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Samia Benhammadi, Adil A. Othman, Kusai Al Omar, Gilles M. Bouet, Mustayeen Ahmed Khan. Synthesis of picolinic acid hydrazide and its complexation with coppe(II) ions in methanol solutions.. 2021. hal-03258144

HAL Id: hal-03258144

https://univ-angers.hal.science/hal-03258144

Preprint submitted on 11 Jun 2021

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Synthesis of picolinic acid hydrazide and its complexation with copper(II) ions in methanol solutions

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Abstract

The picolinic acid hydrazide (APH) was synthesized and characterized by UV-Vis-IR and NMR spectrometry. A complexation study of APH with copper(II) ions was carried out by conductometry and spectrophotometry. The formation of a weak complex of APH-Cu is reported with a stability constant value of 1.58.

Keywords: Picolinic acid, 2-pyridinecarboxylic acid, hydrazide, synthesis, complexation, metal complexes.

En français:

Titre:

Synthèse de picolinique acide hydrazide et son complexation avec cuivre(II) en solution méthanolique

Résumé:

Le picolinique acide hydrazide (APH) a été synthétisé et caractérisé par spectrometrie UV-Vis-IR et RMN. Une étude de complexation d'APH avec le cuivre(II) a été faite par conductométrie et par spectrophotométrie. La faible formation d'un complexe est remarquée dont la constante de stabilité a été calculée par le programme SIRKO avec une valeur de 1,58.

Mots- clés:

Acide picolinique, pyridine-2-carboxylique acide, hydrazide, synthèse, complexation, complexes métalliques.

INTRODUCTION

The importance of aromatic hydrazides is clearly related to their biological activity and to the fact that they can be used for the syntheses of several other compounds for their biological and luminescence properties such as the ligand 5-(2-pyridyl)-1,3,4 oxadiazol-2-thione [1].

The present study was undertaken to investigate the complexation reaction of copper(II) with the 2-pyridinecarboxylic acid hydrazide (APH) in methanol solution. This ligand, synthesized in our laboratory, and structurally similar hydrazides, have great potential owing to their anti-tuberculosis action. This action is enhanced by the presence of metal ions such as cobalt(II) [2-4] and cadmium(II) [5]. In the latter publication, van Hecke et al. have studied in detail the co-ordination geometry of the Cd(II) complexes with this ligand.

The equilibrium of 2-pyridinecarboxylic acid hydrazide, also known as picolinic acid hydrazide and abbreviated here as APH, with copper(II) in aqueous solution and under acidic conditions has already been reported [6]. For this study in methanol solution, copper was retained as the central ion as we have already shown that, in similar systems, the stability of complexes with copper is highest as compared to that of the other 3d transition metals [7].

EXPERIMENTAL

Reagents

Methanol (Merck) was used as solvent without any further treatment. Other details concerning the reagents are given in the paragraph on the synthesis of the picolinic acid hydrazide.

For measurements, stock solutions of all species were prepared by weighing calculated quantities of ligand and copper(II) chloride (Fluka). The conductometric measurements were done with a PHYWE system with R232 integrated interface. The temperature at which all experiments were carried out was maintained at 25.0 ± 0.2 °C.

Spectrophotometric measurements were made immediately after the addition of the last reactant since the mixtures are not very stable. For these measurements the final analytical concentration of copper was maintained at 5.10^{-4} mol L^{-1} for all systems. The ligand concentration varied from zero to 5.10^{-3} mol L^{-1}. The measurements were carried out with the help of a Perkin-Elmer UV-Vis-NIR Lambda 19 Spectrophotometer using spectrophotometric cells of quartz of 1.0 cm.

RESULTS AND DISCUSSION

Synthesis of picolinic acid hydrazide

Ethyl picolinate (Acros), 5 mg, was dissolved in 8 mL ethanol. To this, 2 mL of hydrazine (51%) was added drop wise and the mixture was heated under reflux on an oil bath at 90°C for 20 hours. The solvents were evaporated under vacuum to give yellow crystalline product (4.25 g, 90%, melting point: 107 ± 1°C). The product was washed with small quantity – just a few mL, of ether. The characterization results of the product are given below.

IR: 3309.25 ν cm^{-1}; (N-H): 1677, 77 cm^{-1}.

UV: λmax 218 and 260 nm.

^{1}H-NMR S 8.5 ppm (d, 1H, Hz)
7.9 ppm (m, 2H, H4 & H5)
7.45 ppm (d, 1H, H6)
4.75 ppm (ds, 3H, N-H)

^{13}C NMR S ppm 166.27, 149.2
148.6, 138.7, 127.5 & 122.8.

