Equilibrium and structural studies of copper(II) complexes with a tridentate ligand containing amide, pyrazyl and pyridyl nitrogen donors: Effect of anions coligands on crystal structures of copper(II) complexes

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ABSTRACT

The stability constants of the Cu(II) chelates with the tridentate ligand 2-(N, 2-pyridylmethyl)pyrazinecarboxamide (Hpzpy), determined by potentiometry UV–Vis and mass spectrometries, show the formation of $[Cu(pzpy)]^+$, $[Cu(pzpy)(OH)]$, $[Cu(pzpy)_2]$ and $[Cu(pzpy)_2(OH)]^-$ species (where pzpy is an amide-deprotonated ligand). In the solid state, the synthesis, crystal structures, and electronic and magnetic properties of three new Cu^{II} compounds containing the tridentate pzpy ligand with the general formula $[Cu^{II}(pzpy)(L)(OH_2)_x]$ (where $x = 1$ for $L = CH_3CO_2^-$ and $x = 0$ for $L = N_3^-$ or $NC–N–CN^-$) are reported. The geometries of the Cu^{II} ions are described as a five-coordinate slightly distorted square pyramidal monomeric compound $[Cu(pzpy)(OH_2)(CH_3CO_2)]$ (**1**) and polymeric complexes, $[Cu(pzpy)(N_3)]_n$ (**2**) and $[Cu(pzpy)(N(CN)_2)]_n$ (**3**). Polymerization for complex **2** comes from equatorial–apical bridges of the "naked" pyrazine nitrogen atoms, while in compound **3**, the copper centers were bridged by $NC–N–CN^-$ anions. These three compounds have been characterized in details by infrared, ligand field and EPR spectroscopy; the data are consistent with the single-crystal X-ray structures.

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1. 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-pyrazinecarboxamide are very useful to modulate the structural and electronic properties of first-row transition-metal centers. The ligand 2-(N, 2-pyridylmethyl)pyrazinecarboxamide (hereafter denoted Hpzpy) may adopt both chelating and bis(chelating) coordination modes, and thus has the ability to form mononuclear as well as polynuclear complexes through spare nitrogen of pyrazyl group. A variety of structural motifs, including chain and framework structures are possible, making this ligand an attractive choice in attempts to prepare supramolecules based on the assembly of organic molecules and metal-ion building blocks. The Hpzpy ligand, has been used recently in the construction of some interesting molecular weaving with octahedral metal ions [2]. To the best of our knowledge no published data referring either to the acidity constants of Hpzpy ligand or to the stability constants of its metallic ion complexes have been reported. In solid state, only few

X-ray crystal structures of cobalt and manganese complexes and the Hpzpy ligand have been reported: one mononuclear $[Co^{III}(pzpy)_2]BF_4$ compound [3], one dinuclear $[Mn_2^{II}(Hpzpy)_2(OH_2)_2Cl_4]$ complex [4] and one trinuclear octahedral cobalt compound [2] $[Co_2^{III}(pzpy)_4 Co^{II}(OH_2)_2(Cl)_2]Cl_2$; (pzpy is an amide-deprotonated ligand).

In this paper, we describe the syntheses of the pzpy ligand and their copper(II) complexes as well as the thermodynamic constants of the metal chelates formed by this ligand. A variety of new crystal structures with different coordinating anions as coligand are reported together with their spectroscopic and magnetic properties.

2. Experimental

2.1. Reagents

All the solvents were purified by conventional procedures [5] and distilled prior to use. All the chemicals commercially available (Aldrich) were used as supplied without further purification.

2.2. Synthesis

2.2.1. Synthesis of the ligand 2-(N, 2-pyridylmethyl)pyrazine carboxamide (Hpzpy)

The ligand, described earlier in the literature [2–4,6] was obtained from the coupling of the carboxylate moieties using 1,

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1′-carbonyldiimidazole (CDI) [7]. Recrystallisation from dimethylformamide of the crude product obtained gave Hpzpy as colorless needle crystals, yield: (4.036 g, 82%). *Anal.* Calc. for $C_{11}H_{10}N_4O$: C, 61.67; H, 4.70; N, 26.15. Found: C, 61.55, H, 4.85, N, 26.10%. ^{1}H NMR (D_2O CDCl$_3$, 250 MHz, δ_H/ppm): 4.90 (2H, s, CH$_2$); 7.90 (1H, t, CH$_{py}$); 8.00 (1H, d, CH$_{py}$); 8.50 (1H, t, CH$_{py}$); 8.60 (1H, d, CH$_{py}$); 8.75 (2H, d, CH$_{pz}$); 9.10 (1H, s, CH$_{pz}$). IR (KBr disk, v/cm^{-1}): 3450–3100 (s, v_{N-H}); 3215–3060 (m, v_{C-H}); 2900–2600 (m, v_{CH2}); 1673 (vs, $v_{C=O}$); 1613, 1272, 1188, 999, 615, 445 (s, $v_{aromatic\ rings}$).

2.2.2. Synthesis of metal complexes

2.2.2.1. [Cu(pzpy)(OH₂)(CH₃CO₂)] (1).
An ethanolic solution (10 mL) of copper(II) acetate monohydrate (0.199 g, 1 mmol) was added whilst stirring to an ethanolic solution (40 cm^3) of Hpzpy (0.214 g, 1 mmol). The mixture was maintained at a boil for 10 min; the small amount of precipitate that formed was redissolved by few drops of water. The solution was filtered and left at room temperature and crystals were obtained within 4 weeks, yield: (0.248 g, 70%). *Anal.* Calc. for $C_{13}H_{14}N_4O_4Cu$: C, 44.13; H, 3.99; N, 15.84; Cu, 17.96. Found: C, 44.10; H, 4.10; N, 15.75; Cu 17.70%. IR (KBr disk, v/cm^{-1}): 3307, (s, v_{O-H}); 3086–3030 (m, v_{C-H}); 2890–2830 (m, v_{CH2}); 1636 (versus, $v_{C=O}$); 1287, 467 (s, $v_{aromatic\ rings}$).

2.2.2.2. [Cu(pzpy)(N₃)] (2) and [Cu(pzpy)(N(CN)₂)] (3).
Caution! Azido complexes of metal ions in the presence of organic ligands are potentially explosive. Only a small amount of material should be prepared, and it should be handled with care.

The two complexes were obtained by a similar method described above, but in this case, before filtering the mixture copper(II)–Hpzpy ligand, sodium azide (0.065 g, 1 mmol) dissolved in 5 cm^3 of water (complex **2**), or sodium dicyanamide (0.089 g, 1 mmol) dissolved in 5 cm^3 of water (complex **3**), was added dropwise. The mixture was stirred at room temperature for 20 min. Solutions were filtered and left at room temperature. Crystals suitable for X-ray studies were obtained within 2 months.

2.2.2.3. [Cu(pzpy)(N₃)] (2).
Yield: (0.239 g, 75%). *Anal.* Calc. for $C_{11}H_9N_7OCu$: C, 41.45; H, 2.85; N, 30.76; Cu, 19.93. Found: C, 41.39; H, 2.90; N, 30.65; Cu, 19.75%. Requires IR (KBr disk, v/cm^{-1}): 3070–3025 (m, v_{C-H}); 2880–2820 (m, v_{CH2}); 1640 (versus, $v_{C=O}$); 1610, 1280, 466 (s, $v_{aromatic\ rings}$), 2054 (versus, v_{N3}).

