Liquid- liquid extraction of metals by using new bipyrazolic compounds

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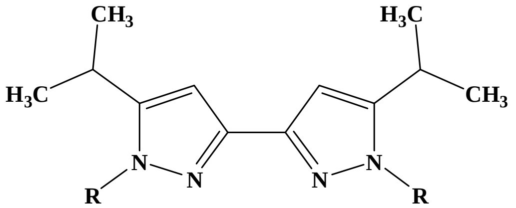
Abstract

The synthesis of new bipyrazole derivatives (**1, 3, 4**) is reported. The structures of these products were confirmed by IR, MS, EA and NMR (^{1}H and ^{13}C) spectroscopy. The extraction behaviour of Cu (II), Cd (II) and Pb (II) from aqueous solution has been investigated with dichloromethane solution for compounds (**1-4**). The percentage of the extracted cation was determined by atomic absorption spectroscopy measurements.

Keywords : Synthesis, Bipyrazole, Extraction, Copper (II), Lead (II), Cadmium (II).

1. Introduction

The Global problems facing society and science are really amazing and huge if we can give list some of them, they can be Food, Energy, Raw materials, Health care, Environment, Information technology, Sustainability, Globalization and Education. In all of these problems without any exception chemistry can provide enable solution to these issues [1]. The environmental damage is one of the important global problems in the present days and many organizations are alert to solve it. Some of the concerning environmental issues are green house effect, water–air pollution and hazardous waste generation of which one major cause is wastewater containing heavy metal ions. A lot of wastewater is disposed to the environment as a result of the growing economy, therefore its treatment is necessary especially to minimize the amount of heavy metals. Industrial and urban activities introduce large amounts of pollutants into the environment, causing significant and permanent disturbances in different systems. In many regions, these activities have increased the industrial wastes. The heavy metals are among the most harmful of the elemental pollutants and are of particular concern because of their toxicities to humans. These elements are, in general, the transition metals, and some of the representative elements, such as copper, cadmium, chromium, mercury and lead are becoming a serious public health concern [2]. Liquid–liquid extraction, based on transfer of analyte from the aqueous sample to a water-immiscible solvent, is being widely employed for sample preparation [3] and is one of the efficient techniques to separate and concentrate metal ions from industrial wastewater [4]. Solvent extraction is one of the common techniques used for their elimination. The use of pyrazole derivatives as chelating ligands is well documented in the literature [5, 6] by the presence of nitrogen electron donation group which can coordinate these analytes. Polydentate pyrazolic receptors are well known for their ability to form stable complexes with transition metal ions [7, 8]. As part of our laboratory research program on the synthesis [9, 10] and on the study [11, 12] of extractive properties of pyrazolic compounds, we report here in this paper, the synthesis method of some new bipyrazole derivatives **1, 3, 4** (**Figure 1**) and their liquid-liquid extraction properties of three metal ions Cu^{2+}, Pb^{2+} and Cd^{2+}.



1- 4

With
1: R = CH_2-Pz
2: R = CH_2-C_6H_5
3: R = $CH_2CO_2CH_2CH_3$
4: R = CH_2CH_2OH

Fig. 1. Molecular structure of compounds **1**, **2** [13], **3**, **4**

2. Experimental

2.1. Apparatus

The uncorrected melting points were determined on a BUCHI 510 Melting Points Apparatus. The ^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a Bruker 300 spectrometer (operating at 300.13 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR). Chemical shifts are listed in ppm and are reported relative to tetramethylsilane. The IR spectra were taken using KBr discs on Perkin-Elmer 1310 spectrometer. The mass spectra have been obtained on a VG7070E spectrometer. The total metal ions concentrations were analysed with the help of a Varian AAS 20 atomic absorption spectrometer using the flame technique.

