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Some Copper(II)-Aminopyridine Complexes in Non-Aqueous Solvents

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Abstract

In the present work the complex formation equilibria in some non-aqueous solvents between copper(II) and 2-aminopyridine or two halide-substituted aminopyridines was investigated. The study was carried out by visible spectrophotometry and flow-microcalorimetry.

We characterized these complexes by their proper parameters as concentration quotients at the equilibrium, molar absorptivities and enthalpy values.

Introduction

In the study of complex equilibria the solvent can strongly influence the distribution and the stability of the species because of its donor, acceptor and dielectric properties. These parameters influence the solvation and ionization of metal, ligand and complex species, as well as the ion pair formation [1–3].

In the present work the complex formation between copper(II) perchlorate and 2-aminopyridine* or 2-amino-5-bromopyridine* or 2-amino-5-chloropyridine* has been studied in order to have information on both the solvent influence and the inductive effects of bromide and chloride substituents on the stability of the complexes. Data about the complexes between copper(II) and this kind of ligand in water are available [4–9].

The study was performed in solvents such as methanol (MeOH), n-propanol (PrOH), N,N-dimethylacetamide (DMA) and dimethylsulphoxide (DMSO). The investigation was carried out by visible spectrophotometry and flow-microcalorimetry.

Experimental

All products used were of analytical grade. The ligands were recrystallized from ligroine up to their proper melting point. The metal solutions were analyzed by complexometric titration.

The spectrophotometric apparatus was a Perkin Elmer 559. Quartz cells with different path lengths (5.0, 1.0 and 0.2 cm) were used.

The flow-microcalorimeter was a LKB 10700 apparatus with two glass syringes on a Braun Melsungen AG injection pump. All measurements were carried out at 25 °C ± 0.1 °C.

Nuclear Magnetic Resonance measurements were carried out on a Bruker WP 80 at 25 °C on DMSO-d_6 solutions, using 2,2-dimethyl-2-silapentane-5-sulphonate sodium salt (DSS) peak as reference, in order to have some information on the nitrogen atom involved in the coordination. Cyclohexane, at the same concentration of the ligand, was used as a reference compound to calculate the number of protons present. The TGA apparatus was a Perkin Elmer TGS-2 thermal analyser. The spectrophotometric and calorimetric data were treated according to the 'straight line' [10] and 'corresponding solution' [11] methods, thus allowing the identification of the prevailing species and calculation of concentration quotients at the equilibrium.

Results

The complexation reaction for every system considered was complete in a few seconds from the mixing of the solutions. The inertness of the compounds obtained was checked by spectrophotometric measurements.

Experimental data were obtained by solutions of different metal concentrations in the range 10^{-3} M ÷ 2.4×10^{-2} M and initial molar ratio C_L/C_M in the range 0 ÷ 50.

The spectra trends suggested that the study was carried out at the wavelengths corresponding to the maximum of solution characterized by an initial molar ratio $C_L/C_M = 10$ (see tables below).

The absorbance values in every considered solvent are reported in Tables I, II, III.

Mathematical elaboration of the absorbance values in MeOH has allowed the identification of two species in all considered systems. The first one, characterized

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*Abbreviations used: Apy = 2-aminopyridine; BrApy = 2-amino-5-bromopyridine; ClApy = 2-amino-5-chloropyridine.

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TABLE I. Absorbance values of copper(II)–2-aminopyridine, copper(II)–2-amino-5-bromopyridine and copper(II)–2-amino-5-chloropyridine systems in methanol at different initial concentration ratios C_L/C_M.

	L = Apy, λ = 588 nm		L = BrApy, λ = 632 nm		L = ClApy, λ = 640 nm	
C_L/C_M	$C_M = 1.00 \times 10^{-3}$ M b = 5.0 cm	$C_M = 4.00 \times 10^{-3}$ M b = 5.0 cm	$C_M = 1.91 \times 10^{-3}$ M b = 5.0 cm	$C_M = 8.00 \times 10^{-3}$ M b = 1.0 cm	$C_M = 2.00 \times 10^{-3}$ M b = 5.0 cm	$C_M = 8.00 \times 10^{-3}$ M b = 1.0 cm
0.5		0.029				
1.0	0.041	0.050	0.058	0.080	0.065	0.090
1.5	0.071	0.082	0.084		0.090	0.125
2.0	0.092	0.117	0.107	0.148	0.110	0.160
2.5	0.125	0.158	0.133		0.133	0.195
3.0	0.138	0.180	0.148	0.207	0.155	0.220
3.5	0.158	0.200	0.170	0.235	0.170	0.245
4.0	0.179	0.222	0.185	0.260	0.190	0.275
4.5	0.190	0.240		0.285	0.210	0.300
5.0	0.198	0.247	0.218	0.307	0.225	0.320
5.5				0.329	0.235	0.340
6.0	0.220	0.268	0.247	0.348	0.250	0.355
8.0	0.259	0.299	0.303	0.406	0.300	0.410
10.0	0.282	0.310	0.350	0.443	0.335	0.450
25.0					0.530	0.570
50.0					0.580	0.620

