Scientific paper

Spectroscopic, Potentiometric and Quantum-Mechanical Studies of S-(-)-Nicotine Complexes with Cu(II) Ion

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Abstract

Copper(II)-nicotine complexes with chelating perchlorate, nitrate, acetate and formate ligands have been synthesized and characterized in solid state by elemental analysis and FT-IR spectroscopy. Coordination of Cu(II) by nicotine molecule has been also studied in water solution of various pH by potentiometry and spectroscopic (VIS, EPR and NMR) methods. Furthermore, quantum-mechanical calculations helped elucidate the experimental data as they provided some information on the energetic of the possible interaction modes of Cu(II) with nicotine. The studies showed that nicotine acts as a monodentate ligand utilizing for this purpose the pyridine nitrogen atom. In the Cu(II)/Nicotine system the MHL and ML type complexes were formed in 1:1 metal:ligand ratio.

Keywords: Nicotine, Cu(II) complexes, potentiometry, spectroscopic methods, quantum-mechanical calculations

1. Introduction

(*S*)-(-)-Nicotine, 3-[(2*S*)-1-methylpyrrolidin-2-yl] pyridine, (**1**) (Fig. 1) has a long history of being produced and used by humans for pharmacological purposes because of its numerous biological properties. Nicotine and its derivatives act as nicotinic acetylcholine or cholinergic agonists modulating neuroendocrine functions to effect cognition, attention, and memory by binding to acetylcholine receptors located throughout the brain. The structure of nicotine has unique functionality. It contains both a pyridine and a pyrrolidine rings connected by a chiral center. Both of the rings contain nucleophillic nitrogen atoms, which act competitively when reacted with electrophiles. Important aspect of nicotine reactivity is its metal complexation. It is known that some metal complexes can modulate biological activity of organic ligands.[1–3] Metal coordination complexes of biological molecules have much potential for design of novel therapeutic and diagnostic agents that target specific properties and show reduced side effects, avoidance of resistance, improved selectivity and can be used for treating a wide range of important human diseases. Several metal complexes of nicotine with a variety of metals have been prepared for different applications,[4–8] e.g. for pharmaceutical use as caged nicotine[9] or for their antibacterial sensitivity against different microorganisms.[10–12]

Additional challenges are the possibility to better understand the mechanism of action of the small molecules, further evaluation and modulation of the chemical composition and reactivity, and even the development or improvements in the methods for detection of biological activity. Of particular importance in the field of synthetic and biological chemistry are copper(II) complexes because of the role this element plays in biological systems.[13–15] The interaction of Cu(II) cation with drugs is a subject of considerable interest.

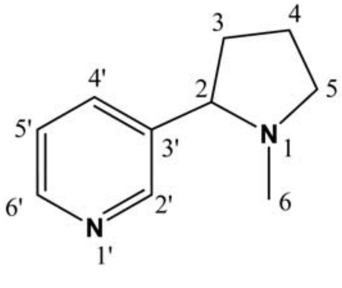

Figure 1. Atom numbering in nicotine.

For example nicotine was reported to form molecular complexes with copper(II) chloride and bromide.[15] Published results were not always in agreement, but a simple stoichiometry, CuX_2/nicotine, could be assumed. Thus the elucidation of the structure of a representative sample became a matter of interest.

Herein we report the synthesis, potentiometric, spectroscopic and quantum-mechanical study of nicotine complexes with Cu(II) ion.

2. Experimental

2. 1. Synthesis

(-)-Nicotine and copper(II) salts were commercial products of Aldrich.

New complexes **2**–**5** were prepared by mixing methanolic solutions of CuX_2 salt (where X = ClO_4,NO_3, CH_3COO, HCOO) and of the alkaloid in 1:1 stoichiometric milimolar quantities. The precipitates settled out immediately or after several minutes. Complexes were recrystallized from ethanol.

$[(C_{10}H_{14}N_2)Cu(ClO_4)_2(H_2O)_3]$ (**2**)

Blue crystals. M.p. 202–204 °C. Yield: 85%. Anal. Calcd. for $C_{10}H_{20}N_2CuO_{11}Cl_2$: C: 25.10; H: 4.18; N: 5.86. Found: C: 25.14; H: 4.21; N: 5.67%.

