalt complex, which is consistent with the larger radius of Ni(II). However, we note that M–N_{amido} bond lengths are shorter than M–N_{amine} and M–N_{py} bond lengths reflecting the stronger σ donor ability of the deprotonated amido nitrogen. This differences in M–N_{amido} bond distances [-0.15 and -0.06 Å, respectively for nickel(II) and cobalt(III) compounds] are more important in the case of the Ni(II) complex, reflecting the fact that **5** has a larger distortion than **6**; the difference between Ni–N (average, 2.147 Å) and Co–N (average, 1.947 Å) distances is *ca.* + 0.200 Å. The bond lengths found for **5** and **6** are entirely consistent with those in other Ni(II) and Co(III) amido complexes.[41] Conversely, the five chelate bond angles of 77.3(7)–79.9(7)° (average, 78.6°) subtended by the ligand at the nickel atom are smaller than their analogues of 82.2(2)–87.8(2)° (average, 85.0°) in the cobalt complex, in agreement with a larger distortion in the nickel compound.

The crystalline structure of complex **5** shows one hydrogen bond between the oxygen atom of one of the picolinamide groups and the water molecule of crystallisation [O(2) ··· H(03) = 2.103 Å]. In the lattice of the cobalt compound, the intermolecular distances between two oxygen atoms of five water molecules [O(17) and O(21)] are less than the sum of their van der Waals radii; the same phenomenum appears between the oxygen atoms of water molecule O(21) and the amidic group O(2). This suggests that these species are involved in the hydrogen bonding interactions, but the disorder exhibited by perchlorate anions prevents a detailed analysis.

Conclusion

The protometry results reveal that only four basic groups are protonated for the potentially hexadendate N_6 ligand, due to the two amidic nitrogens present in pyctrien.

The equilibrium constants of the M(II) chelates with pyctrien determined by potentiometry show the formation of $[MLH_{-1}]^+$ and $[MLH_{-2}]$ (M = Cu and Ni) in all the cases; thus, the chelation of metal ions by the amidic nitrogen promotes an amide hydrogen ionization.[23] Whereas the other detected species depend on the nature of the metallic ion: $[CuLH_2]^{4+}$, $[CuL]^{2+}$, $[NiLH_2]^{4+}$ and $[NiLH]^{3+}$. In addition, the variable pH UV/Vis spectrophotometry has allowed us to determine some complex structures in solution. We can note the preference of the Cu^{2+} ion for an environment with four nitrogen donor atoms with a coordination number of five or six achieved by extra water molecules, in contrast Ni(II) species always have an octahedral geometry. The comparison of the chelating effect of pyctrien with other similar ligands shows that the behaviour of this ligand is interesting for the synthesis of complexes in which the metal ion retains a sufficient availability for interactions with substrates.

X-Ray crystallographic studies show that both cobalt(III) and nickel(II) compounds are octahedral with the same configuration; the two secondary amine nitrogen atoms and the two pyridyl groups are *cis*, whereas the two amido nitrogen atoms are *trans*. The comparison of the bond angles of **5** and **6** with those of similar compounds described earlier[8] indicates that substituting the methylene group by a carbamoyl group leads to a decrease of the bond angle (*ca.* −8.1°) formed by the two axial bond lengths: $[Copytrien]^{3+}$, $N_{pyridyl}$–Co–N_{amine} = 175.6(1)°; $[CopyctrienH_{-2}]^+$, $N_{pyridyl}$–Co–N_{amine} = 167.5(2)°. We can conclude that metal complexes with a bis(pyridylcarbamoyl) N_6 ligand have a more distorted octahedral geometry than those with the bis(pyridylmethyl) N_6 ligand, probably due to the extended π electron delocalisation.

The interpretation of two and three bond coupled proton interactions by one- and two-dimensional NMR techniques allows us to assign the $[CoLH_{-2}]^+$ cation an α-*cis* configuration.

It seems to us worthwhile to obtain a more complete picture of the factors influencing the stereochemical properties of these types of complexes by studying the chelating effect of other analogous ligands possessing other central heteroatoms like thioether sulfur and/or ether oxygen donor atoms. Further work along these lines is in progress.

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