Conductivity of copper(II) solutions with picolinic acid hydrazide and picolinic acid

The determination of the specific conductivity of copper solutions ($CuSO_4.5H_2O$) with two different ligands: picolinic acid (AP) and picolinic acid hydrazide (APH), was carried out for the metal and for the ligands separately and then for the solutions of metal and ligands:

- The determination of the specific conductivity of the metal ($CuSO_4.5H_2O$) in methanolic solutions with copper concentrations of 0.00625, 0.0125, 0.025, 05 and 0.1 mol L^{-1}.
- The determination of the specific conductivity of the ligand: picolinic acid hydrazide and picolinic acid, at different concentrations: 0.00625, 0.0125, 0.025, 05 and 0.1 mol L^{-1}.
- The determination of the specific conductivity of metal/ligand mixtures at different concentrations: 0.00625/0.00625 mol L^{-1}, 0.0125/0.0125 mol L^{-1}, 0.025/0.025 mol L^{-1}, 0.05/0.05 mol L^{-1}, 0.1/0.1 mol L^{-1}.

The principal equation used is $\Lambda = X/C$, where

X: specific conductivity in micro siemens cm^{-1} ($\mu s\ cm^{-1}$),

C: concentration (mol L^{-1}),

Λ: molar conductivity (ms cm^2/mole).

The expression for molar conductivity is: $\Lambda = \Lambda_o - KC^{1/2}$

K: constant

Λ_o: molar conductivity at infinite dilution.

The conductometric method is used to indicate the formation of an ion pair between a cationic metal and an anionic ligand. While this method has been widely used in investigations of the association of simple ions, it has rarely been employed to investigate systems with copper and picolinic acid hydrazide [8]. The specific conductivity of metal-ligand mixture in methanol solution was measured as a function of molar/molar concentration of the mixtures and compared to those of the mixture of copper and picolinic acid. These results are resumed in Tables 1-2 and Figures 1-5.

Tables 1-2

Figures 1-5

If no interaction occurred between the metal and APH, the specific or the molar conductivity would be expected to be the sum of the conductivities of the individual species in the solution. In case there is a reaction, the molar conductivity of the mixture increases linearly with with increasing mixture concentrations, according to the mathematical expression for molar conductivity as given above. Figure 1 shows that the graph of solutions of APH/Cu is clearly distinct from those of the ligand APH and that of the metal ($CuSO_4$) which is a clear indication of of the formation of a new species – a complex APH/Cu. The same phenomenon is observed when molar conductivities of the metal and of picolinic acid, separately and in a mixture, are studied (figure 2). However, when the molar conductivities of APH/Cu and AP/Cu are compared (figure 3), it is remarked that conductivity of the metal with picolinic acid is much superior than the metal with the hydrazide of picolinic acid. This signifies that picolinic acid is a better complexing agent and has a higher complexing ability than its hydrazide. Figure 4 presents the result of a kinetic study of the solutions of APH with the metal for two different sets of concentrations. Both the graphs confirm the complete formation of the complex as soon as the two constituents are mixed together. However, for the same set of concentrations of metal and ligand, the molar conductivity with picolinic acid increases with respect to time when compared to that of picolinic acid hydrazide (figure 5). It is concluded that the complex formed in this instant is either not formed immediately or is unstable.

Spectrophotometric investigation of copper(II) solutions with picolinic acid hydrazide

A rapid investigation of copper(II) solutions of picolinic acid hydrazide was carried out at 25°C. The concentration of the copper solution was kept constant at 5.10^{-4} mol L^{-1} whereas the APH concentration varied from zero to 5.10^{-3} mol L^{-1}. The experimental spectra is presented in figure 6.

Figure 6

The characteristic copper band in the near IR appears around 850 nm. With increasing concentrations of APH this band undergoes a shift towards lower wave numbers and can be seen centred around 710 nm. At still higher concentration of the ligand, the maximum is situated at around 625 nm. This significant hypsochromic shift of about 225 nm is a clear indication of the formation of a new species between copper and APH.

The determination of the stability constant of this complex was done with the computer program SIRKO which was conceived for the calculation for such parameters from spectrophotmetric experimental data [9]. It is based on a least-squares method and its essential details were given in our earlier publicatins [10, 11]. The complex is a weak complex as is indicated by the low calculated value of its stability constant, β, which is 1.58 ($\log \beta = 0.2$). This is calculated with a reliability factor, R, of 17% which is quite high. Normally the R factor should be less than 10%. Taking into consideration the low values of absorbance and the low value of the stability constant, this high value of R factor is not surprising.