$[(C_{10}H_{14}N_2)Cu(NO_3)_2(H_2O)_3]$ (**3**)

Blue crystals. M.p. 172–174 °C. Yield: 86%. Anal. Calcd. for $C_{10}H_{20}N_4CuO_9$: C: 29.70; H: 4.95; N: 13.86. Found: C: 29.81; H: 4.84; N: 13.76%.

$[(C_{10}H_{14}N_2)Cu(CH_3COO)_2(H_2O)_2]$ (**4**)

Green crystals. M.p. 149–151 °C. Yield: 92%. Anal. Calcd. for $C_{14}H_{24}N_2CuO_6$: C: 44.21; H: 6.32; N: 7.37. Found: C: 44.61; H: 6.29; N: 7.26%.

$[(C_{10}H_{14}N_2)Cu(HCOO)_2(H_2O)_3]$ (**5**)

Green crystals. M.p. > 220 °C. Yield: 64%. Anal. Calcd. for $C_{12}H_{22}N_2CuO_7$: C: 38.92; H: 5.95; N: 7.57. Found: C: 39.03; H: 5.87; N: 7.63%.

Melting points were determined on Melt-Temp II apparatus (Laboratory Devices Inc.) Elemental analysis was carried out by means of a Perkin-Elmer 2400 CHN automatic device.

2. 2. Equilibrium Study

The potentiometric measurements were carried out using Titrino 702 Metrohm equipped with an auto-burette with a combined glass electrode – Metrohm 6.233.100. Prior to each series of measurements, the pH-meter indication was corrected with the help of two standard buffer solutions of pH 4.002 and pH 9.225 and electrode was calibrated in terms of H^+ concentration.[16] All potentiometric titrations were made under helium atmosphere, at the constant ionic strength of $\mu = 0.1$ M (KNO_3), temperature 20±1 °C (titration dish placed in thermostatic bath set at this temperature), in the pH range from 2.5 to 7.5 using as a titrant CO_2-free NaOH at a concentration of 0.231 M. Above pH 7.5 value a precipitate appeared. The concentration of nicotine in systems was $2 \cdot 10^{-3}$ mol · dm^{-3} and the metal to ligand ratios used were 2:1, 1:1 and 1:2. The selection of the model and the determination of the stability constants of the complexes were made using the HYPERQUAD program which uses the nonlinear method of least squares.[17] The determined ionic product of water was $pK_w = 13.89$. The calculations were performed using 150–200 points for each job, taking into account only this part of titration curves that corresponded to the conditions in which no precipitate appeared in the solutions. The hydrolysis constant for copper(II) ion was taken from our previous publication.[18] The model assumed was verified by analysis of the standard deviations, the convergence of the experimental data with those obtained for the model was evaluated by the Hamilton test and chi squared test.[19] The distributions of particular species were obtained by the HALTAFALL program.[20]

2. 3. UV-vis, IR, NMR and EPR Spectroscopy

UV-Vis spectra were taken on a UV-Vis Evolution 300 ThermoFisher Scientific spectrometer equipped with a xenon lamp (range 450–950 nm, accuracy 0.2 nm, sweep rate 120 nm/min) for the same ligand concentrations as in the samples for potentiometric titrations, at the metal:ligand ratio 1:1 and 1:2 in the systems. The infrared (IR) spectra were recorded by means of a FT-IR Bruker 113v spectrometer (KBr pellets). The samples for NMR study were prepared by dissolving nicotine and $Cu(NO_3)_2$ in D_2O and adjusting pH with addition of NaOD or DCl. The pH values were corrected according to the formula pD = pH-meter readings + 0.4.[21] The concentration of the ligand in the systems was 0.01 mol · dm^{-3} and the ratio of Cu(II) to ligand was 1:100. The ^{13}C and ^{1}H NMR spectra were recorded on an NMR Gemini 300 VT Varian Spectrometer using dioxane as internal standard. The signal positions were given on the TMS (tetramethylsilane) scale. EPR spectra were recorded at 77 K, in a water–glycol solution (3:3, v/v) on a Radiopan SE/X 2547 spectrometer ($c_{Cu2+} = 1 \cdot 10^{-3}$ mol · dm^{-3} or $5 \cdot 10^{-3}$ mol · dm^{-3}).

