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C,N-Pyridylpyrazole-Based Ligands: Synthesis and Preliminary Use in Metal Ion Extraction

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Abstract: The synthesis of new *N-donor* pyridylpyrazole ligands with a functionalized arm is described. The complexation capabilities of these compounds towards bivalent metal ions (Hg^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+}, and Zn^{2+}) and alkali metal ions (K^{+}, Na^{+}, and Li^{+}) were investigated using the liquid-liquid extraction process. The percentage limits of extraction were determined by atomic absorption measurements.

Keywords: *N-donor* pyridylpyrazole, liquid-liquid extraction, cations, atomic absorption

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INTRODUCTION

Chelating ligands based on the pyrazole ring have been described extensively in the literature (1–6), several of them being reviews (7–9). In our recent work, a series of acyclic pyrazole compounds containing one to four pyrazole rings were prepared and demonstrated to extract only bivalent metal cations (10–15) whereas macrocyclic pyrazolic compounds are expected to also form stable complexes with alkali metals (16–18). This aptitude is mainly owed to the presence of sp2 hybrid nitrogen donors with the involvement of geometry and nature of ligands.

Pyrazoles associated pyridine groups showed also the ability to complex bivalent metal ions (19–22). However, there have been relatively few studies concerning pyridylpyrazole compounds. It was therefore interesting to increase the diversity of pyridylpyrazole-based ligands with a view to study their complexation capabilities compared to ligands with pyrazoles units only.

Here, we report the synthesis of new compounds **4** and **6** Fig. 1 containing pyridylpyrazole arms with a donor heteroatom in the side chain. The complexation capabilities of these two compounds were investigated using liquid-liquid extraction process towards bivalent metal ions (Hg^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+}, and Zn^{2+}) and alkaline metal ions (Li^{+}, Na^{+}, and K^{+}). This was compared to pyrazolylpyrazole ligand **6′** (12) (Fig. 1) and unfonctionalized compound **4′** (23) (Fig. 1) which is also studied here for the first time. The relative capabilities of these receptors in extracting the selected cations were determined by the measurement of the percentage of extracted cation using atomic absorption spectrometry.

EXPERIMENTAL

Reagents and Apparatus

All solvents and other chemicals, obtained from usual commercial sources, were of analytical grade and used without further purification. The proton

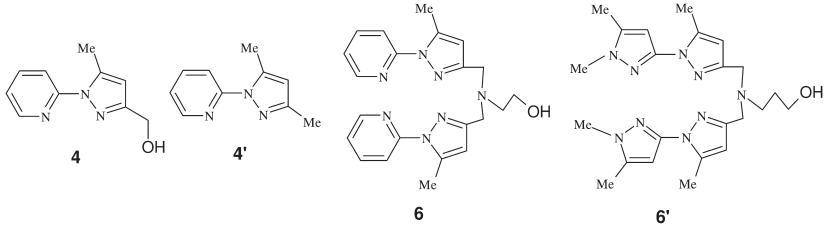


Figure 1. Structures of the synthesised pyridylpyrazoles **4** and **6** and the literature compounds **4′** (23) and **6′** (12).

NMR spectra were obtained with a Bruker AC 300 spectrometer. Elemental analyses were performed by Microanalysis Central Service (CNRS France). Molecular weights were determined on a JEOL JMS DX-300 Mass Spectrometer. Atomic absorption measurements were performed using a double beam Varian AA 20 Spectrophotometer.

Ethyl 5-methyl-1-pyridin-2-yl-1*H*-pyrazole-3-carboxylate (3)

To a solution of ethyl acetylpyruvate **1** (1.45 g, 9.2 mmol) in absolute ethanol (10 ml), was slowly added a mixture of 2-hydrazinopyridine **2** (1 g, 9.2 mmol) and hydrochloric acid (0.29 g) in absolute ethanol (20 ml). The mixture was then heated to 60°C during 3 h. The solvent was eliminated under reduced pressure and the residue obtained was taken by some millilitres of distilled water and neutralized by a solution of sodium carbonate. The solution was extracted with dichloromethane and the solvent was eliminated. The obtained oil was chromatographed on silica using the mixture ethyl acetate/CH_2Cl_2 (5/95) as eluant to give a 60% yield of **3** as a white solid and its regioisomer **3′** as yellow oil (2%):

