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Inclusion properties of 3-amino-5-methypyrazole towards some metal cations

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ABSTRACT

The inclusion properties of 3-amino-5-méthypyrazole (pyrazole) toward the alkali, alkaline earth cations, some transition, heavy metals and some lanthanides have been investigated in acetonitrile and methanol, followed by UV Spectrophotometry Absorption and conductivity. Thus, the stoichiometries of complexes formed and their stability constants were determined by digital processing of data.

The results of liquid-liquid extraction show that the ligand extracted only a Cs^+ and Mg^{2+} in the series of the picrate salts considered.

KEYWORDS

Inclusion properties;
Heterocyclic amine;
Pyrazole;
Stoichiometry;
Complexation;
Extraction;
Stability constants.

INTRODUCTION

Heterocyclic containing nitrogen atoms have common features integrated into the structures of many natural products and pharmaceutical compounds. The multidentate ligands are widely used in coordination chemistry. Among these ligands include derivatives of pyrazole because of their biological importance as constituents of many biomolecules and drogues.[1] Heterocyclic amines have attracted much interest in the metabolism of drugs and therapeutic effects. These heterocyclic amines are metabolically activated by the mixed function oxidase system to produce genotoxic hydroxylamines ends[1].

The biological activity of pyrazole and its derivatives is well known[2]. These compounds have many applications, for example they have a role of inhibitor of alcohol déshydrogénase[2] for their antiallergic action potentielle[2].

Some derivatives of pyrazole may be inhibiting the same mutation induction of certain cancérogènes[2], and can also be an intermediate in the synthesis of pharmaceutiques[3]. The pyrazoles amines have various domains of applications, they are frequently found in pharmaceuticals and ligands protéines[4]. Pyrazole derivatives are also used as pesticides[5]. Heterocyclic amines have a power saw with their complexing affinity with cations métalliques[6-9].

In some cases, structural and biological properties of organic ligands can be modified or even improved when an ion coordination métallique[10]. It was found that metal cations are the most studied metals transition[6,9,11].

Given the above, we recently studied the coordination chemistry of compounds containing this hétérocycles[12].

EXPERIMENTAL

Materials and products

The UV spectra were recorded on a Perkin Elmer Lambda 11 spectrophotometer. Methanol (Riedel-deHaën for HPLC), Acetonitrile (SDS for HPLC, 0.03% water content) and dichloromethane (Fluka, purum) were commercial and used without further purification. The supporting electrolyte used in the stability constant determinations was NEt_4Cl and NEt_4ClO_4 (Acros Organics). The metal salts chosen were chlorides or perchlorates (Fluka, purum). The picrate salts employed in extraction were prepared as described in literature[13].

Extraction studies

The extraction experiments of alkali, alkali earth, transition metal picrate from water into dichloromethane, were performed according to a procedure described in the literature[14]. Equal volumes (5 mL) of neutral aqueous solution of alkali metal picrate (3×10^{-4} $mol.L^{-1}$) and CH_2Cl_2 solution (5 mL) of heterocyclic amines (3×10^{-4} $mol.L^{-1}$) were mixed, magnetically shaken in a thermoregulated water bath at 25° C for 30 min, and then left standing for 2 to 6h in order to obtain a complete separation of the two phases. The concentration of metal picrate remaining in the aqueous phase was determined from the absorbance (A) at 355 nm. The percentage extraction (%E) was derived from the following expression in which A_0 is the absorbance of the aqueous solution of a blank experiment without heterocyclic amines:

$$\%E = 100(A_0 - A)/A_0$$

Stability constant measurements

The stability constants β_{xy} being the concentration ratios $[M_xL_y^{xn+}]/[M^{n+}]^x[L]^y$ and corresponding to the general equilibrium:

$$yL + xM^{n+} \Leftrightarrow M_xL_y^{\ xn+}$$

(where M^{n+} = metal ion, L = ligand) were determined in acetonitrile and methanol by UV-absorption spectrophotometry at 25°C.

The ionic strength was been maintained at 0.01 $mol.L^{-1}$ using Et_4NClO_4. The spectra of ligand solutions of concentrations ranging between 10^{-4} and 2×10^{-4} $mol.L^{-1}$ and increasing concentration of metal ion was recorded between 220 nm and 320 nm. Generally, the metal to ligand ratio R at the end of the titration did not exceed 20 and the equilibrium was quasi-instantaneous for all the systems. Addition of the metal salts to the ligand induced spectra changes large enough to allow the analysis of the resulting data using the program "Letagrop"[15]. Best values for the formation constants β_{xy} of the various complex species and their molar absorptive coefficients for various wavelengths, are deduced from the best fit between the experimental and calculated UV spectra.