2. 4. Quantum-mechanical Calculations

The density functional theory calculations with full geometry optimization at M06/SDD level were carried out. We selected M06 functional as it was parameterized including both transition metals and non-metals, and is recommended for application in organometallic and inorganometallic chemistry and for noncovalent interactions.[22] Due to the presence of copper atom we used SDD basis set which includes Stuttgart/Dresden pseudopotentials.[23] To account for aqueous solvation we included there explicit water molecules to suffice coordination sphere of Cu(II)cation and employed the usual Polarizable Continuum Model (PCM).[24]

3. Results and Discussion

The results show that all complexes synthesized in solid state exhibit the 1:1 stoichiometry, as shown by the results of elementary analysis. The stretching vibration of the C=N of the pyridine ring appears at around 1590 cm^{-1}, and on complexation a shift to higher frequencies is observed. In the present examples this shift (to about 1607 cm^{-1}) may suggest bond formation by the metal atom to the pyridine ring nitrogen atoms, thereby increasing the dipolar contribution of $C{=}N^+$ in the heterocyclic ring. Of particular interest is the assignment of metal-ligand stretching absorptions below 500 cm^{-1}. The occurrence of the absorption bands in the 410–450 cm^{-1} region have been assigned to ν(Cu-N) modes.

According to Lewis and co-workers[25] the only infrared-active bands in the spectrum of an uncoordinated perchlorate are the modes found in the regions near 1100 and 620 cm^{-1}. In unidentate and bidentate perchlorate, each of these modes is split into another infrared-active mode. In the IR spectra of **2** there is considerable broadening and splitting in the region centered around 1100 cm^{-1}, with at least two peaks at 1110 and 1190 cm^{-1} ascribable to the perchlorate group. Examination of the region of the spectrum between 600 and 700 cm^{-1} shows bands at 605 and 625 cm^{-1}. This observation indicates monodentate coordination of perchlorate group and confirms the presence of a significant interaction between the ClO_4^- group and the cation, but does not allow us to distinguish between the various possible types of such interactions. In a nitrato complex, the nitrate group may be present as a free ion, or as a coordinated ligand, bound in a monodentate or bidentate or intermediate fashion or may be bridging. Moreover, in complexes containing several nitrate groups, more than one coordination mode may be present. Nitrate complexes are known to give rise to combination frequencies near 1750 and near 2400 cm^{-1}.[26] The bands near 1750 cm^{-1} are generally clearly defined and often relatively strong, whilst those near 2400 cm^{-1} are weaker. So, useful information can be derived from consideration of the combination bands exhibited by nitrato complexes in the 1700–1800 cm^{-1} region. The magnitude of the splitting depends on the metal-nitrate interaction and is generally larger for bidentate than for monodentate coordination. The separation for the monodentate nitrate group lies in the range 5–26 cm^{-1} whilst for the bidentate complexes it is 20–66 cm^{-1}. For complex **3** this separation takes the value 20 cm^{-1}. Moreover, in **3** a splitting of $\nu(NO_3^-)$ was observed at 1380 and 1290 cm^{-1}. The magnitude of the separation of these bands was ca. 100 cm^{-1} and is consistent with the monodentate nature of the coordinated NO_3^- ions.[27–29]

The metal acetates are very interesting compounds due to their coordination possibility through the carboxylate group. The carboxylate group can show monodentate, bidentate or bridge type coordination. The most widely studied metal acetates are those of Zn(II) dehydrate and Cu(II) monohydrate. The binding in metal carboxylates has often been distinguished by their IR spectra. The acetate ion has symmetric stretching frequency $\nu_s(COO^-)$ and asymmetric stretching frequency $\nu_a(COO^-)$ modes at ~1450 and 1570 cm^{-1}, respectively. According to Deacon and Philips,[30] the monodentate acetato complexes exhibit Δ values $[\nu_a(COO^-) - \nu_s(COO^-)]$ which are greater than for ionic complexes. Bidentate complexes exhibit Δ values which are significantly less than the ionic values. The Δ value for ionic acetate is 164 cm^{-1}.[31] For complex studied, the Δ value is 145 cm^{-1} [$\nu_a(COO^-)$ at 1580 cm^{-1}, and $\nu_s(COO^-)$ at 1435 cm^{-1}]. This small separation indicates bidentate coordination.

The frequencies ν_s(COO) and ν_a(COO) of the symmetric and antisymmetric O–C–O stretching modes of the coordinated formate ion in **5** are assigned at 1356 and 1637 cm^{-1}, respectively. Values of $\Delta\nu$ between ν_a(COO) and ν_s(COO) for **5** is higher than that found in the free formate, taken as those for the sodium (Δ = 241 cm^{-1})[32] or potassium (Δ = 233 cm^{-1})[33] salts. Thus, we state that carboxylate groups in these complexes are probably monodentate. The presence of water molecules in isolated complexes is shown by a strong and broad band in the region 3400–3200 cm^{-1}.