2.2. Synthesis of 1,1'-di(1,5-dimethylpyrazol-3-yl)-5,5'-diisopropyl-3,3'-bipyrazole **1**

A mixture of 5,5'-diisopropyl-3,3'-bipyrazole **5** (218 mg, 1 mmol) and potassium tert-butoxide (224 mg, 2 mmol) in 20 mL of dry THF was stirred under reflux for 30 min [14]. After cooling the mixture to 0°C, the 3-chloromethyl-1,5-dimethylpyrazol (288 mg, 2 mmol) in THF (10 mL) was then added drop by drop. After stirring under reflux for 3 h, the mixture was filtered, evaporated and recrystallized from ethanol, to give product **1** as a white solid. Yield : (0.178 g , 41 %) ; Melting point : 184 - 185°C (EtOH); IR (KBr, cm^{-1}) : 3070 ($\nu_{C-H,\ arom.}$); 2930 (ν_{C-H}, CH_3); 2910; 2830 (ν_{C-H}, $CH(CH_3)_2$); 1584 ($\nu_{C=N}$); 1565 ($\nu_{C=C}$); 1485 ; 1410; 1390; 1334; 1180; 1145; 1085; 1082; 1050; 830; 775; ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm) : 6.43 (s, 2 H, C4-$\underline{H}$) ; 5.76 (s, 2 H, C4'-$\underline{H}$) ; 5.25 (s, 4H, $C\underline{H}_2$) ; 3.68 (s, 6H, N-$C\underline{H}_3$) ; 2.99 (m, 2 H, $C\underline{H}(CH_3)_2$, J = 8.7 Hz) ; 2.13 (s, 6H, C5'-$C\underline{H}_3$) ; 1.17 (d, 12 H, $CH(C\underline{H}_3)_2$, J = 6.8 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$, δ, ppm) : 150.94 (C5); 148.05 (C3); 139.85 (C3'); 143.50 (C5'); 104.58 (C4'); 100.22 (C4); 47.78 ($\underline{C}H_2$); 36.23 (N-$\underline{C}H_3$); 25.64 ($\underline{C}H(CH_3)_2$); 23.16 ($CH(\underline{C}H_3)_2$) ; 11.55 (C5'-$\underline{C}H_3$) ; Anal. Calcd for $C_{24}H_{34}N_8$: C 66.33, H 7.89, N 25.78, Found: C 66.23, H 7.90, N 25.73; MS (EI), m/z : 434 ; 398 ; 368 ; 326 ; 311 ; 283 ; 231; 217 ; 203 ; 175 ; 144 ; 109 ; 83 ; 43.

2.3. Synthesis of 1,1'-di(ethyl-ethanoate-yl)-5,5'- diisopropyl-3,3'-bipyrazole **3**

A mixture of 5,5'-diisopropyl-3,3'-bipyrazole **5** (218 mg, 1 mmol) and potassium tert-butoxide (246 mg, 2.2 mmol) in 25 mL of dry THF was stirred under reflux for 30 min [13]. After cooling the mixture to 0°C, the ethyle chloroacetate (257 mg, 2.1 mmol) in THF (10 mL) was then added drop by drop. After stirring under reflux for 3 h, the mixture was filtered, evaporated and recrystallized from ethanol, to give product **3** as a white solid. Yield : (0.370 g , 95 %) ; R_f : 0,6 (Silice / éther + hexane; 8:2, v/v); Melting point : 118 - 120°C (EtOH); IR (KBr, cm^{-1}) : 2850 ; 2830 ($\nu_{C-H,\ CH3}$); 2775 ($\nu_{C-H,\ CH2}$) ; 2685 ($\nu_{C-H,\ CH(CH3)2}$); 1715 ($\nu_{C=O}$); 1510 ($\nu_{C=N}$); 1455 ($\nu_{C=C}$); 1410 ; 1350; 1320; 1284; 1183; 1175 (ν_{C-O-C}); 1078; 1035; 1014; 935; 805; 781 ; ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm) : 6.42 (s, 2 H,C4-$\underline{H}$) ; 4.87 (s, 4 H, N-$C\underline{H}_2$-CO_2Et) ; 4.20 (q, 4 H, $C\underline{H}_2$-CH_3, J = 7.2 Hz) ; 2.79 (sept, 2 H, $C\underline{H}(CH_3)_2$, J = 6.9 Hz) ; 1.22 (m, 18 H, $CH(C\underline{H}_3)_2$, CH_2-$C\underline{H}_3$); ^{13}C-NMR (75 MHz, $CDCl_3$, δ, ppm) : 168.43 ($\underline{C}$=O); 151.64 (C5); 146.36 (C3); 100.63 (C4); 62.07 (N-$\underline{C}H_2$-CO_2Et); 51.02 (O-$\underline{C}H_2CH_3$); 25.95 ($\underline{C}H(CH_3)_2$); 23.11 ($CH(\underline{C}H_3)_2$); 14.49 (CH_2-$\underline{C}H_3$) ; Anal. Calcd for $C_{20}H_{30}N_4O_4$: C 61.53, H 7.69, N 14.35. Found: C 61.21, H 7.93, N 14.12; MS (EI), m/z : 390; 375; 317; 303; 290; 243; 229; 201; 173; 149; 120; 97; 71; 57; 40.