The best fit is reflected by the lowest value of U (the sum of U values for all given lambda) corresponding to the square sum of a differences between experimental and calculated absorbances ($U = \Sigma\ (Acal - Aexp)^2$). The β_{xy} values correspond to the arithmetic means of at least three independent experiments.

Conductimetric studies

While complexation by a neutral ligand is not expected to dramatically alter the molar conductivity of a cationic species, the differences can usually be detected and so the measurement of conductance of a solution of a ligand into which a metal ion is added can be a useful rapid means of establishing the stoechiometry of a complex ion species. Thus, this procedure was followed to obtain preliminary estimates of the metal:ligand ratio in the complexes formed by the heterocyclic amine.

RESULTS AND DISCUSSION

Complexation of metal cations in methanol and acetonitrile

We evaluated the thermodynamic parameters of complexation on pyrazole in a homogeneous medium limited to acetonitrile and methanol. The stability constants in acetonitrile and in methanol were determined by UV absorption spectrophotometry at 25°C. The procedure consisted of adding increasing amounts of metallic perchlorates to a solution of pyrazole. The resulting changes were analysed by the program

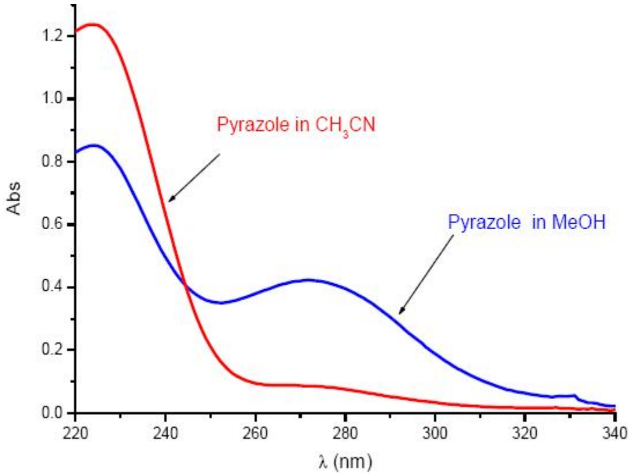

Figure 1 : Absorption spectra in the UV at 25 °C at a concentration of the pyrazole 2x10^{-4} mol.L^{-1}

Letagrop–Spefo.

The logarithms of the stability constants logβ_{xy} and the stoechiometries for the different complexes formed by ligand with alkali metal, alkaline-earth metal, some transition metal and some lanthanide metal cations in methanol and acetonitrile are given in TABLES 1,2.

The profile of the spectrum of pyrazole changes with the nature of the solvent, in fact the secondary maximum to disappear from methanol to acetonitrile.

In the series of the alkali and alkaline earth metal cations only Mg which forms a complex with the pyrazole in both solvents considered. So, Pyrazole has no affinity with the other elements of these cation series. The addition of magnesium perchlorates solution at the pyrazole solution shown a lowering of the intensities and provides two isosbestic points. It was noted that the Mg complex in acetonitrile is more stable than the corresponding in methanol.

TABLE 1 : Stability constants logβ_{xy} of the complexes of pyrazole with alkali and alkaline earth cations (a) in methanol and (b) in acetonitrile at 25 °C, I = 10^{-2} M, 0.01 ≤σ_{n-1}≤ 0.10.

	M :L	Li$^+$	Na$^+$	K$^+$	Rb$^+$	Cs$^+$	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
^{a}pyrazole	11	c	c	c	c	c	3.21	c	c	c
^{b}pyrazole	1:1	c	c	c	c	c	3.71	c	c	c

c: Absorbance changes too small to enable satisfactory fitting

TABLE 2 : Stability constants log β_{xy} of the complexes of pyrazole with some transition, have and lanthanide metal (a) in methanol and (b) in acetonitrile at 25 °C, I = 10^{-2} M, 0.01≤σ_{n-1}≤0.16.