Computer analysis of the results of potentiometric measurements data for the system Cu(II)/nicotine confirmed the occurrence of CuH(nicotine) and Cu(nicotine) complexes with overall stability constants (logβ) 11.50 and 6.75, respectively (Table 1). For all metal to ligand ratio (Cu(II):nicotine, 2:1, 1:1 and 1:2), in the tested pH range, CuH(nicotine) and Cu(nicotine) forms were found.

CuH(nicotine)species binds about 50% of copper ions at pH about 4.0 and occurs in the system to pH about 6.5, see Fig. 2. The equilibrium constant for CuH(nicotine) complex formation Cu + H(nicotine) $\rightleftarrows$ CuH(nicotine) calculated according to the formula: $\log K_{\mathrm{CuH(nicotine)}} = \log\beta_{\mathrm{CuH(nicotine)}} - \log\beta_{\mathrm{Hnicotine}}$ takes the value 3.20. The protonation constants values of nicotine calculated in this study are in good agreement with those reported in the li-

Table 1 Overall stability constants (logβ) of Cu(II) complexes of nicotine and spectral data (Vis and EPR) and modes of coordinations in the complexes studied.

Species	pH	logβ	$\lambda_{\max}$ [nm]	$g_\parallel$	$A_\parallel$ [10^{-4} cm^{-1}]	Chromophore
CuH(nicotine)	3.8	11.50(4)	795	2.31	168.8	{1N}
Cu(nicotine)	6.0	6.75(3)	728	2.30	175.6	{1N}

terature and equal: H-nicotine = 8.30(1) and H_2-nicotine = 11.70(1).[34] The first one corresponds to proton attachment to pyrrolidine ring, the second to protonation of the pyridine ring.[34,35] Thus, in CuH(nicotine) complex the nitrogen atom of pyridine ring (N1') is involved in the formation of complex and the pyrrolidine nitrogen atom (N1) is protonated. Cu(nicotine) species start to form at pH ~3.0 and dominates in the system from pH ~ 5.0 (Figure 2). Equilibrium constant for such type of coordination $\log K_{\mathrm{Cu/nicotine}} = \log \beta_{\mathrm{Cu/nicotine}}$ is 6.75 (Table 1).

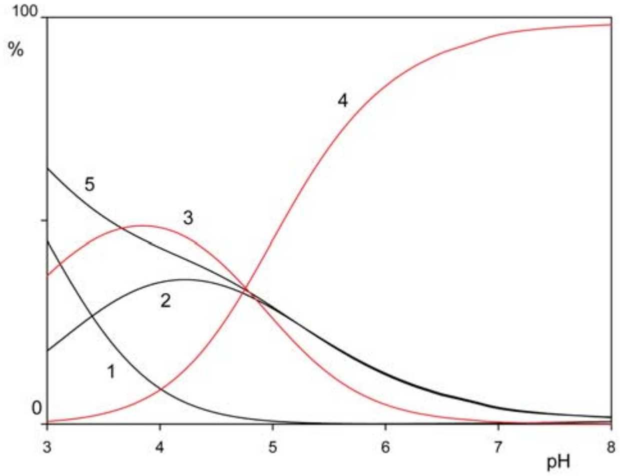

Figure 2. Distribution diagram for the Cu/nicotine system; the percentage of the species refers to total nicotine:1-H_2nicotine, 2–Hnicotine, the percentage of the species refers to total metal: 3–CuH(nicotine), 4–Cu(nicotine), 5–Cu^{2+}; $C_{Cu2+} = 210^{-3}$ M; $C_{nicotine} = 210^{-3}$ M.