2.2.2.4. [Cu(pzpy)(N(CN)₂)] (3).
Yield: (0.240 g, 70%). *Anal.* Calc. for $C_{13}H_9N_7OCu$: C, 45.55; H, 2.65; N, 28.60; Cu, 18.54. Found: C, 45.77; H, 2.84; N, 28.45; Cu, 18.65%. IR (KBr disk, v/cm^{-1}): 3237–3090 (m, v_{C-H}); 2877–2826 (m, v_{CH2}); 1643 (versus, $v_{C=O}$); 1610, 1275, 467 (s, $v_{aromatic\ rings}$); 2301, 2248, 2177 (versus, $v_{(C\equiv N)}$).

2.3. Measurements

Elemental analyses (C, H and N) were carried out on a Perkin-Elmer 2400 C, H, N element analyzer. The metal analysis was performed on an ICP AES Liberty Series II Varian apparatus and chloride ions were determined potentiometrically using silver nitrate.

2.3.1. Potentiometric technics

2.3.1.1. Protometric.
Distilled and argon-bubbled water was used for the preparation of all solutions. Stock solutions of metal nitrate were prepared from commercially available reagents (Fluka) of the highest purity (>99%) and were used without further purification. The titrating solutions of carbonate-free base NaOH and nitric acid 0.1 M were prepared from standardized molar solutions (Prolabo).

All solutions were prepared with glass-distilled, de-ionized water and degassed by argon saturation in order to remove all dissolved CO_2.

Protometric titrations were carried out with an automatic titrator composed of a microprocessor burette Metrohm Dosimat 665 and a pH-meter Metrohm 713 connected to a computer. All measurements were performed within a thermoregulated cell at 25 °C under an argon stream to avoid the dissolution of carbon dioxide. The ionic strength was adjusted to 0.1 with potassium nitrate. A HNO_3 solution at exactly 10^{-2} mol dm^{-3} was used to calibrate the electrode. The titrant, a carbonate-free KOH solution (Normadose), was standardized against a 0.05 mol dm^{-3} potassium hydrogen phthalate solution by pH-potentiometry. The ionic product of water was determined under these conditions (pK_w = 13.76) and used in the calculations.

For a classical titration, a total of 120–150 points (volume of titrant, pH) was taken. The protonation constants of the ligand Hpzpy were determined from 7 titrations in the presence of HNO_3. The concentration of the ligand and the ratio of the concentration [HNO_3]/[Hpzpy] were in the range of 0.8–4 × 10^{-3} mol dm^{-3} and 1–5, respectively. The stability constants of Cu(II) complexes were determined from 8 titrations in which 4 titrations were performed at constant ligand concentration (1.6×10^{-3} mol dm^{-3}) and variable [Hpzpy]/[Cu^{2+}] ratios from 1 to 4, in the pH range from 2 to 11. The 4 remaining titrations were performed with equimolar ligand and the metal solutions in the concentration range from 0.8 to 2.4×10^{-3} mol dm^{-3}.

2.3.1.2. Protometric computations.
The protonation constants of the ligand and overall stability constants (β_{mlh}) of the metal complexes were calculated with the general computation program **hyperquad** [8,9]:

$$mM + lL + hH \rightleftharpoons M_mL_lH_h, \quad \beta_{mlh} = \frac{[M_mL_lH_h]}{[M]^m[L]^l[H]^h}$$
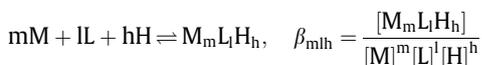
(with M the metal ion, L the ligand and H the proton, the charges are omitted). The computer program HYSS [18,19] was used to obtain the species distribution curves.

2.3.1.3. Aqueous spectroscopic titration of Hpzpy–Cu species.
The visible spectra of copper(II) complexes were recorded in aqueous solution using a Shimadzu UV-2401-PC spectrophotometer equipped with a standard syringe sipper and a temperature-controlled cell holder TCC-240A. The experiments were monitored in the same concentration range as used for pH titration. An average of 40 spectra was recorded in the pH range of 2.5–11.5.

2.3.2. Electrospray ionization mass spectrometry (ESI-MS)

All experiments (MS and MS/MS) were carried out on a hybrid tandem quadrupole/time-of-flight (Q-TOF) instrument, equipped with a pneumatically assisted electrospray (Z-spray) ion source (Micromass, Manchester, UK) operated in positive mode. The solutions of complexes were prepared in similar conditions to the ones set out for the potentiometric study and were introduced using a syringe pump with a flow rate 5 µl/min.

The peaks corresponding to the complex species were identified by analyzing their specific isotopic profile due the different Cu isotopes (e.g. ^{63}Cu, ^{65}Cu). The stoichiometries of the molecular associations were determined in accordance with the greater isotopic peak (e.g. ^{63}Cu) and further checked by simulating the different parts of the spectrum with the Isopro 3.0 piece of software [10]. The difference between experimental and calculated m/z values was less than or equal to 0.1 unit.

2.3.3. Spectroscopic technics

The UV–Vis spectra for solid compounds in solution were recorded on a Perkin-Elmer Lambda 6 spectrophotometer. In the solid state, the visible spectra were obtained on a Beckman 5240 spectrophotometer by depositing the compound on a Schleicher and Schul ash-free filter paper. The paper was used as the 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. X-band EPR spectra were recorded on polycrystalline samples at room temperature and as frozen solutions (dimethylformamide) at 77 K with a Jeol RE2X electron spin resonance spectrometer using DPPH (g = 2.0036) as a standard. Magnetic susceptibility measurements (5–300 K) were carried out using a Quantum Design MPMS-5 5T SQUID magnetometer (measurements carried out at 0.1 T). Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from Pascal's constants.

2.3.4. Crystal structure determination

In Table 1 are summarized the pertinent crystallographic data together with refinement details for [Cu(pzpy)(OH₂)(CH₃CO₂)] (1), [Cu(pzpy)(N₃)] (2) and [Cu(pzpy)(N(CN)₂)] (3).

The intensity data were collected in the phi scan mode, at 293 K for all three compounds, on a Bruker-Nonius Kappa-CCD diffractometer, equipped with a graphite monochromator, using Mo Kα radiation (k = 0.71073 Å).

The structures were solved by direct methods using the SIR92 software package [11] and refined by full matrix least-squares on F^2 using SHELXL97 [12]. The intensities were corrected for Lorentz and polarization effects. In both crystal structure determinations, non-hydrogen atoms were located in the difference Fourier syntheses and were refined with anisotropic thermal parameters. Observed hydrogen atoms were placed at calculated positions using a riding model.

3. Results and discussion

3.1. Synthesis

The tridentate ligand (Hpzpy) containing pyridyl and pyrazyl rings described earlier in the literature [2–4,6] was prepared with suitable modifications. This ligand is obtained in a single-step synthesis from pyrazine-2-carboxylic acid and 2-aminomethylpyridine, activated by 1,1-carbonyldiimidazole (CDI) (Scheme 1).