by complexation ratio $L/M = 1$, prevailed in the range $C_L/C_M = 0.5 \div 2.2$ in the case of Apy, $C_L/C_M = 1 \div 2.5$ in the case of BrApy, in the range $C_L/C_M = 1.4 \div 3.6$ in the case of ClApy.

The concentration quotients at the equilibrium and molar absorptivities of the evidenced species are respectively: β_1(Apy) = 4.3 × 10^2 mol l^{-1}, ϵ_1 = 33 mol^{-1} l cm^{-1}; β_1(BrApy) = 3.4 × 10^2 mol l^{-1}, ϵ_1 = 19 mol^{-1} l cm^{-1}; β_1(ClApy) = 3.3 × 10^2 mol l^{-1}, ϵ_1 = 17 mol^{-1} l cm^{-1}.

The second species, characterized by a complexation ratio L/M = 2, prevailed in the range 2.5 ÷ 6 in the case of Apy, in the range 2.7 ÷ 7 in the case of BrApy and in the range 4 ÷ 10 in the case of ClApy.

The concentration quotients at the equilibrium and molar absorptivities of these species are respectively: β_2(Apy) = 4.7 × 10^5 mol^2 l^{-2}, ϵ_2 = 52 mol^{-1} l cm^{-1}; β_2(BrApy) = 1.3 × 10^5 mol^2 l^{-2}, ϵ_2 = 22 mol^{-1} l cm^{-1}; β_2(ClApy) = 6.5 × 10^4 mol^2 l^{-2}, ϵ_2 = 29 mol^{-1} l cm^{-1}.

In PrOH the complex copper(II)–Apy was scarcely soluble. In order to have more information about these species, the solid compound was examined by TGA and showed a ligand/metal ratio = 2, and the reflectance spectrum showed a wavelength maximum at 560 nm.

The other two complexes were soluble and the mathematical elaboration of the obtained absorbance values confirmed the presence of two species.

The first, characterized by the complexation ratio $L/M = 1$, prevailed in the range $C_L/C_M = 1 \div 2$ in the case of Apy, in the range $C_L/C_M = 1 \div 2$ in the case of BrApy and in the range $C_L/C_M = 1 \div 1.5$ in the case of ClApy.

The concentration quotients at the equilibrium and molar absorptivities of these complexes are respectively: β_1(BrApy) = 4.1 × 10^2 mol l^{-1}, ϵ_1 = 46 mol^{-1} l cm^{-1}; β_1(ClApy) = 4.0 × 10^2 mol l^{-1}, ϵ_1 = 37 mol^{-1} l cm^{-1}.

The second species, characterized by complexation ratio $L/M = 2$, prevailed in the range $C_L/C_M = 2.5 \div 6.3$ in the case of BrApy and in the range $C_L/C_M = 2 \div 5$ in the case of ClApy. The concentration quotients at the equilibrium and molar absorptivities of these complexes are respectively: β_2(BrApy) = 1.9 × 10^5 mol^2 l^{-2}, ϵ_2 = 57 mol^{-1} l cm^{-1}; β_2(ClApy) = 2.4 × 10^5 mol^2 l^{-2}, ϵ_2 = 41 mol^{-1} l cm^{-1}.

In DMA, complex species were noted only when the ligand was Apy. These complexes were characterized by the following concentration quotients at the equilibrium and molar absorptivities: β_1(Apy) = 4.0 × 10^2 mol l^{-1}, ϵ_1 = 17 mol^{-1} l cm^{-1}; β_2(Apy) = 3.4 × 10^5 mol^2 l^{-2}, ϵ_2 = 88 mol^{-1} l cm^{-1}.

The other two ligands give very weak complexes.

The same problem exists in DMSO. In fact the complex formation started only at C_L/C_M ratio >

TABLE II. Absorbance values of copper(II)–2-amino-5-bromopyridine and copper(II)–2-amino-5-chloropyridine systems in n-propanol at different initial concentration ratios C_L/C_M.