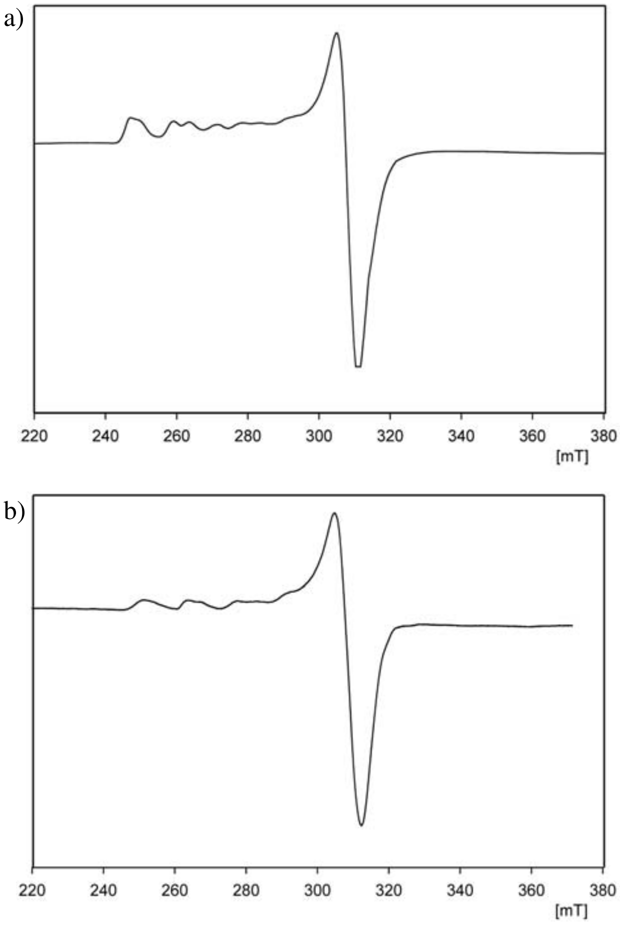

Figure 3. EPR spectra of Cu(II)/nicotine system (ratio 1:1) at pH = 3.5 (**3a**) and 6.0 (**3b**) (apart of signal of the complex the Cu^{2+} signal exists).

The protonation constant of CuH(nicotine) complex: Cu(nicotine) + $H^+ \rightarrow$ CuH(nicotine) calculated according to the formula: $\log K_{\mathrm{CuH(nicotine)}}{}^{\mathrm{H}} \rightleftarrows \log \beta_{\mathrm{CuH(nicotine)}} - \log \beta_{\mathrm{Cu(nicotine)}}$ takes the value 4.75. The lower value of $\log K_{\mathrm{CuH/nicotine}}{}^{\mathrm{H}}$ compared with the value of first protonation constant of nicotine (8.30) reflects the influence of copper ions on the proton liability in the ligand. The EPR, Vis and NMR spectral data suggest that in both types of Cu-nicotine complexes, the same type of coordination is present. The spectral parameters $g_{\|}$ and $\lambda_{\max}$ for CuH(nicotine) and Cu(nicotine) complexes ($g_{\|}$2.31 and 2.30, $\lambda_{\max}$ 795 and 728 nm, respectively, Table 1, Figures. 3a and 3b, indicate type of coordination (one nitrogen atom for both CuH/nicotine and Cu/nicotine species).[36,37] As follows from the distribution form (Figure 2) in a pH range in which the complex CuH/nicotine is dominant, about 50% copper ions in solution are uncomplexed. The presence of copper ions in two different forms is supported by EPR methods. At pH = 3.5 apart from the signal corresponding to the CuH/nicotine species, signal for Cu(II) aqua ion is also identified (Figure 3).

Similarly the results from quantum-mechanical calculations suggest that nicotine acts as a monodentate ligand utilizing for this purpose the pyridine nitrogen atom rather than the pyrrolidine one. However, the energy difference favoring Cu(II) coordination mode by the pyridine nitrogen atom over pyrrolidine one was quite small, about 1.5 kcal/mol. All efforts to obtain nicotine acting as bidentate ligand failed leading to the monodentate nicotine structure most likely because the relative orientation of nitrogen atoms in nicotine molecule is such that only significant strain on nicotine molecule might force it to chelate metal cations. In the case of the protonated nicotine the energy difference favoring Cu(II) coordination mode by the pyridine nitrogen atom was larger, of about 10 kcal/mol suggesting that proton attachment to the pyrrolidine ring nitrogen is preferred also in the case of CuH(nicotine) complex. Moreover in the case of the lowest energy structure of the Cu(II)-protonated nicotine complex one of the nitrate anions forms strong hydrogen bonding with the protonated nitrogen atom. The donor-acceptor distance is 2.661 Å, proton-acceptor distance 1.674 Å, and donor-proton-acceptor angle 164.8°. As the protonated nitrogen center bears formal positive charge while nitrate anion has formal negative charge the values of these para-

Table 2 Selected geometrical parameters in Å for the Cu(nicotine) and CuH(nicotine) complexes