The potentiometric titration by silver nitrate of the precipitated ligand in concentrated HCl confirmed that this compound was isolated as the dihydrochloride salt and the recrystallisation from dimethylformamide allows isolating of the free ligand Hpzpy as white needle crystals. The result of single X-ray measurements is in agreement with that described by Khavasi and co-workers [6].

Three new copper(II) complexes with deprotonated forms of the ligand were synthesized by treating an ethanolic solution of the ligand with copper(II) acetate monohydrate and azide, thiocyanate or dicyanamide ion as coligand. The acetate ion acts as a base to deprotonate the NH amido groups of the ligand. One mononuclear compound (1) and two polynuclear complexes (2 and 3) were isolated as crystals suitable for X-ray structure determinations. The variation of the copper/ligand ratios in the synthesis has no influence on the stoichiometry of the final compounds. The crystal and molecular structures depend on the coligand anion, from case to case, as will be described below.

3.2. Solution equilibria

The affinity of Hpzpy (L) towards copper(II) ions was studied in aqueous solution. The chemical model was established on the basis of potentiometric, UV–Vis spectrophotometric and mass spectrometric studies. Representative titration curves of the ligand alone and in the presence of the Cu^{2+} ion are depicted as ℏ versus pH curves; ℏ is the mean number of bound protons per mol of ligand:

Table 1
X ray experimental data.

Compound	1	2	3
Formula	$C_{13}H_{14}CuN_4O_4$	$C_{11}H_9CuN_7O$	$C_{13}H_9CuN_7O$
Molecular weight	353.82	318.79	342.81
Crystal system	monoclinic	othorhombic	triclinic
Space group	$P2_1/m$	$Pbca$	$P\bar{1}$
a (Å)	8.2540(2)	9.63270(10)	7.405(5)
b (Å)	13.6553(3)	14.0345(2)	7.855(5)
c (Å)	13.1504(3)	18.3967(2)	12.379(5)
α (°)	90.00	90.00	102.512(5)
β (°)	94.6880(10)	90.00	95.582(5)
γ (°)	90.00	90.00	102.822(5)
V (Å³)	1477.23(6)	2487.05(5)	677.4(7)
Z	5	8	2
D_{calc}, (g cm⁻³)	1.591	1.703	1.681
$F(000)$	724	1288	346
μ (cm⁻¹)	1.502	1.763	1.625
Crystal size (mm)	$0.315 \times 0.250 \times 0.185$	$0.310 \times 0.090 \times 0.050$	$0.270 \times 0.250 \times 0.095$
Color, shape	blue-green, block	blue-green, needle	blue, plate
T (K)	293(2)	293(2)	293(2)
θ_{min}, θ_{max} (°)	2.89, 27.88	3.06, 27.87	3.41, 30.12
Total reflections	6824	5534	6974
Total unique reflections (R_{int})	3490 (0.03)	2955 (0.03)	3978 (0.04)
No of refined data, parameters	3490, 207	2955, 181	3978, 199
R [a], wR_2 [b]	0.0330, 0.0939	0.0325, 0.0835	0.0392, 0.0956
Goodness-of-fit (GOF) on F^{2} [c]	1.022	1.038	1.037
min. and max. resd. dens. (e Å⁻³)	−0.496, 0.463	−0.358, 0.373	−0.418, 0.411
CCDC number	786207	786208	786210

[a] $R_1 = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$.
[b] $wR_2 = [\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]]^{1/2}$.
[c] Goodness-of-fit GOF = $[\Sigma_w(F_o{}^2 - F_c{}^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p the number of parameters.
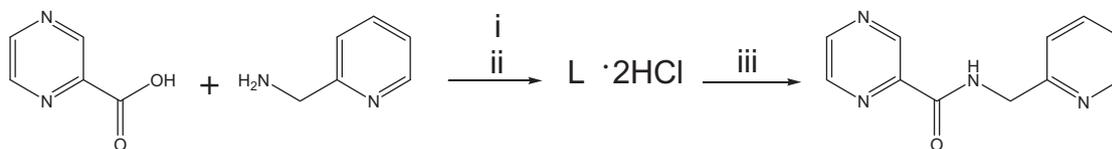
Scheme 1. Synthesis of the ligand Hpzpy. (i) = +CDI in THF; (ii) = +HCl conc in EtOH; (iii) = recryst. DMF.

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

where n is the number of protons in the neutral form of the ligand, C_L is the total concentration of the ligand, C_B is the concentration of the strong base added and C_H is the concentration of the strong acid initially added. Fig. 1 represents the $\bar{h}$ variation for a solution of ligand alone and for metal–ligand solutions with the ratio $R = [Hpzpy]/[Cu^{2+}] = 1$ or 2.

3.2.1. Ligand protonation constant

The acid–base behavior of the ligand showed that the full protonated ligand has one dissociable proton bound to the pyridinic nitrogen atoms (H_2pzpy^+). The deprotonation of the pyridinium group is almost complete (corresponding to $\bar{h} = 0$) above pH 6, with the protonation constant value of log $\beta_{011} = 4.187$ (Table 2). As expected, no protonation of pyrazine function was detected in the pH range investigated. The protonation constant of an amide nitrogen ($-C(O)NH_2^+-$) has been estimated to be $pK_a = -8$, whereas the pK_a value of the amide hydrogen ($-C(O)N^--$) falls outside the upper pH limit of this measurement ($pK_a \approx 15$) [13–15].

3.2.2. Major complex species in aqueous solution

The potentiometric titrations showed that the interaction of the ligand Hpzpy with copper(II) ions enables the extra-deprotonation of the amide group and/or coordinated water molecules (Fig. 1). For the ratio $R = 1$, the $\bar{h}$ versus pH curve displays two plateaus,
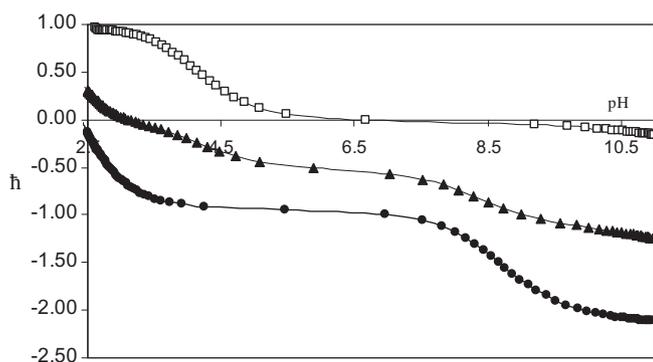

Fig. 1. Average number $\bar{h}$ of protons bound per mole of Hpzpy ligand as a function of pH: (□) ligand alone, (●) $R = 1$ and (▲) $R = 2$.

Table 2
Logarithms of equilibrium constants[a] of Hpzpy alone and Cu(II) complexes; $I = 0.1$ mol dm^{-3} (NaCl); $T = 298$ K.

