

Pyrazolic tripods synthesis and cation binding properties

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The synthesis of two new bipyrazolic tripods with different functionalised arms is described. The complexing properties of these compounds towards heavy metal ions (Hg^{2+} , Cd^{2+} , Pb^{2+}) and alkaline metal ions (K^+ , Na^+ , Li^+) were studied by a liquid–liquid extraction process and the extracted cation percentage was determined by atomic absorption measurements.

Keywords: bipyrazolic tripods, liquid–liquid extraction, cations

For many years, the ability of pyrazole and its derivatives to act as ligands with sp^2 hybrid nitrogen donors has been the subject of research of many coordination chemists. This is evident from the large number of articles, several of them being reviews.^{1,2} In our recent work, a series of acyclic pyrazole compounds containing one, two, three or four pyrazole rings was prepared and demonstrated to extract only the transition metal cations^{3,4} whereas macrocyclic pyrazolic compounds were expected to form stable complexes both with transition and alkali metals.^{5,6}

We now describe the synthesis of two new pyrazolic tripods (Fig. 1) containing mobile chains attached at a nitrogen with or without a donor heteroatom and we study their binding ability towards alkali and transition metal ions. It has been found that a donor atom in a side chain of lariat ethers increases the binding ability of the macrocycle.^{7–9} Furthermore, structures with side arms attached at a nitrogen (N-pivot lariat ethers) instead of a carbon (C-pivot lariat ethers) have stronger binding properties because of greater flexibility, allowing the donor site to have the best binding position.¹⁰

Results and discussion

The route that we used to prepare the pyrazole compounds is shown in Scheme 1. 3-Chloromethyl 1,5-dimethylpyrazole¹¹ was prepared as shown in Scheme 1.

Compound **1** was obtained in a 90 % yield by reacting the chloro derivative with commercially available *para*-aminophenyl ethanol in a ratio of 2:1 under reflux using sodium carbonate as base. Compound **2** was prepared in a 80 % yield in a similar procedure by reacting propylamine with the synthon chloride.

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

Liquid–liquid extraction of individual cations

We used this method in order to study the relative capabilities of pyrazolic tripods **1** and **2** compared to the known compound **3**.^{3,4}

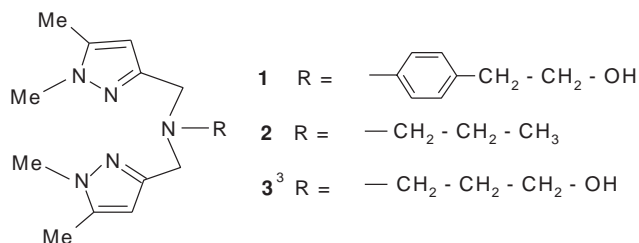


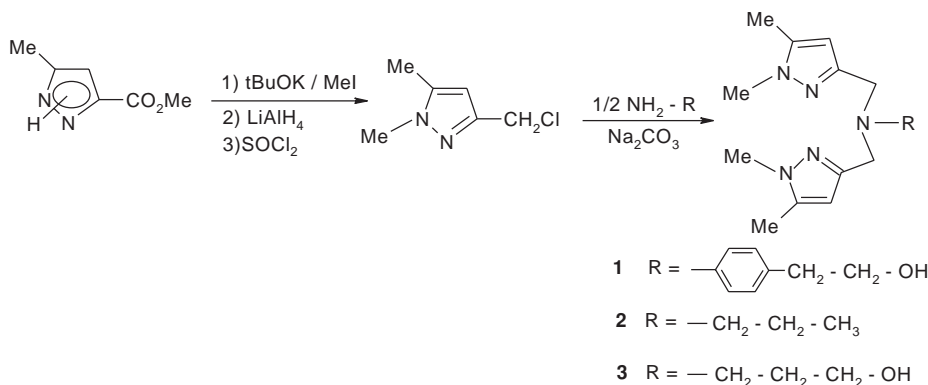
Fig. 1

in extracting Hg^{2+} , Cd^{2+} , Pb^{2+} , K^+ , Na^+ and Li^+ cations. Metal picrates were extracted into the organic phase by complex formation with tripods. The percentage limits of extraction determined by atomic absorption measurements are given in the Table 1.