	Protonated nicotine		**Nicotine**	
	N-pyridine	**N-pyrrolidine**	**N-pyridine**	**N-pyrrolidine**
Cu–N(nicotine)	1.964	2.053	1.936	2.025
Cu–O(NO_3)	2.338	2.115	2.136	2.147
Cu–O(NO_3)	1.974	2.216	2.185	2.660
Cu–O(H_2O)	2.164	2.001	1.993	1.977
Cu–O(H_2O)	2.134	2.180	2.186	2.081
Cu–O(H_2O)	2.059	2.192	2.193	1.977

meters characteristic for very strong hydrogen bonding are of no surprise. The attraction of one nitrate anion by the protonated nitrogen center shifts this nitrate anion away from the Cu(II) center, thus the other nitrate anion uses its both oxygen atoms to coordinate Cu(II) cation in bidentate mode. The Table 2 presents selected structural parameters for the modeled complexes. The optimized structures are presented in Figure 4. The Cu–N(pyridine) distances are 1.936 Å and 1.964 Å for the nicotine and protonated nicotine, respectively. In energetically less favored interaction mode between Cu and N-pyrrolidine atom the Cu–N distances are slightly larger 2.025 Å and 2.053 Å for the nicotine and protonated nicotine, respectively. The distance between Cu(II) center and oxygen ligands (nitrate anion and water molecule) were in the range from 1.974 Å to 2.660 Å. In all the cases the calculated spin densities on Cu atom were larger than 0.7 suggesting strong localization of unpaired electron on Cu center.

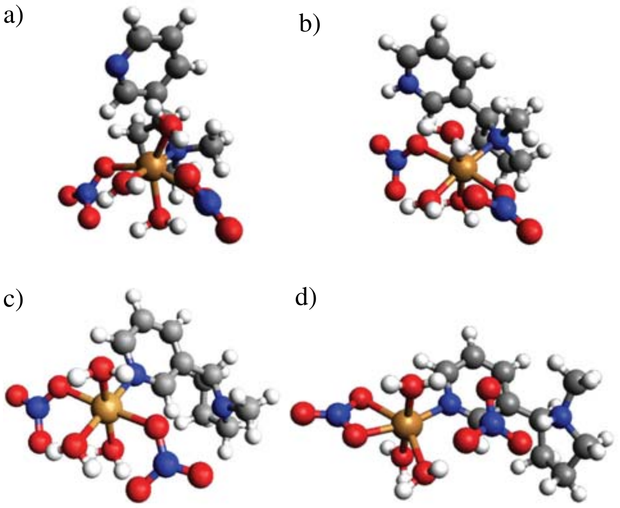

Figure 4. The optimized structures of the modeled nicotine complexes: Cu(nicotine) N-pyrrolidine coordination mode (**a**), CuH(nicotine) N-pyrrolidine coordination mode (**b**), Cu(nicotine) N-pyridine coordination mode (**c**) and CuH(nicotine) N-pyridine coordination mode (**d**). The studied complex **3** corresponds most likely to the structure (**c**).

Analysis of ^{13}C NMR spectra of Cu(II)/nicotine system and free isolated ligand indicates the coordination through the nitrogen atom N1' in both types of complexes. The ^{13}C NMR spectrum of the complex recorded at the pH of the CuH(nicotine) complex domination (pH = 3.8) showed changes in the chemical shifts of carbon atoms C6', C2' and C3' by 0.64 ppm, 0.66 ppm and 0.58 ppm, respectively (Figure 5a, Table 3). Relatively small changes in the chemical shift of the carbon atoms in the direct neighborhood of the nitrogen atom N1 (C2, C5 and C6: 0.39 ppm, 0.01 ppm and 0.01ppm, respectively) indicate that nitrogen atom N1 is excluded from involvement in the formation of complexes. The copper ion is coordinated only by pyridine nitrogen atom which is the main coordination center. Analogously as for the system discussed above, also the ^{13}C NMR spectrum of the complex Cu(nicotine), recorded at the pH = 6.0 (Figure 5b), reveal significant changes in the chemical shifts for C6', C2' and C3', by 0.71 ppm, 0.61 ppm and 0.51ppm, respectively and insignificant shifts of the signals assigned to carbon atoms C2, C5 and C6 from the neighborhood of nitrogen atom N1, by 0.34 ppm, 0.05 ppm and 0.01 ppm, respectively (Table 3). Due to the size of the copper(II) ion and distance between nitrogen atoms in the nicotine molecule con-