Data for **3**

Mp = 79–81°C (CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ: 1.33 (t, 3H, CH_2-CH_3, $J = 7$ Hz); 2.63 (s, 3H, -CH_3); 4.21 (q, 2H, -CH_2-CH_3, $J = 7$ Hz); 6.42 (s, 1H, Pz-H); 7.08 (m, 1H, Py-Hβ); 7.70 (m, 1H, Py-Hγ); 7.82 (m, 1H, Py-Hδ); 8.23 (m, 1H, Py-Hα); ^{13}C NMR ($CDCl_3$) δ : 14.56 (-CH_2-CH_3); 14.63 (-CH_3); 61.23 (-CH_2-CH_3); 110.82 (Pz C-H); 117.43 (Py C-Hδ); 122.61 (Py C-Hβ); 138.83 (Py C-Hγ); 142.53 (Pz CC=O); 144.34 (Pz CCH_3); 147.82 (Py C-Hα); 153.23 (Py C); 162.64 (C=O); Anal. Calcd. for $C_{12}H_{13}N_3O_2$:C 62.33, H 5.67, N 18.17. Found: C 62.40, H 5.65, N 18.06; IR: ν(C=O) = 1710 cm^{-1}; m/z: 232 (MH^+).

Data for **3′**

^{1}H NMR ($CDCl_3$) δ: 1.23 (t, 3H, CH_2-CH_3, $J = 7$ Hz); 2.29 (s, 3H, -CH_3); 4.24 (q, 2H, -CH_2-CH_3, $J = 7$ Hz); 6.53 (s, 1H, Pz-H); 7.23 (m, 1H, Py-Hβ); 7.77 (m, 1H, Py-Hδ); 7.80 (m, 1H, Py-Hγ); 8.40 (m, 1H, Py-Hα); ^{13}C NMR ($CDCl_3$) δ: 13.71 (CH_3); 14.20 (-CH_2-CH_3); 61.52 (-CH_2-CH_3); 111.86 (Pz C-H); 118.03 (Py C-Hδ); 123.04 (Py C-Hβ); 135.11 (Pz CC=O); 138.49 (Py C-Hγ); 148.28 (Py C-Hα); 150.12 (Py C); 152.17 (Pz CCH_3); 160.66 (C=O); Anal. Calcd. for $C_{12}H_{13}N_3O_2$: C 62.33, H 5.67, N 18.17. Found: C 62.45, H 5.61, N 18.10; IR: ν(C=O) = 1720 cm^{-1}; m/z: 232 (MH^+).

(5-Methyl-1-pyridin-2-yl-1*H*-pyrazol-3-yl) Methanol (4)

To a suspension of $LiAlH_4$ (0.65 g, 17.1 mmol) in anhydrous THF (15 ml), cooled to 0°C, was slowly added compound **3** (1.94 g, 8.4 mmol) in anhydrous THF (20 ml). The mixture was stirred at 0°C during 30 mn. The excess of $LiAlH_4$ was destroyed by the slow addition of water (0.65 ml), 15% aqueous sodium hydroxide (0.65 ml) and then water (1.95 ml). The solid material was filtered and the residue was washed with hot THF. The filtrate and THF washings were concentrated under reduced pressure and the obtained oil was organized in diethyl ether to give a 70% yield of **4** (white solid): Mp = 57–59°C (Ether); ^{1}H NMR ($CDCl_3$) δ: 2.62 (s, 3H, -CH_3); 4.52 (s, 2H, -CH_2-OH); 6.08 (s, 1H, Pz-H); 7.06 (m, 1H, Py-Hβ); 7.78 (m, 2H, Py-Hγ, δ); 8.29 (m, 1H, Py-Hα); ^{13}C NMR ($CDCl_3$) δ: 14.65 (-CH_3); 58.75 (-CH_2-OH); 107.74 (Pz C-H); 116.50 (Py C-Hδ); 121.50 (Py C-Hβ); 138.66 (Py C-Hγ); 142.11 (Py C-Hα); 147.76 (Pz CCH_2-); 153.45 (Py C); 153.90 (Py CCH_3); Anal. Calcd. for $C_{10}H_{11}N_3O$: C 63.48, H 5.86, N 22.21. Found: C 63.39, H 5.85, N 22.26; IR: ν(OH) = 3240 cm^{-1}; m/z: 190 (MH^+).