	M:L	Cr^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	Pb^{2+}	Hg^{2+}	La^{3+}	Nd^{3+}
^{a}pyrazole	1:2	8.01	6.02	6.32	9.24	7.01	c	c	9.10	-	-
^{b}pyrazole	1:2	9.02	7.01	6.03	9 .60	6.08	c	c	8.30	7.02	6.03

c: Absorbance changes too small to enable satisfactory fitting

The transition metal cations studied show affinities of complexation with the pyrazole despite of its total absence with the monovalent cations (alkaline) and divalent (alkaline earth). This is likely due to the difference in hardness considered cations. The profiles of selectivity of the pyrazole in the series of transitions metals do not change in passing the acetonitrile in the methanol and the complexes formed are biligands, we signaled a good selectivity of Cu^{2+} in methanol and in acétonitrile, ($S_{Cu/Ni}$>3700 and $S_{Cu/Ni}$=389).

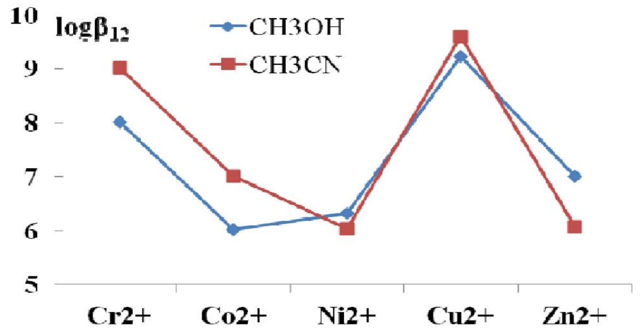

Figure 2 : Stability constants log β_{12} (determined in methanol and acetonitrile) for some transition metals series–with pyrazole

About Heavy metal cations, the cadmium and lead have no affinity with pyrazole, while only mercury is complexed.

Complexation of lanthanide metals studied by the pyrazole leads to significant changes in the appearance of the spectra that arise by hypsochromic shifts, the appearance of isosbestic points and the absorbance decreases in some areas of wavelengths and an increase in other areas.

Regarding the lanthanum and neodymium complexes are formed in acetonitrile biligand species with improved stability for the complexes of lanthanum with respect to neodymium.

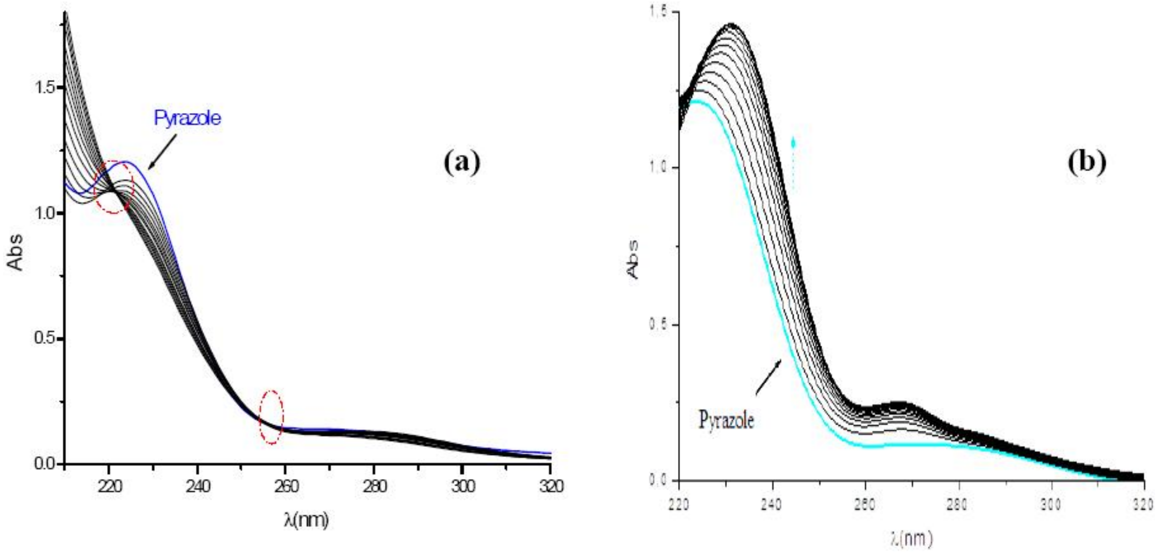

Figure 3 : UV absorption spectra on complexation of (a) zinc (II) perchlorate ($Zn(ClO_4)_2$) with pyrazole in acetonitrile and (b) nickel(II) with pyrazole in methanol) ($0 \leq R_{M/L} \leq 4$) at 25°C.