Table 3. The ^{13}C NMR signal positions of the nicotine ligand in the the Cu(II)/nicotine system and their differences in relation to the metal-free system [ppm].

	pH	**C2'**	**C3'**	**C4'**	**C5'**	**C6'**	**C5**	**C4**	**C3**	**C2**	**C6**
Nicotine		149.53	138.21	129.55	125.60	148.23	56.17	21.47	30.36	69.97	38.31
CuH(Nicotine)	3.8	148.87	137.63	129.40	125.40	157.59	56.18	21.49	30.43	70.36	38.30
Δδ		**0.66**	**0.58**	**0.15**	**0.20**	**0.64**	**–0.01**	**–0.02**	**–0.07**	**–0.39**	**0.01**
Nicotine		151.23	138.08	129.74	125.76	149.92	56.86	22.29	30.91	70.70	38.96
Cu(Nicotine)	6.0	150.58	137.57	129.54	125.51	149.21	56.91	22.23	31.02	71.04	38.97
Δδ		**0.65**	**0.51**	**0.20**	**0.25**	**0.71**	**–0.05**	**0.06**	**–0.11**	**0.34**	**–0.01**

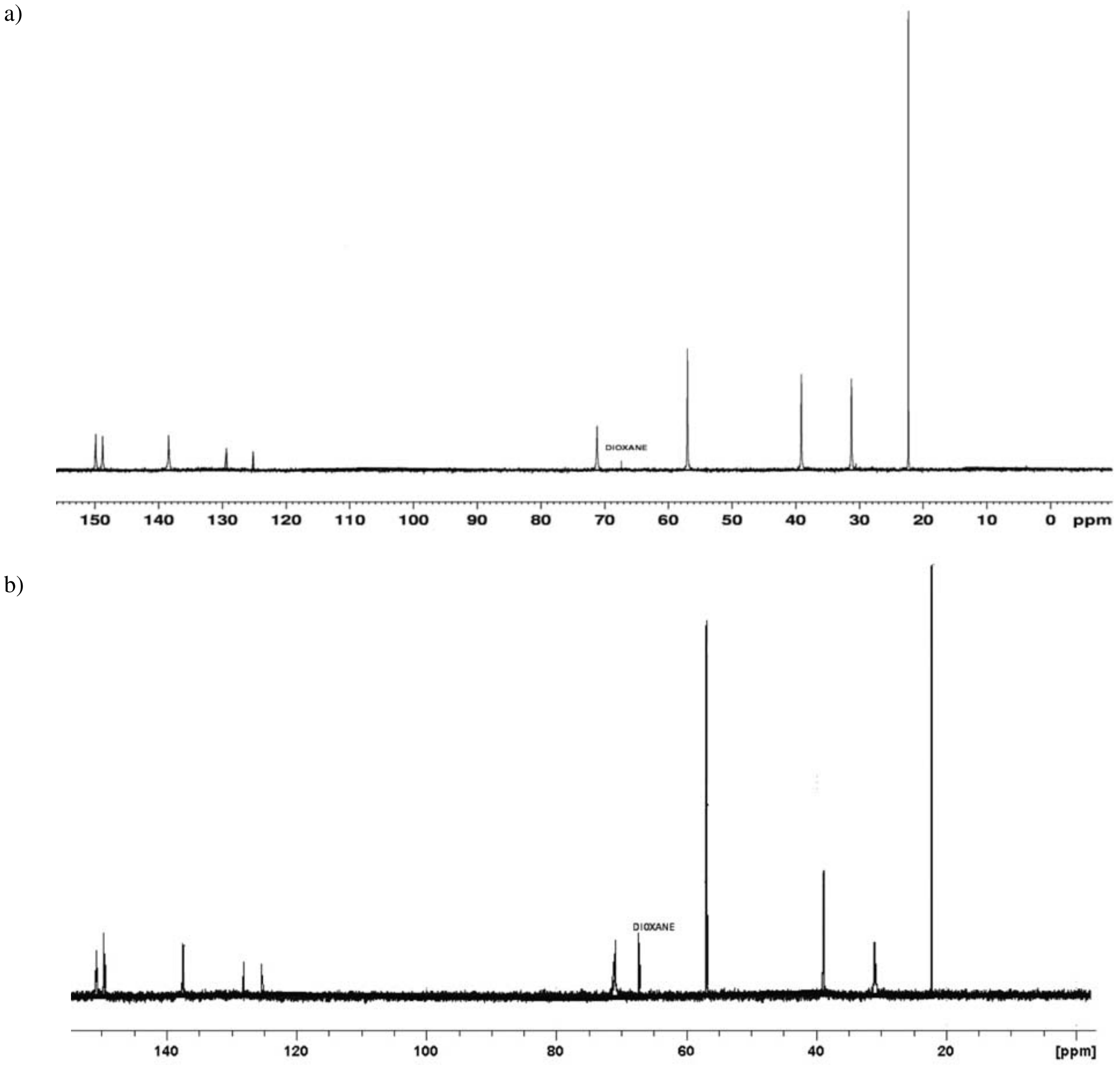

Figure 5. The ^{13}C NMR spectra of Cu(II)/nicotine system at pH = 3.8 (A) and at pH = 6.0 (B).

tribution of both donor nitrogen atoms of nicotine in coordination is impossible. The lack of coordination dichotomy (formation of isomeric Cu(nicotine) complexes with coordinated pyridine or pyrrolidine nitrogen atoms) can be explain by the presence of methyl group at nitrogen atom N1.

^{1}H NMR spectra of complexes show large shifts, when they are compared with free nicotine, for the H6' and H2' protons of aromatic pyridine ring which move downfield at about +0.60 and +0.80 ppm, for H2' and H6' respectively.

Taking into regard the limitations in the use of NMR in investigation of paramagnetic ions, the NMR spectra of the species were recorded by the decoupling technique at low concentrations of the metal ions. The pH ranges of the complex dominance in the distribution diagram of the species are practically the same as for systems of higher concentrations of the metal ions and the ligand. Significant changes in the chemical shifts were observed only in the pH ranges in which the occurrence of the complexes was deduced on the basis of the potentiometric measurements. The results were also carefully verified with the equilibrium data and electronic spectra observations. The NMR method has been earlier applied to the study of similar systems.[39–43]