2-[3-(Chloromethyl)-5-methyl-1*H*-pyrazol-1-yl] Pyridine (5)

To a solution of alcohol **4** (0.5 g, 2.64 mmol) in dichloromethane (15 ml), cooled to 0°C, was slowly added thionyl chloride (0.4 ml) in dichloromethane (10 ml). The mixture was then refluxed for 4 h and the solvent was eliminated under reduced pressure. The obtained residue was neutralized with a solution of sodium bicarbonate. After extraction with diethyl ether, the organic phase was dried on sodium sulphate then concentrated to dry. The chlorinated product **5** was obtained as a brown solid (87%): Mp = 65–66°C (Ether); ^{1}H NMR ($CDCl_3$) δ: 2.65 (s, 3H, -CH_3); 4.62 (s, 2H, -CH_2Cl); 6.27 (s, 1H, Pz-H); 7.20 (m, 1H, Py-Hβ); 7.80 (m, 2H, Py-Hγ,δ); 8.43 (m, 1H, Py-Hα); ^{13}C NMR ($CDCl_3$) δ: 14.85 (-CH_3); 39.40 (-CH_2-Cl); 108.55 (Pz C-H); 116.47 (Py C-Hδ); 122.20 (Py C-Hβ); 138.71 (Py C-Hγ); 142.71 (Py C-Hα); 147.76 (Pz CCH_2Cl); 150.06 (Py CCH_3); 153.58 (Py C); IR: ν(C-Cl) = 1250 cm^{-1}; m/z: 208.6 (MH^+).

2-{bis[(5-methyl-1-pyridin-2-yl-1*H*-pyrazol-3-yl)methyl]amino}Ethanol (6)

A solution of 2-aminoethanol (0.07 g, 1.15 mmol) in acetonitrile (5 ml), was slowly added to a suspension of anhydrous sodium carbonate (1.47 g, 13.86 mmol) and of chlorinated product **5** (0.48 g, 2.3 mmol) in acetonitrile (25 ml). The mixture was, then, heated to 70°C during 24 h. After filtration, the solvent was eliminated under reduced pressure and the obtained residue

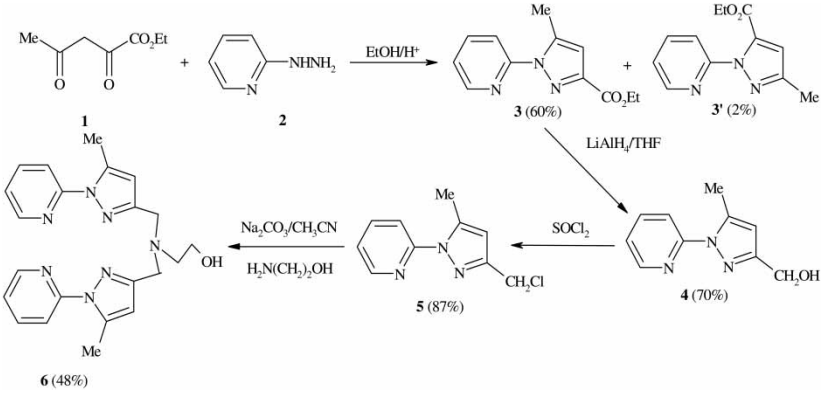
was purified on silica using the mixture $EtOH/CH_2Cl_2$ (2/98) as eluant to give a 48% yield of *6* as a yellow viscous: ^1H NMR ($CDCl_3$) δ : 2.62 (s, 6H, - CH_3); 2.79 (t, 2H, N-CH_2-CH_2-OH, $J = 4.77$ Hz); 3.64 (t, 2H, N-CH_2-CH_2-OH, $J = 4.77$ Hz); 3.81 (s, 4H, N-CH_2-Pz); 6.18 (s, 2H, Pz-H); 7.14 (m, 2H, Py-Hß); 7.78 (m, 4H, Py-Hγ, δ); 8.40 (m, 2H, Py-Hα); ^{13}C NMR ($CDCl_3$) δ: 17.97 (-CH_3); 54.79 (N-CH_2-CH_2-OH); 58.32 (N-CH_2-Pz); 62.32 (-CH_2-OH); 112.14 (Pz C-H); 119.56 (Py C-Hδ); 124.45 (Py C-Hβ); 141.73 (Py C-Hγ); 145.21 (Py C-Hα); 150.91 (Pz CCH_2-N); 154.28 (Pz CCH_3); 156.88 (Py C). Anal. Calcd. for $C_{22}H_{25}N_7O$: C 65.49, H 6.25, N 24.30. Found: C 65.40, H 6.25, N 24.36; IR: ν(OH) = 3400 cm^{-1}, ν(tertiary nitrogen) = 1130 cm^{-1}; m/z: 404.3 (MH^+).