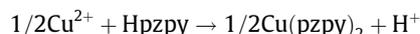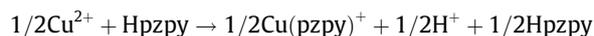|	Hpzpy	Hpzpy–Cu^{2+}
log β_{011}	4.18 (2)	
log β_{11-1}		2.43 (1)
log β_{11-2}		−6.26 (2)
log β_{12-2}		−2.74 (8)
log β_{12-3}		−13.75 (6)

[a] Values in parentheses refer to estimated standard deviations for the last significant digit.

pH 6 and 10, corresponding to $\bar{h}$ values of −1 and −2, respectively. These values correspond to the neutralization of 1 and 2 protons per copper ion. The ESI-MS analysis in the positive mode (Fig. 2) shows the main formation of 1:1 species detected as proton adduct at m/z 276.1 ($Cu + L - H$) and 294.1 ($Cu + L + H_2O - H$). Consequently, these plateaus are attributed to the formation of $[Cu(pzpy)]^+$ and $[Cu(pzpy)(OH)]$, according to the following reaction schemes:

$$Cu^{2+} + Hpzpy \rightarrow Cu(pzpy)^+ + H^+$$

$$Cu_{2+} + Hpzpy \rightarrow Cu(pzpy)(OH) + 2H^+$$
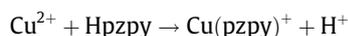
At the ratio $R = 2$, the two plateaus observed at pH 6 and 9 for a $\bar{h}$ value of −0.5 and −1 correspond to the lost of one and two protons per Cu^{2+} ion, respectively.

Two different stoichiometries (1:1 and 1:2) of copper(II) species, are detected by ESI-MS analysis as proton or potassium adduct [$m/z = 276.1$ ($Cu + L - H$), 490.2 ($Cu + 2L - H$) and 528.3 ($Cu + 2L - 2H + K$)]. These peaks are ascribed to the formation of $[Cu(pzpy)]^+$ and $[Cu(pzpy)_2]$ species according to the reaction scheme:

$$1/2Cu^{2+} + Hpzpy \rightarrow 1/2Cu(pzpy)^+ + 1/2H^+ + 1/2Hpzpy$$

$$1/2Cu^{2+} + Hpzpy \rightarrow 1/2Cu(pzpy)_2 + H^+$$

Spectrophotometric titrations of Hpzpy–Cu solutions were carried out for the ratio $R = 1$ and $R = 2$ with the same experimental conditions than those used for protometric titrations. Examination of the λ_{max} versus pH curves (Fig. 3), shows that for both ratios the 1:1 species predominate in the pH range 2–9. Above pH 9, the slight shift of λ_{max} observed for $R = 1$, seems to indicate only weak change in coordination sphere of the Cu^{2+} ion. In the case of $R = 2$, as suggested from potentiometry and ESI-MS studies, the significant increase of λ_{max} is in accordance with a significant change of geometry or coordination mode around the metal center induced by the coordination of a second ligand.

3.2.3. Equilibrium constants

Considering the whole results obtained on the Hpzpy–Cu system, the best chemical model corresponds to the formation of $[Cu(pzpy)]^+$, $[Cu(pzpy)(OH)]$, $[Cu(pzpy)_2]$ and $[Cu(pzpy)_2(OH)]^-$. Computations were monitored taking into account the soluble hydroxo species $Cu(OH)^+$ and $Cu_2(OH)_2^{2+}$. The formation constants of the hydroxo species were available in the compilation "critical stability constants [16]. The low values (Table 2) of the estimated standard deviation of the β_{mlh} constants (<0.95) are indicative of the validity of the model for the fitting procedure. These results are illustrated by the speciation curves reported in Fig. 4.

3.2.4. Metal complexes structures in aqueous solution

The refinement of the spectrophotometric titrations enabled us to deduce the electronic spectra of the main Hpzpy–Cu(II) complexes. These copper(II) species show only one single d–d transition in the visible region. The spectra of $[Cu(pzpy)]^+$ ($\lambda_{max} = 638$ nm; $\varepsilon = 99$ dm^3 mol^{-1} cm^{-1}) and $[Cu(pzpy)(OH)]$ ($\lambda_{max} = 651$ nm; $\varepsilon = 93$ dm^3 mol^{-1} cm^{-1}) are similar to that of solid complex
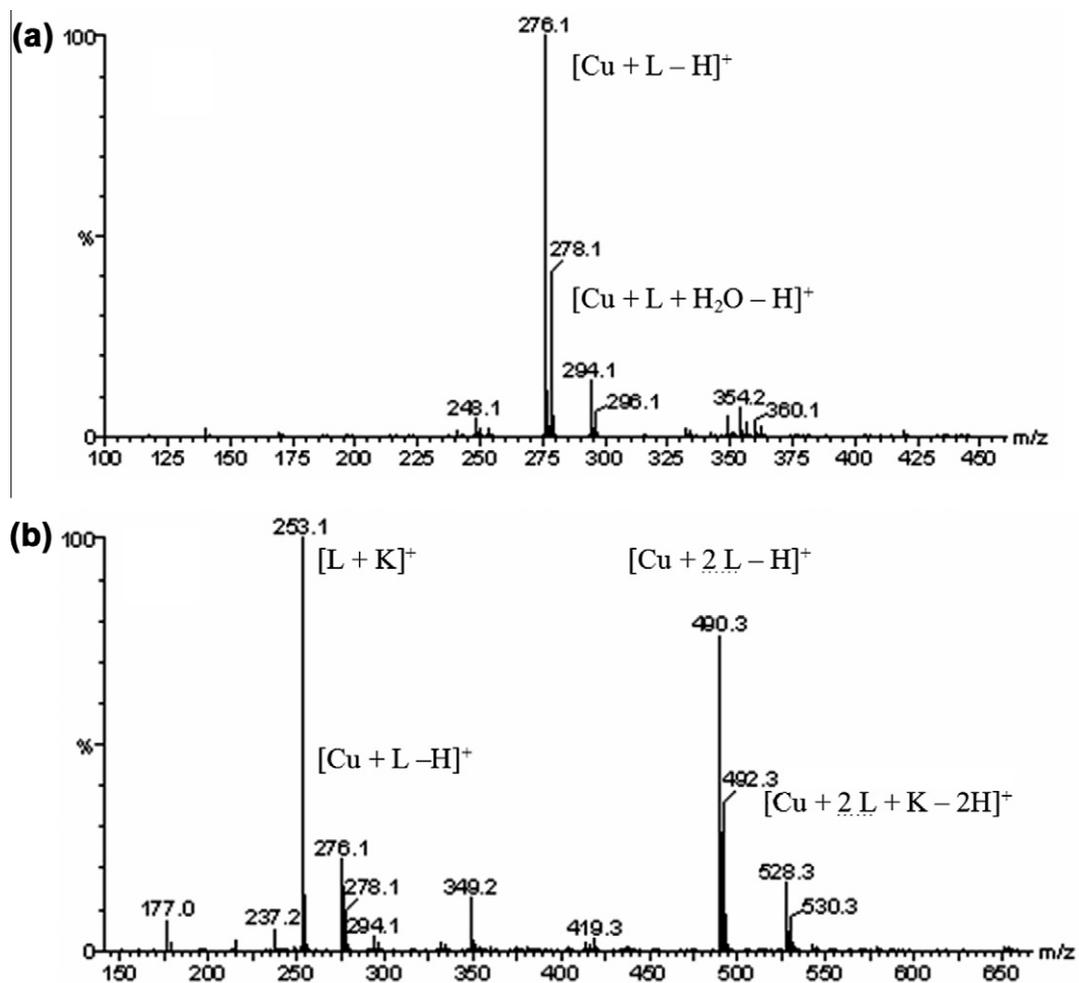
Fig. 2. Mass spectrum of a Hpzpy–copper(II) system at different ratios R. ($C_L = 1.65 \times 10^{-4}$ mol dm^{-3}): (a) $R = 1$, pH 6, in the range of $m/z = 100$–450; (b) $R = 2$, pH 10, in the range of $m/z = 150$–650.
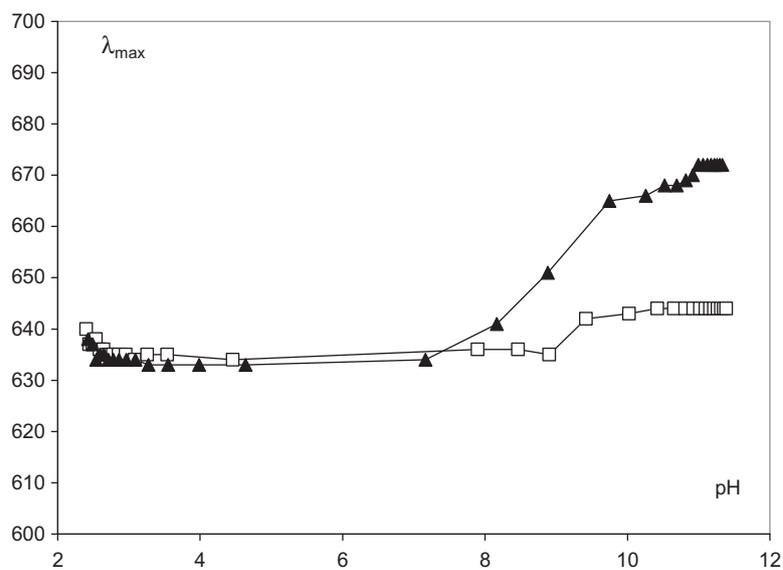