CONCLUSION

The picolinic acid hydrazide, APH, was synthesized and characterized in our laboratory. It was complexed with copper(II) in methanol solutions by conductometric and spectrophotometric methods. The complexation of copper(II) with APH was also compared to the complexation of copper(II) with picolinic acid (AP). It appears that the complex formed with APH is more stable though its stability constant, β, calculated with the help of the computer program SIRKO, has a low value of only 1.58.

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List of Tables

TABLE 1:

Molar conductivities of solutions of copper ($CuSO_4$), picolinic acid (AP), picolinic acid hydrazide (APH), and their mixtures at different molar concentrations, C.

TABLE 2:

Molar conductivities of solutions of copper ($CuSO_4$) and picolinic acid (AP), and copper ($CuSO_4$) and picolinic acid hydrazide (APH), at different intervals of time.

Figure Legends

FIGURE 1

Molar conductivities of solutions of copper, of picolinic acid hydrazide, and of mixtures of APH/Cu at different concentrations.

FIGURE 2

Molar conductivities of solutions of copper, of picolinic acid, and of mixtures of AP/Cu at different concentrations.

FIGURE 3

Comparison of molar conductivities of solutions of AP/Cu and of APH/Cu.

FIGURE 4

Kinetics of molar conductivities of solutions of APH/Cu at two sets of concentrations (M = molar concentration).

FIGURE 5

Comparison of kinetics of molar conductivities of solutions of AP/Cu and APH/Cu copper, of picolinic acid hydrazide, and of mixtures of APH/Cu at the same concentration (M= molar concentration).

FIGURE 6

Experimental absrption spectra of solutions of APH/Cu between 500 and 900 nm.
$[Cu^{2+}] = 5.10^{-4}$ mol L^{-1}, $l_{cell} = 1$ cm.

Table 1

$C^{1/2}$	Λ (Cu)	Λ (AP)	Λ (APH)	Λ (AP/Cu)	Λ (APH/Cu)
0.316	10240	898	846		16900
0.224	11240	972	936	35780	22120
0.158	11000	1048	984	44240	26400
0.112	10480	1119	1057	52160	32000
0.079	10128	1227	1178	60000	38100
0.056	10592	1360		64960	
0.039	11200	1792		66200	

Table 2

Temps (min)	Λ (AP/Cu) (0.05M/0.05M)	Λ (APH/Cu) (0.05M/0.05M)	Λ (APH/Cu) (0.1M/0.1M)
1	35780	22120	16900
5	36080	21760	16800
10	36320	21560	16700
15		21540	16600
20	36760	21440	16650
25	36980	21340	16670
30	38000	21340	16660