Lower log*K* (equilibrium constant) value for Cu-H(nicotine) complex than that for Cu(nicotine) species (3.30 and 6.75, respectively) can be interpreted as a result of deprotonation of nitrogen atom N1 and, consequently, greater efficiency of pyridine nitrogen atom in Cu(nicotine) complex than in protonation form.

4. Conclusion

The nicotine molecule is found to coordinate exclusively *via* its pyridine N atom, both in solid state and in solution. In solution Cu(nicotine) and CuH(nicotine) species are present. Cu(nicotine) species start to form at pH ~3.0 and dominates in the system from pH ~5.0. CuH(nicotine)species binds about 50% of copper ions at pH about 4.0 and occurs in the system to pH about 6.5. The presence of these two different complexes is supported by EPR methods. Quantum-mechanical calculation has shown that the arrangement of the Cu(II) cation in Cu(nicotine) and CuH(nicotine) complexes is different, which is manifested in UV measurements (λ_{max}= 728 and 795 nm, respectively). The energy difference favouring Cu(II) coordination mode by the pyridine nitrogen atom over pyrrolidine one in Cu(nicotine) complex was quite small about 1.5 kcal/mol, but in the case of the protonated nicotine the energy difference favouring Cu(II) coordination mode by the pyridine nitrogen atom was larger, of about 10 kcal/mol, suggesting that proton attachment to the pyrrolidine ring nitrogen is preferred also in the case of CuH(nicotine) complex.

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Povzetek

Baker(II)-nikotin kompleksi s kelatnimi perklorato, nitrato, acetato in metanoato ligandi so bili sintetizirani in okarakterizirani v trdnem stanju z elementno analizo in FT-IR spektroskopijo. Koordinacija Cu(II) z molekulo nikotina je bila proučevana v vodnih raztopinah različnih pH vrednosti s potenciometričnimi in spektroskopskimi (VIS, EPR in NMR) metodami. Nadalje, kvantno-mehanski računi so pomagali razložiti ekperimentalna opažanja, saj lahko s pomočjo podatkov o energijah pridemo do informacij o možnih interakcijah Cu(II) z nikotinom. Študije so pokazale, da je nikotin monodentatni ligand, ki je vezan na bakrov ion preko piridinskega dušikovega atoma. V sistemu Cu(II)/nikot z množinskim razmerjem kovina:ligand 1:1so prisotni MHL in ML kompleksi.