Fig. 3. Variation of λ_{max} as a function of pH for Hpzpy–Cu solutions at variable [Hpzpy]/[Cu^{2+}] ratios: (□) $R = 1$; (▲) $R = 2$.
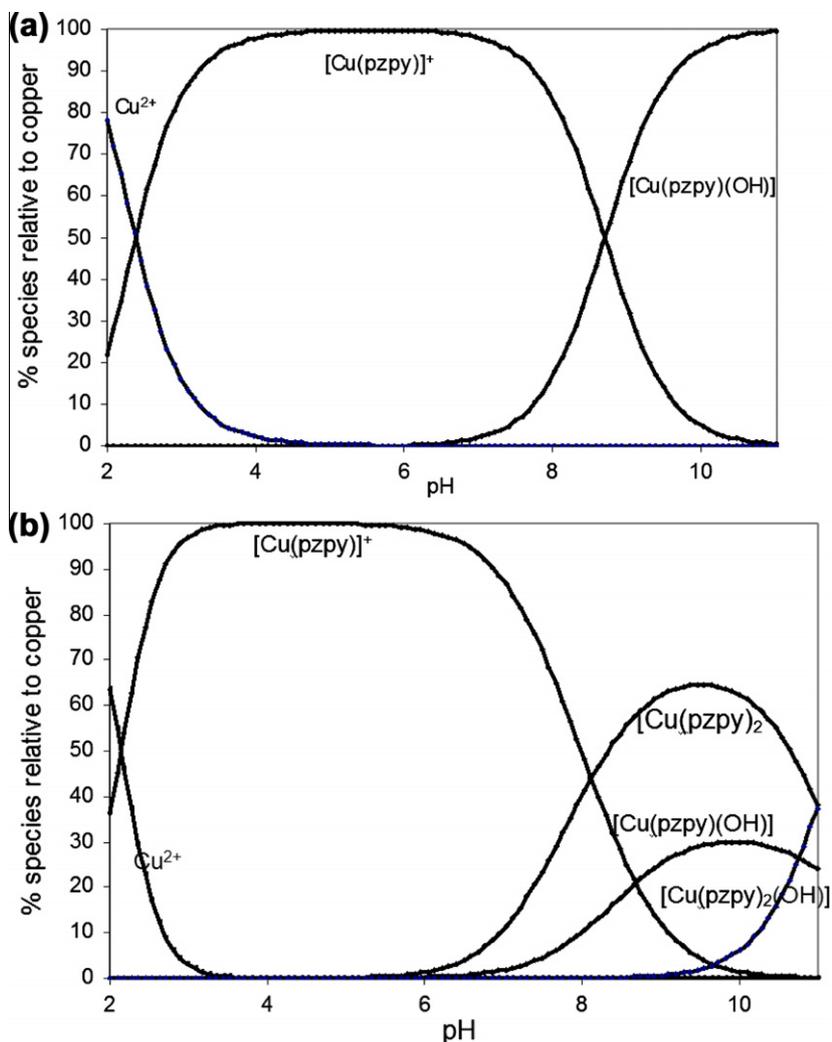
Fig. 4. Distribution curves of the Hpzpy–Cu(II) complexes. (a) $R = 1$, ($C_L = 2 \times 10^{-3}$ mol dm^{-3}, $C_M = 2 \times 10^{-3}$ mol dm^{-3}); (b) $R = 2$ ($C_L = 4 \times 10^{-3}$ mol dm^{-3}, $C_M = 2 \times 10^{-3}$ mol dm^{-3}).

[Cu(pzpy)(OAc)(OH$_2$)] described below. This suggests that the coordination mode and geometry of aqueous soluble complexes are nearly identical than those of solid compounds which are square

pyramidal. The Cu^{2+} ion could be coordinated by the nitrogen atoms of pyridyl and pyrazyl moieties and the deprotonated amidic nitrogen atom giving two five-chelate rings. The remaining two
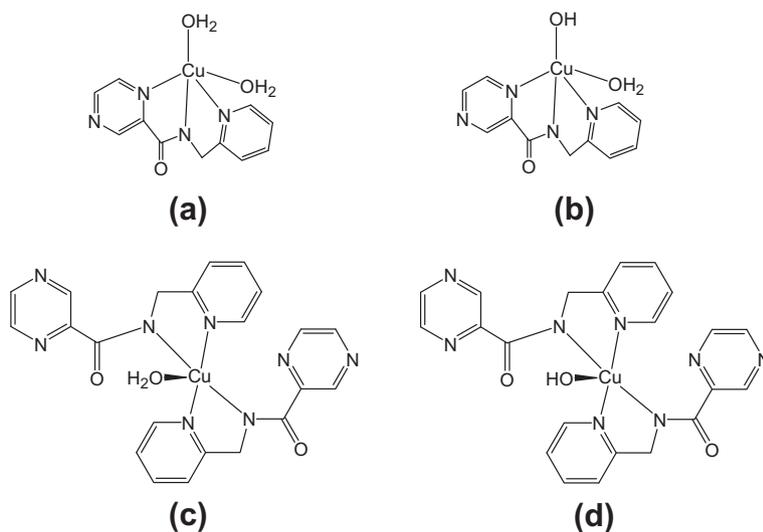
Scheme 2. Proposed structure for pzpy–Cu species.