2.4. Synthesis of 1,1'-di(2-hydroxy-ethyl)-5,5'-diisopropyl-3,3'-bipyrazole **4**

To a solution of $LiAlH_4$ (120 mg, 3.07 mmol) in 10 mL of THF was slowly added **3** (300 mg, 0.76 mmol) in 10 mL of THF. The mixture was stirred under reflux for 1h. After cooling, water (0.12 mL), 10% aqueous sodium hydroxide (0.12 mL) and then water (0.36 mL) were added successively to the mixture at 0°C. The solid material was filtered and the residue was washed with hot THF. The filtrate and THF washings were concentrated under reduced pressure, to give product **4** as a white solid. Yield : (0.223 g, 96 %) ; R_f : 0,4 (Silice / CH_2Cl_2 + EtOH : 90 / 10); Melting point : 205 - 206°C (EtOH); ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm) : 6.38 (s, 2 H, C4-$\underline{H}$) ; 4.16 (t, N-C$\underline{H}_2$, 4 H, J = 5.4 Hz) ; 4.01 (t, C$\underline{H}_2$-OH, 4 H, J = 4.5 Hz) ; 2.96 (sep, 2 H, C$\underline{H}$(CH_3)$_2$, J = 6.9 Hz) ; 1.27 (d, 12 H, CH(C$\underline{H}_3$)$_2$, J = 6.9 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$, δ, ppm) : 151.52 (C5) ; 145.69 (C3) ; 99.83 (C4) ; 62.08 (N-$\underline{C}H_2CH_2OH$); 50.45 ($CH_2\underline{C}H_2$-OH); 25.63 ($\underline{C}H(CH_3)_2$) ; 22.97 ($CH(\underline{C}H_3)_2$); IR (KBr, cm^{-1}) : 3340 (ν_{N-H}); 2880 ($\nu_{C-H, CH3}$); 2865 ($\nu_{C-H, CH2}$); 2805 ($\nu_{C-H, CH(CH3)2}$); 1535 ($\nu_{C=N}$); 1450 ($\nu_{C=C}$); 1375; 1330; 1312 (δ_{O-H}); 1285; 1249; 1186; 1158; 1075 (δ_{C-O}); 1058; 1045; 952; 875; 810; Anal. Calcd for $C_{16}H_{24}N_4O_2$: C 62.72, H 7.84, N 18.28. Found: C 62.61, H 7.97, N 18.36; MS (EI), m/z : 306 ; 291 ; 275 ; 262; 248 ; 231 ; 217; 188 ; 161; 136 ; 107 ; 67 ; 54 ; 43.

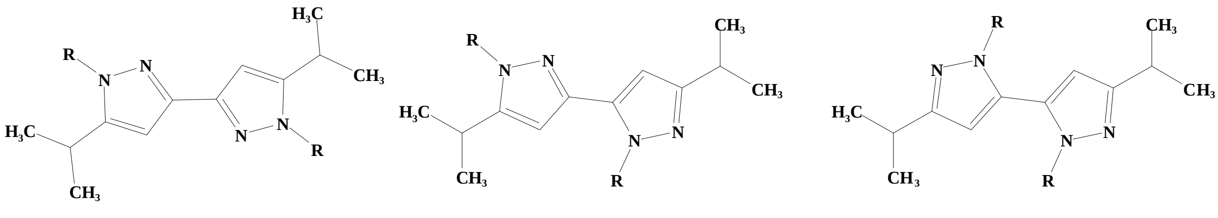
25.5. Extraction experiments

The extraction of metal ions was investigated using nitrate salts. The organic solutions were made by dissolving a weighed amount of the compound in dichloromethane. Liquid-liquid extraction experiments were carried out in a flask by shaking for 2 hours in a thermostated bath [12]. The temperature was maintained constant at 25°C during all the experiments and the pH of 7.00 was controlled with a pH-meter. A solution of (7. 10^{-5} M) of bipyrazole in 25 mL of CH_2Cl_2 was stirred for 2 h with 25 mL of an aqueous solution of metal salt (7. 10^{-5} M). The aqueous phase was separated and analyzed by atomic absorption spectrometry with an air-acetylene flame. Cadmium, copper and lead analysis were performed using Varian A20 double beam Spectrometer equipped with a Varian hollow cathode and a Deuterium background corrector. Single element standards were prepared for these metals from a Merck 1000 µg/mL stock solutions. All standards were made sufficiently acidic to avoid metal hydrolysis and to match content in the sample using nitric acid 65% Suprapur from Merck. All dilutions were made in 50 ml polypropylene tubes (Sarstedt).