Extraction Experiments

A solution of 7×10^{-5} M of each pyridylpyrazole in CH_2Cl_2 (25 ml) was stirred for 2 h with an aqueous solution (25 ml) of metal nitrates 7×10^{-5} M; the complexation was followed by measuring the concentration of cations in the aqueous phase by atomic absorption. The temperature was maintained constant during all the experiments at 25°C and at pH 7 measured by a pH-meter.

RESULT AND DISCUSSION

Our strategy was to develop a simple and high yielding procedure, in few steps, to prepare the desired pyridylpyrazole ligands. The results of our investigation are summarized in Scheme 1. The preparation of the structure **6** was carried out in four steps from the diketone **1**. The first step consists in the



Scheme 1.

condensation of the corresponding 1,3-disubstituted diketone **1** and 2-hydrazinopyridine **2** in acidic media under refluxing ethanol to give a mixture of two regioisomers **3** (60%) and 3′ (2%). These compounds were separated on silica gel column using the mixture: ethyl acetate/CH_2Cl_2 (5/95) as eluant. Compound **3** was then converted in the presence of $LiAlH_4$ as a reduction agent in THF to give a 70% yield of hydroxy product **4**. The chlorination of the resulting product carried out in dichloromethane and thionyl chloride gave the compound **5** with a good yield (87%). Two equivalents of the last product **5** were condensed with one equivalent of 2-aminoethanol in the presence of an excess of sodium carbonate as a base to give compound **6** with a 48% yield.

Structures of all compounds were determined on the basis of the corresponding analytical and spectroscopic data.

Liquid-Liquid Extraction of Individual Cations

We have used this method in order to determine and thereafter to compare the relative complexing capabilities of pyridylpyrazole derivatives **4**, **4′**, and **6** towards bivalent and alkali metal ions (Hg^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, Li^{+}, Na^{+} and K^{+}). Metal nitrates were extracted into the organic phase by complex formation with pyridylpyrazoles. The percentage limits of extraction were determined by atomic absorption and the results are given in Table 1.

The results in Table 1 show that in analogy to our previous work (10–18), in which acyclic pyrazoles extract only bivalent metal ions when the macrocyclic pyrazolic compounds are expected to form stable complexes both with bivalent and alkali metals, we demonstrate also here an affinity of these new acyclic ligands type sp2 nitrogen only with the bivalent metal ions, with no complexation being observed toward alkali cations.

The affinity of these ligands is especially high for mercury (II). This is not surprising if the high donor properties of nitrogen towards this metal are considered.

We noticed for all bivalent metal under study that the extraction yield is high only for Hg^{2+} and Pb^{2+} with no complexation being observed toward

Table 1. Yields of extraction of alkali and bivalent metal ions

	Hg^{2+}	Cd^{2+}	Pb^{2+}	Cu^{2+}	Zn^{2+}	Li^{+}	Na^{+}	K^{+}
4	38	2	19	26	0	0	0	0
4′ (23)	32	1	13	9	0	0	0	0
6	29	1	26	2	0	0	0	0
6′ (12)	50	30	35	—	—	0	0	0

Cd^{2+}, Cu^{2+}, and Zn^{2+}. We can thus conclude here that there is a selectivity of these ligands towards Hg^{2+} and Pb^{2+}.

On the other hand, compound **6** is more efficient for the extraction of Pb^{2+} compared to **4** and **4′**. This is probably due to the presence of two pyridylpyrazole arms and a nitrogen amine.

Concerning the extraction of Cu^{2+}, compound **4** presents a good efficiency compared to the compounds **4′** and **6**. This may be explained by the contribution of the oxygen of the hydroxyl group in the coordination of this metal ion. These results seem to correlate with the copper (II) complex L-Cu where one of the two ligands 5-methyl-1-(pyridin-2-yl)-1H-pyrazole-3-carboxamide (L) acts in N,N′-bidentate and the other in a N,N′,O-tridentate fashion with the amide O-atom participating in the latter case (24).

Furthermore, we noticed a high affinity for pyrazolylpyrazole ligand **6′** compared to its homologue pyridylpyrazole **6** towards bivalent metals, we can thus emphasize the novel complexation properties of the ligands containing linked pyrazole groups compared to the pyridinic groups.

CONCLUSION

In conclusion, new acyclic pyridylpyrazole-based ligands were prepared and proved to form complexes only with bivalent metal cations with no complexation being observed for alkali metal ions. A good affinity was observed towards mercury and lead; however, ligands with pyrazole-type sp2 nitrogen are more effective.

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