coordination sites are occupied by the oxygen atoms of water molecules ([Cu(pzpy)(OH$_2$)$_2$]$^+$). The formation of the neutral [Cu(pzpy)] species corresponds to the deprotonation of a water molecule bound to the metallic center and should be written [Cu(pzpy)(OH)(OH$_2$)], leading for both species to CuN$_3$O$_2$ chromophore (Scheme 2a and b). The feature of the band and λ_{max} value (λ_{max} = 701 nm; ε = 85 dm^3 mol^{-1} cm^{-1})) for [Cu(pzpy)$_2$] are similar to those obtained by Vagg and co-workers [17,18] for analogous CuN$_4$O chromophores, characteristic of a square pyramidal geometry with probably four equatorial nitrogen donors (2 N$_{pyridyl}$ and 2 N$_{amido}$) and a water molecule in the apical position (Scheme 2c). The deprotonation of this water molecule should imply the formation of [Cu(pzpy)$_2$(OH)] species (Scheme 2d) detected in basic medium (pH > 9.5).

3.3. Spectroscopic studies

3.3.1. IR spectra

IR spectra of these complexes show the disappearance of the stretching frequency C=O of the ligand, confirming the deprotonation of the amide group. Small shifts to lower energies for the characteristic C=N aromatic bands at *ca.* 1610 cm^{-1}, with decreasing intensity are also observed. The azide anion in the compounds **2**, has been characterized by a very strong band at 2054 cm^{-1}; whereas in complex **3**, dicyanamide anion exhibit three bands with a strong absorption in the 2310–2170 cm^{-1} region characteristic of the $v_{s(C-N)}$ + $v_{as(C-N)}$ and $v_{(C\equiv N)}$ vibrations. The frequencies of these vibrations, in good agreement with those reported in the literature [19,20], indicate the coordination of these anions.

3.3.2. Electronic spectra

To investigate whether or not the solid state structure is retained in solution, the UV–Vis spectral behavior was investigated in solution (DMF) as well as in the solid state. The overall pattern for both spectra corresponding to each complex is closely similar. The absorption spectra for these complexes essentially exhibit similar patterns in the 250–450 nm region, with strong bands that may be due to intraligand [21] and charge transfer transitions. In the visible region, the spectra of these copper(II) complexes exhibit

Table 3
Selected bond lengths (Å) and angle (°) for complexes **1**, **2** and **3**.

[Cu(pzpy)(OH$_2$)(CH$_3$CO$_2$)] (**1**)			
Cu–N(1)	2.0429(15)	Cu–O(2)	2.2574(15)
Cu–N(3)	1.9180(15)	Cu–O(3)	1.9347(13)
Cu–N(4)	2.0193(15)		
N(1)–Cu–N(3)	80.61(6)	N(3)–Cu–O(2)	100.80(7)
N(1)–Cu–N(4)	161.56(6)	N(3)–Cu–O(3)	169.09(6)
N(1)–Cu–O(2)	94.76(6)	N(4)–Cu–O(2)	93.80(7)
N(1)–Cu–O(3)	96.42(6)	O(3)–Cu–N(4)	99.91(6)
N(3)–Cu–N(4)	81.76(6)	O(3)–Cu–O(2)	89.88(6)
[Cu(pzpy)(N$_3$)] (**2**)			
Cu–N(2)	2.0549(19)	Cu–N(4)	2.0153(19)
Cu–N(2A)	2.375(2)	Cu–N(5)	1.9510(19)
Cu–N(3)	1.9182(19)		
N(1)–Cu–N(2A)	86.78(8)	N(2A)–Cu–N(4)	100.56(7)
N(1)–Cu–N(3)	80.92(7)	N(2A)–Cu–N(5)	91.86(8)
N(1)–Cu–N(4)	161.90(7)	N(3)–Cu–N(4)	81.54(8)
N(1)–Cu–N(5)	101.19(8)	N(3)–Cu–N(5)	168.66(9)
N(2A)–Cu–N(3)	99.41(8)	N(4)–Cu–N(5)	95.16(8)
[Cu(pzpy)(N(CN)$_2$)] (**3**)			
Cu–N(1)	2.031(2)	Cu–N(5A)	1.982(2)
Cu–N(3)	1.914(2)	Cu–N(5B)	2.227(3)
Cu–N(4)	2.007(2)		
N(1)–Cu–N(3)	81.04(8)	N(3)–Cu–N(5A)	152.60(10)
N(1)–Cu–N(4)	162.53(8)	N(3)–Cu–N(5B)	113.40(10)
N(1)–Cu–N(5A)	97.46(8)	N(4)–Cu–N(5A)	97.32(9)
N(1)–Cu–N(5B)	92.57(9)	N(4)–Cu–N(5B)	95.674(9)
N(3)–Cu–N(4)	81.55(9)	N(5A)–Cu–N(5B)	93.98(10)

Table 4
Spectroscopic parameters of copper(II) complexes.

Complex	λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})	$g_{//}$	$g_{\perp}$	$10^4 A_{//}$ (cm^{-1})
1	625 (106)	2.22	2.04	182
2	590 (120)	2.18	2.06	187
3	585 (135)	2.19	2.05	190

only one single d–d transition with λ_{max} ranging between 585 and 625 nm (Table 4). These bands have a symmetrical shape with the molar extinction coefficient ε ranging between 106 and 135 dm^3 mol^{-1} cm^{-1}.

3.4. X-ray diffraction studies

The crystal structures of complexes [Cu(pzpy)(OH$_2$)(CH$_3$CO$_2$)] (**1**), [Cu(pzpy)(N$_3$)] (**2**) and [Cu(pzpy)(N(CN)$_2$)] (**3**) were determined by single crystal X-ray diffraction.