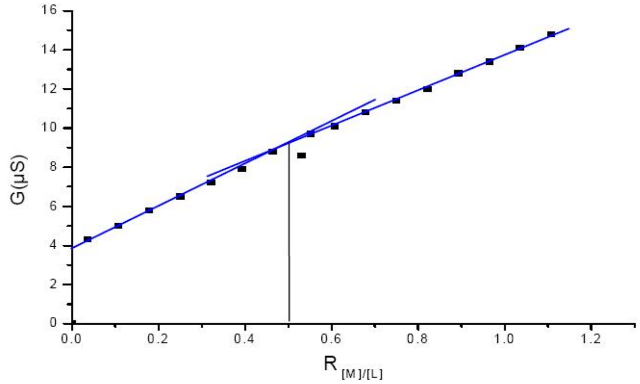

Figure 4 : Conductometric titration in the case of pyrazole with Cu^{2+}

In the other hand, the 1:2 stoichiometry of the complexes with pyrazole were confirmed by conductimetric studies in the case of Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}. For example Figure 4 show the curve change of the conductometric titration in the case of pyrazole with Cu^{2+} at the ratio M/L = 0.5.

Extraction of metal picrates

A preliminary evaluation of the binding efficiency of pyrazole was carried out by solvent extraction of metal picrates into dichloromethane at 20°C under neutral conditions. The Extraction percentages (%E) of alkali, alkaline earth and transition metal cations by pyrazole from Water into dichloromethane are given in TABLE 3.

In the series of alkali cations, pyrazole extract selectively the Cs^+ with 25%. This result is particularly interesting for the extraction of radioactive $^{137}Cs^+$ is in the waters of discharges from nuclear power plants accompanied by Na^+[16-18].

In the series of alkaline earth the pyrazole extracts only the Mg^{2+} with percentages of 67%. However, pyrazole show no affinity extraction towards the transition metals and lanthanide studied. So the pyrazole exhibe an important selectivity of extraction of the Mg^{2+} in the series of the cations M^{II} studied (Alkaline earth and Transition metals cations), this result is in accordance with the complexation study.

Complexation studies of pyrazole with $Mg^{2+}(Pic^-)_2$, $Ca^{2+}(Pic^-)_2$ and $Ni^{2+}(Pic^-)_2$ were monitored by means of ^1H NMR. $CDCl_3$ solutions of pyrazole (10^{-3} mol L^{-1}) were reacted with the solid picrates (directly introduced in the NMR tube) until the spectra of the resulting solutions remained unchanged (7 days). The formation of a complex induced changes in the ^1H NMR patterns with the appearance of a singlet corresponding to the ex-

TABLE 3 : Extraction percentages (%E) of metal picrates by pyrazole from water into dichloromethane, at 25° C ($C_L = C_M = 2.5 \times 10^{-4}$ mol L^{-1}).

	Alkali cations					Alkaline earth cations			Transition metals cations					
cations	Li^+	Na^+	K^+	Rb^+	Cs^+	Mg^{2+}	Ca^{2+}	Ba^{2+}	Co^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	Hg^{2+}	Pb^{2+}
% E	3	≤1	≤1	9	25	67	≤1	≤1	4	≤1	4	8	≤1	11

tracted picrate at 8.70–8.80 ppm.

The ratio of the extracted species to ligand in solution was estimated by calculating the integration ratio of the picrate proton resonances vs those of the protons of the ligand. Mg^{2+}, Ca^{2+} and Ni^{2+} induced changes of the spectrum of ligand with the formation of the following 1:1 complexe $Mg^{2+}(Pic^-)_2$.pyrazole, absence of complex formation with calcium and 1:2 complexe $Ni^{2+}(Pic^-)_2$.(pyrazole)$_2$.

CONCLUSION

The results show important complexation selectivity with Mg^{2+} in the alcalins and alkaline-Earth cations, the formation of biligands species to a ligand complex with transition metals, heavy metals and lanthanides. The conductimetric titration and ^{1}H NMR solid-liquid extraction confirmed mainly stoichiometries of complexes formed in solution with pyrazole determined by the UV Spectrophotometric study.

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