Results in Table 1 show that by analogy to our previous work^{3–6} in which acyclic pyrazoles extract only the transition metal cations and where the macrocyclic pyrazolic compounds are expected to form stable complexes both with transition and alkali metals, we demonstrate here an affinity of these new acyclic tripods only with the transition metal cations and no complexation was observed toward alkali cations. Their affinity is especially high for mercury. This is not surprising if the high donor properties of nitrogen towards this metal are considered.

Contrary to the literature in which a donor atom in a side chain of a lariat ethers increases the binding ability of the macrocycle,^{7–9} the comparison between **3** with a donor atom in a side chain and **2** without a donor atom shows that there is practically no change in the percentage of complexation. Indeed, we can conclude here that the complexation was due to the tripod nitrogens without contribution of a side arm.

We also notice a small increase of complexation towards Cd^{2+} and Hg^{2+} for the compound **1** probably due to its lipophilic



Scheme 1

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Table 1 Yields of extraction of various heavy and alkali metal ions

	Mercury (1.10 Å)	Cadmium (0.92 Å)	Lead (1.20 Å)	Potassium (1.33 Å)	Sodium (0.98 Å)	Lithium (0.60 Å)
1	50	30	20	0	0	0
2	45	20	20	0	0	0
3 ⁴	42	21	15	0	0	0

character (phenyl), which prevents its dissolution and its loss in the aqueous phase at the time of liquid–liquid extraction.

In conclusion, metal cations and macrocyclic pyrazolic compounds are expected to form stable complexes both with transition and alkali metals, but these new acyclic tripod ligands only form complexes with transition metal cations. They do not complex with alkali metal cations.

Experimental

Synthesis of 1: To acetonitrile (150 ml) containing 3-chloromethyl-1,5-dimethyl pyrazole (4.1×10^{-2} mole) and sodium carbonate (16×10^{-2} mole) was added slowly (2.0×10^{-2} mole) of *para*-aminophenyl ethanol. The mixture was stirred under reflux for 12 h. the solid material was filtered and the filtrate was concentrated under reduced pressure. The residue was purified on alumina using 99/1 $\text{CH}_2\text{Cl}_2/\text{MeOH}$ as eluant to give a 90 % yield of **1** as a viscous oil: ^1H NMR (CDCl_3) δ : 2.20 (s, 6H); 2.72 (t, 2H); 3.70 (s, 6H); 3.75 (t, 2H); 4.45 (s, 4H); 5.91 (s, 2H); 6.80 (d, 2H); 7.00 (d, 2H); Anal. Calc. for $\text{C}_{20}\text{H}_{27}\text{N}_5\text{O}$: C 67.99, H 7.65, N 19.83, Found: C 68.09, H 7.72, N 19.91; m/z : 354 (MH^+); IR: $\nu(\text{OH}) = 3300 \text{ cm}^{-1}$, $\nu(\text{tertiary nitrogen}) = 1100 \text{ cm}^{-1}$.

Synthesis of 2: In similar procedure **2** was obtained in a 80 % yield as a viscous oil: ^1H NMR (CDCl_3) δ : 0.86 (t, 3H); 1.56 (q, 2H); 2.25 (s, 6H); 2.42 (t, 2H); 3.60 (s, 4H); 3.72 (t, 6H); 6.01 (s, 2H); Anal. Calc. for $\text{C}_{15}\text{H}_{25}\text{N}_5$: C 65.45, H 9.09, N 25.45, Found: C 65.52, H 9.12, N 25.36; m/z : 276 (MH^+); IR: $\nu(\text{tertiary nitrogen}) = 1100 \text{ cm}^{-1}$.

Extraction experiments: A solution of 7.10^{-5} M of tripod in 50 ml of CH_2Cl_2 was stirred for 2 h with an aqueous solution (50 ml) of

metal picrates 7.10^{-5} M; the complexation was followed by measuring the concentration of cations in an aqueous solution by atomic absorption. The temperature was maintained constant at 25°C and pH 7 during all the experiments.

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