3.4.1. [Cu(pzpy)(CH$_3$CO$_2$)(OH$_2$)] (**1**)

A perspective view of the complex **1** together with the atom numbering scheme is given in Fig. 5, and selected bond distances and angles for this compounds are listed in Table 3. The structure of **1** consists of molecular compound with the formula [Cu(pzpy)(CH$_3$CO$_2$)(OH$_2$)]. The coordination polyhedron of the CuN$_3$O$_2$ chromophore has a distorted SP geometry with the structural index τ = 0.13; [τ = ($\beta - \alpha$)/60, where β is the largest *trans* angle and α the smallest one]; for perfect square pyramidal and trigonal bipyramidal geometries the value of τ is zero and unity, respectively [22]. The basal sites are occupied by three nitrogen atoms (N$_{pz}$, N$_{py}$ and N$_{amido}$ atoms of a chelating Hpzpy ligand) and one oxygen atom O$_{acetato}$ of the coordinated acetato group. The basal Cu–N/O bond lengths are in the 1.9180(15)–2.0429(15) Å range and the basal *trans* angle are 161.56(6)° and 169.09(6)°, respectively. The aqua ligand in the apical position has the longest Cu–O(2) bond distance of 2.2574(15) Å. The copper center is shifted by 0.1837 Å from the basal CuN$_3$O plane towards O(2). The crystal lattice is stabilised by hydrogen bonds of type O–H···O between hydrogen atoms of coordinated water molecule and the adjacent acceptor free oxygen atoms (O$_{amido}$ and O$_{acetato}$) belonging the two neighbouring complexes; the bond distance OH···O$_{amido}$ and OH···O$_{acetato}$ being 2.759 and 2.730 Å. These hydrogen bonds of type OH···O build up a supramolecular 2 D network (Fig. 6).
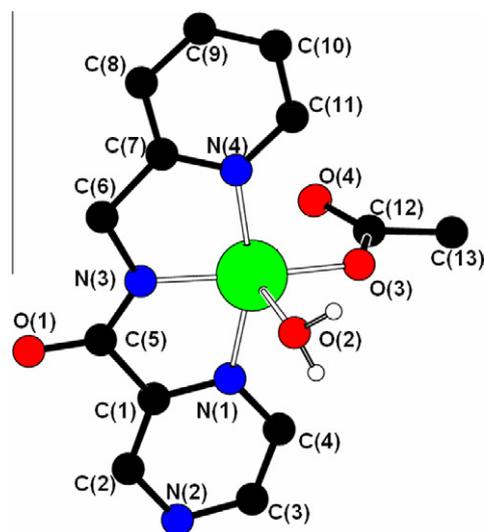

Fig. 5. A PLUTON projection of the molecular compound of **1** and the atom labelling-scheme. For clarity, only hydrogen atoms of coordinated water molecule are shown.
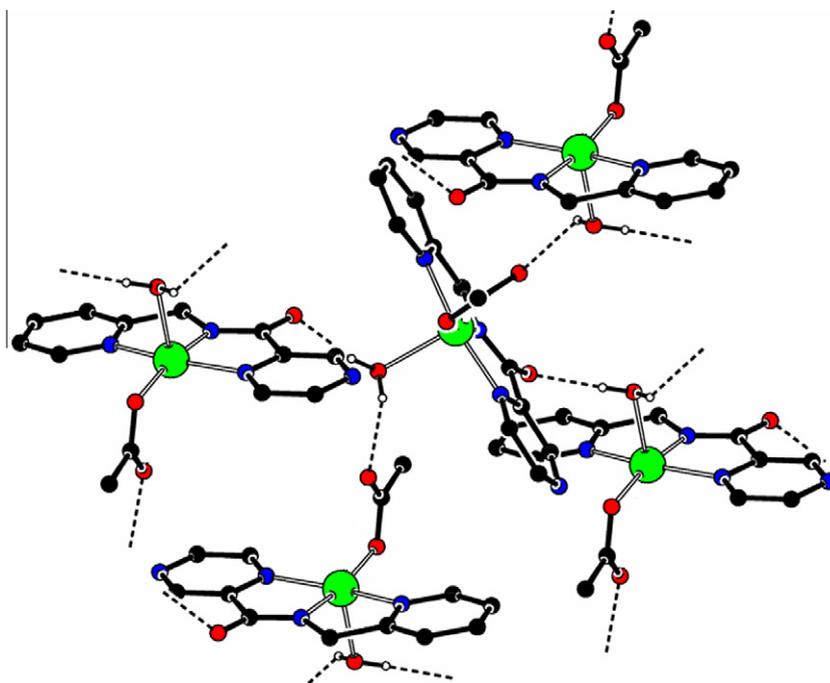
Fig. 6. Packing diagram of **1**, showing the supramolecular 2D network and the hydrogen bonding contacts; all hydrogen atoms not involved in hydrogen bonding have been omitted for clarity.

3.4.2. [Cu(pzpy)(N₃)] (2)

Atomic displacement plots with the numbering scheme for the compound **2** are given in Fig. 7, and its selected bond distances and angles are listed in Table 3.

The asymmetric unit of compounds **2** includes one [Cu(pzpy)N₃] fragment in which the copper(II) complex has a distorted square pyramidal geometry with the structural index τ of 0.11. The base of a square pyramid is formed by four nitrogen atoms from the pyrazine-2-carboxamido moiety [N(1) and N(3)], one pyridyl nitrogen [N(4)] and one nitrogen from an azide ion. The apical position is occupied by the second pyrazyl nitrogen [N(2)] of the neighbouring complex. The Cu–N$_{pyridyl}$ bond length (average, 2.011 Å) is comparable to those observed in other five coordinate complexes where Cu^{2+} ion is bound to pyridine [23–25]. The Cu–N$_{amido}$ bond length (average, 1.919 Å) is shorter than the Cu–N$_{aromatic}$, which is consistent with the stronger donor ability of
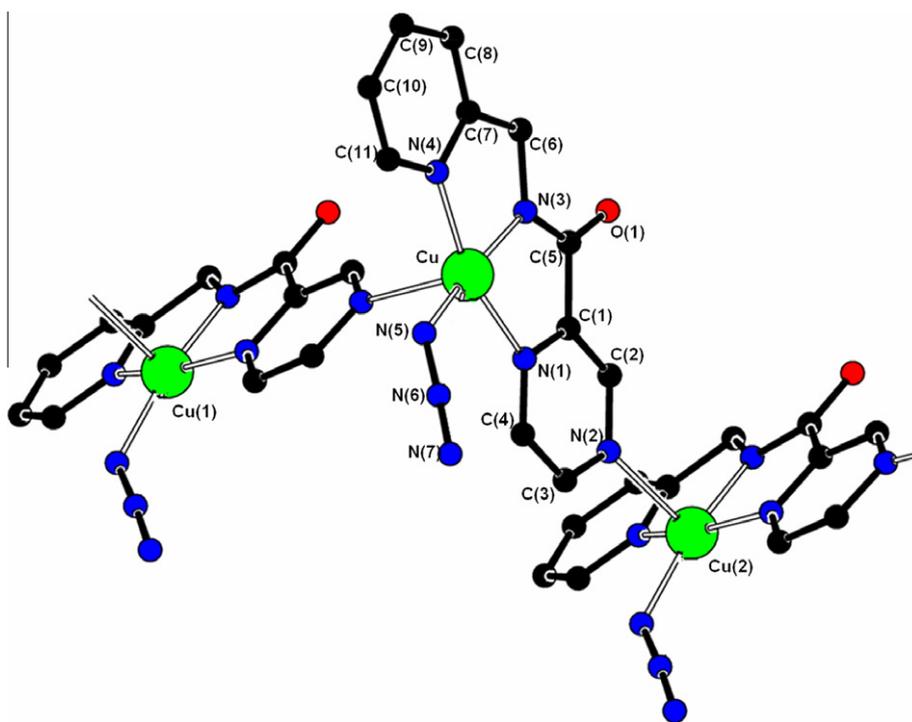