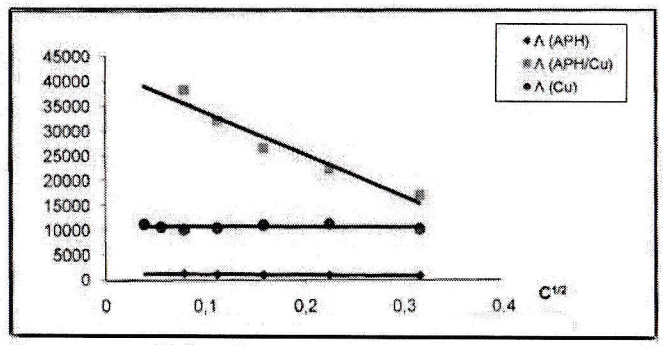


Figure 1

Figure 2

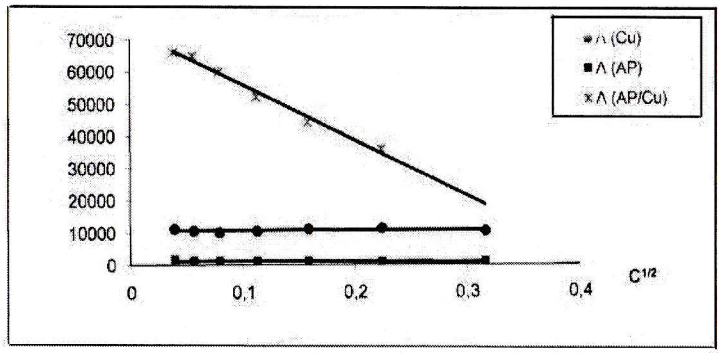


Figure 2

Figure 3

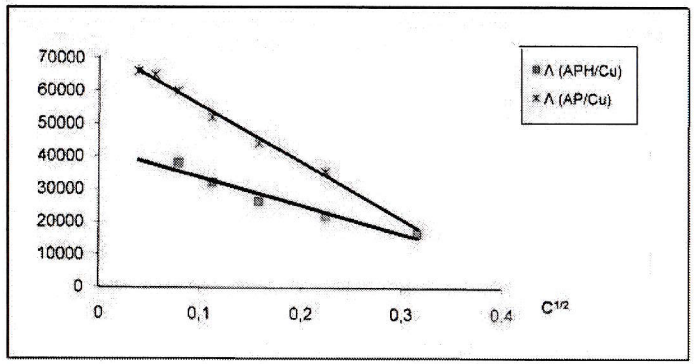


Figure 3

Figure 4

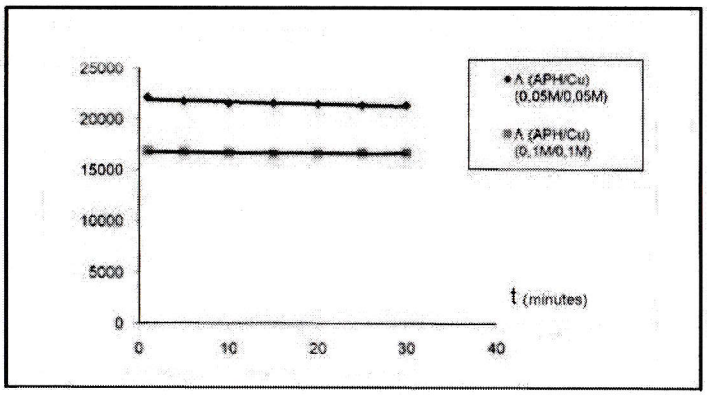


Figure 4

Figure 5

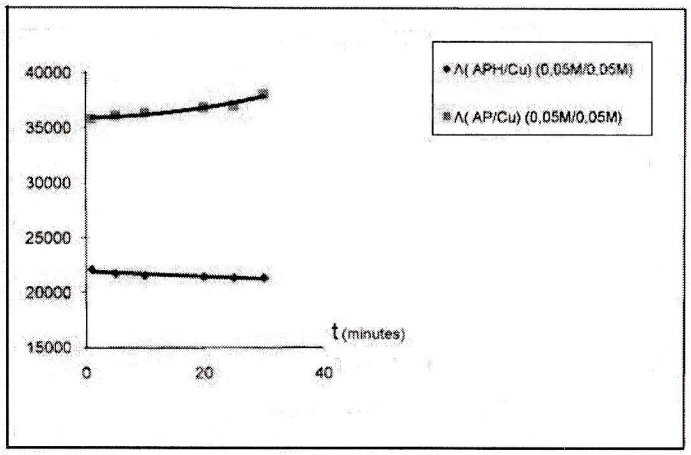
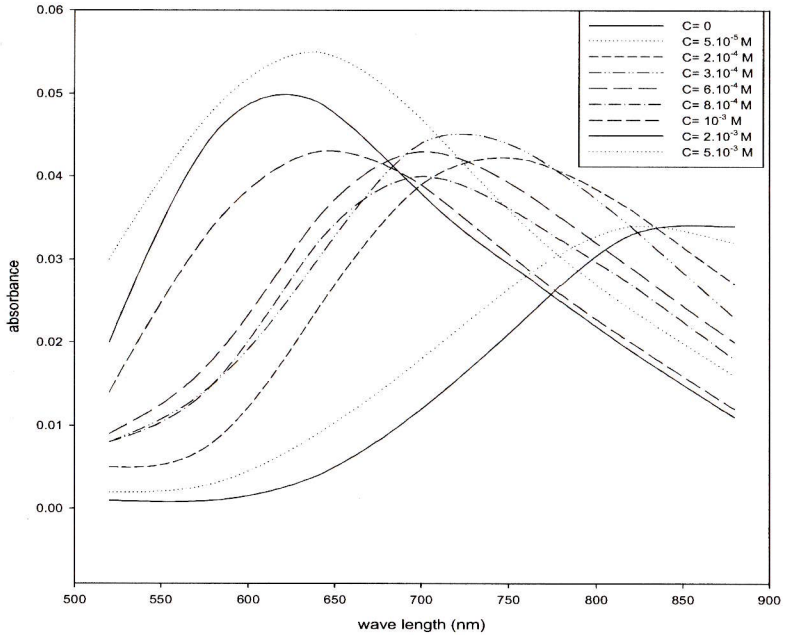


Figure 5

Figure 6


0.06
0.05
0.04
0.03
0.02
0.01
0.00
absorbance
500
550
600
650
700
750
800
850
900
wave length (nm)
C= 0
C= 5.10-5 M
C= 2.10-4 M
C= 3.10-4 M
C= 6.10-4 M
C= 8.10-4 M
C= 10-3 M
C= 2.10-3 M
C= 5.10-3 M