3. Results and discussion

3.1. Synthesis of bipyrazole derivatives

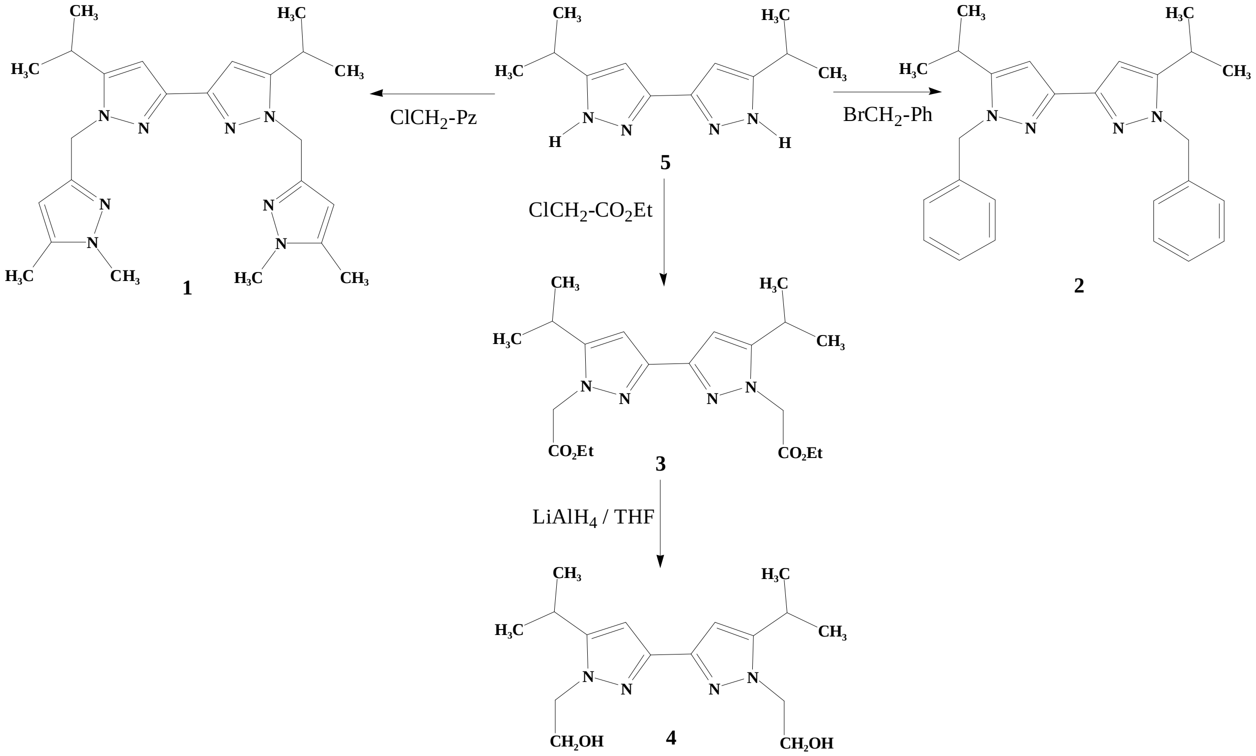
Compounds **2** and **5** have been already reported in an earlier study [13]. Different methods can be used for the synthesis of the final products **1** and **3**. The condensation of alkylhydrazine with 2,9-dimethyl-3,5,6,8-decanetetrone [14] can be used but it gives product mixtures. Since, other method consists on the N-alkylation of 5,5'-diisopropyl-3,3'-bipyrazole **5**. Following this method, we found that the previously reported conditions, such as KI/DMF, K_2CO_3/DMF, K_2CO_3/DMSO, K_2CO_3/THF, tBuOK/DMF, and tBuOK/DMSO gave unsatisfactory low yields and led to the formation of regioisomers mixtures. So the nucleophilic centre is not located on one nitrogen atom; indeed both nitrogen atoms can react. The orientation of the N-alkylation reaction depends strongly on the method used [7, 15]. For the bipyrazole anion of **5** there are three resonance forms, and therefore a regioisomeric mixture of **I**, **II** and **III** would be expected from N-alkylation (**Figure 2**).