Fig. 7. A PLUTON projection of the molecular compound of **2** and the atom labelling-scheme. For clarity, hydrogen atoms are omitted.
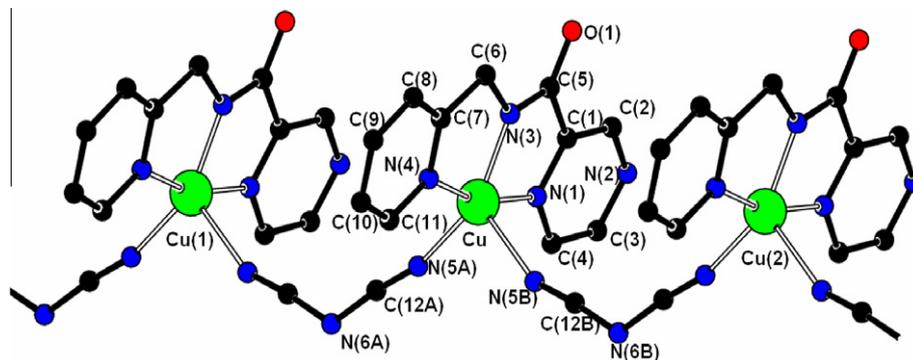
Fig. 8. A PLUTON projection of the molecular compound of **3** and the atom labelling-scheme. For clarity, hydrogen atoms are omitted.

the deprotonated amido nitrogen compared to the aromatic nitrogen [26]. This amido bond length is well within the range of Cu–N_{amido} distances noted in similar complexes [27,28]. The long apical bond Cu–N_{pz} [Cu–N(2) = 2.375(2) Å] reflects a weak axial interaction as expected for Jahn–Teller sensitive copper(II) complexes. The chelate bite angles of the two five-membered rings formed by the pyrazyl-N, the amido-N and the pyridyl-N are practically similar (average, 80.66°). The angles between the *trans* basal nitrogens [N(1)–Cu–N(4) and N(3)–Cu–N(5)], although less than the expected 180°, is in the range for SP Cu(II) complexes (155–170°) in which the Cu(II) center lies slightly above the basal plane [29,30]. In the crystalline structure, compound **2** forms one-dimensional chain of copper(II) ions via equatorial–apical bridges, giving a polymeric species with the inter-monomer Cu···Cu distance of 7.176 Å. The four equatorial coordinating atoms N_{pz}, N_{amido}, N_{py} and N_{azide} are nearly coplanar. In the polymeric species, the azide anions are oriented in the same direction (Fig. 7).

3.4.3. [Cu(pzpy)(N(CN)₂)] (**3**)

An atomic displacement plot showing the numbering scheme is given in Fig. 7 and selected bond distances and angles are given in Table 3. The geometry around the copper(II) ion is a slightly distorted square pyramidal which can be best described by the structural parameter τ of 0.17. The basal plane [with *trans* angles of 152.60(10)° and 162.53(8)°] consists of three nitrogen atoms of one Hpzpy ligand [Cu–N_{pz} = 2.031(2) Å, Cu–N_{amido} = 1.914(2) Å and Cu–N_{py} = 2.007(2) Å] and one nitrile nitrogen atom of the $\mu_{1,5}$-bridging N(CN)₂ (dca) anion [Cu–$N_{dca(A)}$ = 1.982(2) Å]. The apical position is occupied by one nitrile nitrogen atom of the second dca anion with the longest bond distance of Cu–$N_{dca(B)}$ = 2.227(3) Å. The geometry around the copper(II) ion for complexes **3** is a distorted square pyramidal. In crystalline structure, each nitrile nitrogen atom of both dca molecules are connected in an end-to-end fashion to two neighbouring Cu(II) complexes via equatorial–apical bridges, and giving in this way a 1D polymeric chain (Fig. 8) of polyhedra which is oriented along the *b*-axis of the unit cell. The inter-monomer Cu···Cu distance is 7.405 Å and the NC–N–CN angle is 121°. The donor atoms of the tridentate Hpzpy ligand N(1), N(3) and N(4) are nearly coplanar.

3.5. EPR and magnetic susceptibility studies

The EPR spectra of **1**, **2**, and **3** are obtained in frozen dimethyl-formamide and the data are summarized in Table 4. The EPR 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 [31]. A small anisotropy is also observed in the perpendicular part of the spectrum. The hyperfine coupling constant and g values are very close to those found for the

copper–bleomycin complex [32] and are in agreement with a square pyramidal coordination geometry [33] for **1**, **2**, and **3**. It has been demonstrated [28] 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: τ_{max} = 0.17; see above) and the strong in-plane ligand strength shown by UV–Vis analysis of the three compounds in dimethylformamide (λ_{max} ranging from 585 to 625 nm) is corroborated by the large $A_{//}$ values. These facts are in full agreement with the X-ray structures of these compounds and show that the structural arrangement is maintained in solution.

For two of the new compounds with potential magnetic exchange as a result of their structure, detailed variable-temperature magnetic susceptibility studies were performed. The magnetic susceptibility of the powdered samples of **2**, and **3** were measured from 5 to 300 K. The inverse susceptibility versus temperature plot shows that the curve follows the Curie–Weiss law. For these Cu(II) compounds, the μ_{eff} versus temperature plot shows hardly any changes at lower temperatures and remains constant at a value of 1.76–1.66 BM down to 5 K, which is close to the spin-only value for copper(II) (1.73 BM). Given the fact that the magnetic (d$x^2 - y^2$) orbitals of copper(II) ions within the sheet are mutually orthogonal (the 4 short Cu–N bonds are within the same planes) and that the other Cu···Cu distances are fairly large, one would not expect any significant interactions [34,35].

4. Conclusion

The protometry results reveal that only one basic group is protonated for the tridendate N_3 ligand due to the weak basic pyrazyl nitrogens and the amidic nitrogen atom present in Hpzpy. The equilibrium constants of the Cu(II) chelates with Hpzpy determined by potentiometry show the formation of [Cu(pzpy)]⁺, [Cu(pzpy)(OH)],[Cu(pzpy)₂] and [Cu(pzpy)₂(OH)]⁻ species, thus, the chelation of metal ions by the amidic nitrogen promotes an amide hydrogen ionization [36]. 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 Cu²⁺ ion for an environment with three or four nitrogen donor atoms with a coordination number of five achieved by extra water molecules or hydroxyl group.

In the solid state, the present work shows that the coordination mode of Hpzpy allows the preparation one mononuclear compound and two polynuclear "naked" pyrazine pzpy-bridged copper(II) molecular chains of formula [Cu(pzpy)Anions] with a variety of coordinating ions (azide and dicyanamide). The arrange-

ments of the chains in the crystals create supramolecular networks with channels extending in one direction through the crystals. In these polymer compounds, no magnetic exchange between copper(II) ions have been observed.

It seems to us worthwhile to get more complete picture of the factors influencing the building higher dimensionality polymers with two- or three-dimensional framework structures by studying the chelating effect of other metal ions with more than one unpaired electron to check the efficiency of both σ and π pathways. Further work along this line is in progress.

Acknowledgements

Appendix A. Supplementary material

CCDC 786207, 786208 and 786210 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.11.016.

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