	L = BrApy, λ = 620 nm		L = ClApy, λ = 592 nm	
C_L/C_M	$C_M = 2.00 \times 10^{-3}$ M b = 5.0 cm	$C_M = 1.200 \times 10^{-2}$ M b = 1.0 cm	$C_M = 8.00 \times 10^{-3}$ M b = 1.0 cm	$C_M = 2.400 \times 10^{-2}$ M b = 0.2 cm
1.0	0.202	0.260	0.144	0.095
1.55	0.240	0.382	0.213	0.140
2.0	0.300	0.531	0.266	0.175
2.55	0.340	0.588	0.319	0.210
3.0	0.369	0.624	0.365	0.240
3.5	0.408		0.407	0.268
4.0	0.430	0.676	0.433	0.285
4.5	0.452	0.718	0.451	0.297
5.0	0.470	0.748	0.471	0.310
5.5	0.489		0.486	0.320
6.0	0.495	0.780	0.494	0.325
7.0	0.507	0.780	0.524	0.345
8.0	0.530	0.782	0.525	0.375
10.0	0.554	0.782	0.570	0.375
25.0	0.560		0.620	
50.0			0.660	

TABLE III. Absorbance values of copper(II)–2-aminopyridine system in N,N-dimethylacetamide at different initial concentration ratios C_L/C_M.

	L = Apy, λ = 736 nm	
C_L/C_M	$C_M = 2.00 \times 10^{-3}$ M b = 5.0 cm	$C_M = 7.99 \times 10^{-3}$ M b = 1.0 cm
1.0	0.405	0.306
2.0	0.634	0.576
2.5		
3.0	0.807	0.618
3.5		0.627
4.0	0.980	0.632
4.5		0.641
5.0	1.014	0.645
5.5		0.650
6.0	1.030	0.655
8.0	1.044	0.660
10.0	1.060	0.662
20.0	1.070	
25.0	1.070	0.665
50.0	1.080	0.670

50. Moreover, the absorbance of copper(II) interferes very strongly with that of the complex.

Calorimetric investigations, carried out at the same systems in the same experimental conditions, have given suitable data in PrOH and DMA while in MeOH they did not provide any useful results [12, 13].

In Fig. 1 the reaction heats at various C_L/C_M ratio are reported for solutions with initial metal concentration $C_M = 2 \times 10^{-3}$ mol l^{-1} in PrOH and in DMA.

Mathematical elaboration of calorimetric data allows us to calculate the enthalpy of the reactions. The calculated values were: ΔH_1(BrApy) = −2.4 Kcal/mol; ΔH_2 = −5.8 Kcal/mol; ΔH_1(ClApy) = −2.3 Kcal/mol, ΔH_2 = −6.2 Kcal/mol in PrOH and they were: ΔH_1(Apy) = −3.6 Kcal/mol, ΔH_2 = −9.7 Kcal/mol in DMA.

Concerning which atom bonds the copper(II) ion, NMR measurements have evidenced that the nitrogen atom involved in the coordinating bond is the pyridinic one.

Discussion

The data summarized in Table IV allow us to formulate some hypotheses about the influence of the solvent and of the substituents in the pyridine moiety on the complexation equilibria. With regard to the solvent influence, the comparison of the results obtained in MeOH and in PrOH can evidence the effect of the dielectric properties of the medium, whereas the comparison of the data obtained in MeOH and DMA show the influence of donor and acceptor properties on the complexation equilibria.

The dielectric constant seems to be unrelated to the stability of the complex species, while it strongly affects their solubility and ionization. The stability is probably not influenced because of the high rate of 'soft' character of the complexes [14].

The values of the concentration quotients at the equilibrium obtained in MeOH and DMA are not so different as would be expected in respect to the