I (3, 3') **II (3, 5')** **III (5, 5')**

Fig. 2. Possible isomeric forms

This paper reports direct 3,3'-dialkylation of a 5,5'-diisopropyl-3,3'-bipyrazle **5** with 3-chloromethyl-1,5-dimethylpyrazol [9a, 16] and ethyle chloroacetate using tert-butoxide as a base. This was done in refluxing THF for three hours, which yielded to the corresponding regioselective bipyrazole derivatives **1** and **3**, respectively. Compound **3** was then converted in the presence of lithium aluminium hydride to give a 96 % yield of the hydroxy product **4**.



Scheme 1. General pathway for preparing bipyrazolic compounds

In order to confirm the **1, 3** and **4** tautomeric forms; comparative NMR studies were carried out. Proton NMR spectra of these compounds revealed one signals at 5.42 - 6.52 ppm (**Table 1**) corresponding to the vinylic protons.

Table 1: Comparative study between bipyrazole derivatives

Compd.	*R*	*Yields*	*m.p.(°C)*	*δ C4-H (ppm)*	δ C5 (ppm)	δ C3 (ppm)	δ C4 (ppm)
1	CH_2-pz	41	184	6.43	150.94	148.05	100.22
2	CH_2-ph	92	201	6.52	150.01	143.32	100.50
3	CH_2-CO_2Et	93	120	6.42	151.64	146.36	100.63
4	CH_2CH_2OH	96	205	6.38	151.52	145.69	99.83

Carbone NMR spectra showed one signal at 99.83 - 100.63 ppm corresponding to the pyrazolic carbone at position 4, which clearly exclude the unsymmetrical **II (3,5')** form. Moreover, the **III (5,5')** regioisomer is destabilised by a steric effect. Moreover ^{13}C NMR spectra, revealed signals at 150.01 - 151.61 ppm corresponding to the signal of C5 in the **I (3,3')** form, whereas the corresponding isomer appeared at lower field. The products adopt the **I (3,3')** tautomere forms. These results are in good agreement with the literature [14]. Our new bipyrazolic **1, 3** and **4** as well as compound **2** [13] will be examined for their metal ion extraction ability. All of these compounds are stable at room temperature and their structures have been determined by IR, MS, NMR (^{1}H and ^{13}C) spectroscopy and elemental analysis.

3.2. Liquid-liquid extraction of individual cations

The results given in **Table 2** correspond to the percentages (E%) of extracted cations from solutions of bipyrazoles derivatives **1-4.** The E% of the selected transition metal ions (Cu^{2+}, Pb^{2+}, Cd^{2+}) at pH = 7.00 and t = 25°C were calculated. As can be deduced from **Table 2**, our compounds have no affinity for Cd^{2+}. But bipyrazole compounds **1, 2** and **4** extract copper (II) approximately twice more than the lead (II) cations. The modification of the structure due to the aryl group of the ligand **1** which possesses pyrazolyl nitrogen has no effect on the extraction percentage compared with ligand **2**. These results show that the E% of the selected cations is not affected by the R moieties. The complexation in these conditions is probably controlled by the acyclic bipyrazolic geometries. These modest results don't stop us to look for more and more new efficient extractor nitrogen heterocyclic compounds [17].

Table 2: Extraction percentages (E%) of some metal ions by bipyrazoles derivatives.

Cations	**1**	**2**	**3**	**4**
Cu^{2+}	13	14	18	14
Pb^{2+}	5	7	3	7
Cd^{2+}	1	5	3	2

4. Conclusion

In conclusion, we have prepared a new 3,3'-bipyrazole derivatives. N-alkylation of 5,5'-diisopropyl-3,3'-bipyrazole yields a target products 1,1'-disubstited-5,5'-diisopropyl-3,3'-bipyrazole in regioselective manner. Our results show that copper (II), lead (II) and cadmium (II) are poorly extracted from aqueous solution by bipyrazole derivatives in the present condition of pH and temperature.

5. References

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