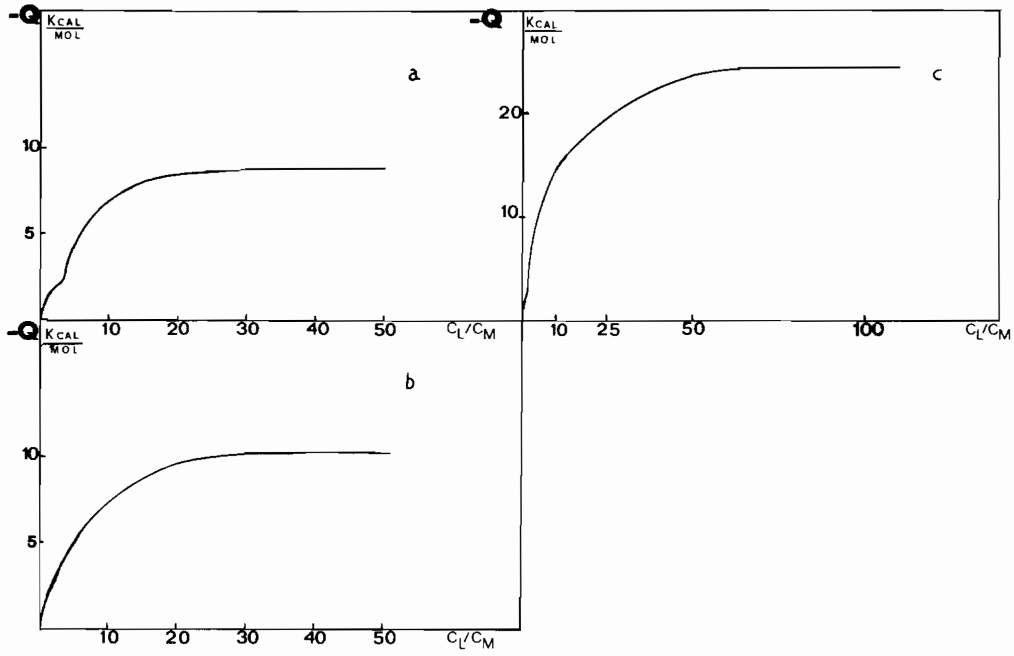

Fig. 1. Heat values at $C_M = 2 \times 10^{-3}$ mol l^{-1} and various initial concentrations of the ligands in the range $C_L = 10^{-3} \div 10^{-1}$ mol l^{-1} of following systems: a) Copper(II)–2-amino-5-bromopyridine in propanol; b) Copper(II)–2-amino-5-chloropyridine in propanol; c) Copper(II)–2-aminopyridine in N,N-dimethylacetamide.

TABLE IV. Values of concentration quotients at the equilibrium, molar absorptivities and enthalpies of copper(II)–2-aminopyridine, copper(II)–2-amino-5-bromopyridine and copper(II)–2-amino-5-chloropyridine systems in methanol, propanol and N,N-dimethylacetamide.

Solvent:	MeOH		PrOH		DMA	
Parameters of the solvent:	DN = 19.1,	AN = 41.5, DEC = 32.6	DN = 19.6,	AN = 37.3, DEC = 20.1	DN = 27.8,	AN = 13.6 DEC = 37.9
Copper pyridine complex						
Cu(II)–Apy	$\log \beta_1 = 2.63$ $\log \beta_2 = 5.67$	$\epsilon_1 = 33$ $\epsilon_2 = 52$	$ML_2 \downarrow$		$\log \beta_1 = 2.60$ $\log \beta_2 = 5.53$ $\Delta H_1 = -3.6$ $\Delta H_2 = -9.7$	$\epsilon_1 = 17$ $\epsilon_2 = 88$
Cu(II)–BrApy	$\log \beta_1 = 2.54$ $\log \beta_2 = 5.13$	$\epsilon_1 = 19$ $\epsilon_2 = 22$	$\log\beta_1 = 2.61$ $\log\beta_2 = 5.28$ $\Delta H_1 = -2.4$ $\Delta H_2 = -5.8$	$\epsilon_1 = 46$ $\epsilon_2 = 57$		
Cu(II)–ClApy	$\log \beta_1 = 2.52$ $\log \beta_2 = 4.81$	$\epsilon_1 = 17$ $\epsilon_2 = 29$	$\log \beta_1 = 2.60$ $\log \beta_2 = 5.38$ $\Delta H_1 = -2.3$ $\Delta H_2 = -6.2$	$\epsilon_1 = 37$ $\epsilon_2 = 41$		

values of the donor numbers. This fact can be explained by the large difference between their acceptor numbers, which affects this kind of ligand. In MeOH the acceptor number is low, and the affinity of the solvent for the ligand is also low. Consequently the formation of a complex species is more favorable in DMA than in MeOH, even if the donor properties of the solvent act in the opposite way.

Regarding the influence of substituents on the pyridine moiety, some suppositions can be formulated on the stability order of the concentration quotients at the equilibrium obtained in MeOH. The observed order is: CuApy > CuBrApy > CuCl-Apy, the same sequence as the Lewis basicity of the ligands. Moreover the comparison of concentration quotients at the equilibrium of substituted ligands shows that the influence of halides on the stability of the complexes is higher on K_2 than on K_1 values.

The microcalorimetric results obtained in MeOH have always shown endothermic reactions for the formation of the complexes with the three different ligands. These reaction heats cannot be assigned to the complex formation, but probably can be ascribed to the breaking of the self-association bounds among the ligands molecules [15].

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