

Synthesis and Cation Binding Properties of a New Bipyrazolic Tripodal Ligands

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Nitrogenous systems have attracted more attention in these last years due to their interesting properties in coordination chemistry.^{1,2} This aptitude is mainly owed to the presence of sp² hybrid nitrogen donors³⁻⁶ with the involvement in some cases, of other sites donors as oxygen and sulphur atoms.^{7,8} Moreover, polydentate pyrazolic receptors are well known for their ability to complex not only alkali cations⁹⁻¹³ but also to form stable complexes with transition metal ions.¹⁴⁻¹⁷ These complexes are so stable that it is often difficult to obtain the free macrocycles from them.

In our recent work, a series of acyclic pyrazole compounds containing one, two, three or four pyrazole rings were prepared and demonstrated to extract only transition metal cations¹⁸⁻²³ whereas macrocyclic pyrazolic compounds are expected to also form stable complexes with alkali metals.²⁴⁻²⁶

In this paper we describe the synthesis of a new bipyrazolic tripods (Fig. 1) containing a mobile chain attached to the nitrogen with or without a donor heteroatom and we study their binding ability towards alkali and transition metal ions.

Results and Discussion

The route that we used to prepare the target ligands **5-8** is shown in Scheme 1. The development of these structures pass first through the preparation in two steps of the precursor *N*-(2-*p*-toluenesulfonylethyl)-3,5-dimethylpyrazole **4** that possesses a good leaving group, as described in the

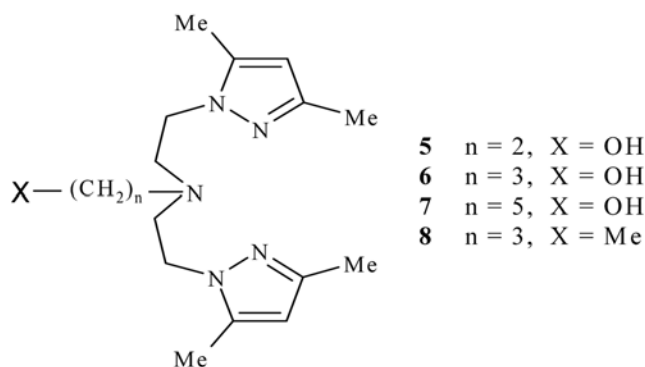


Figure 1. Structures of synthesized bipyrazolic tripods.

literature.²⁷ The condensation of the resulting compound **4** with a series of *n*-aminoalkanols ($n = 2, 3$ and 5) in the presence of an excess of anhydrous sodium carbonate, during 4 days under refluxing acetonitrile afforded the expected tripods with a good yield. Compound **5** was already reported under another way and after 2 weeks of reaction.²⁸

In order to verify the possible effect of the donor heteroatom in the end of the flexible side chain on the cations binding, we have prepared another new tripodal compound **8** without a donor atom in a side arm. This last new compound was obtained using a modified literature method²⁹ owing to the condensation of **4** with butyl amine in presence of sodium hydroxide as a base.

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

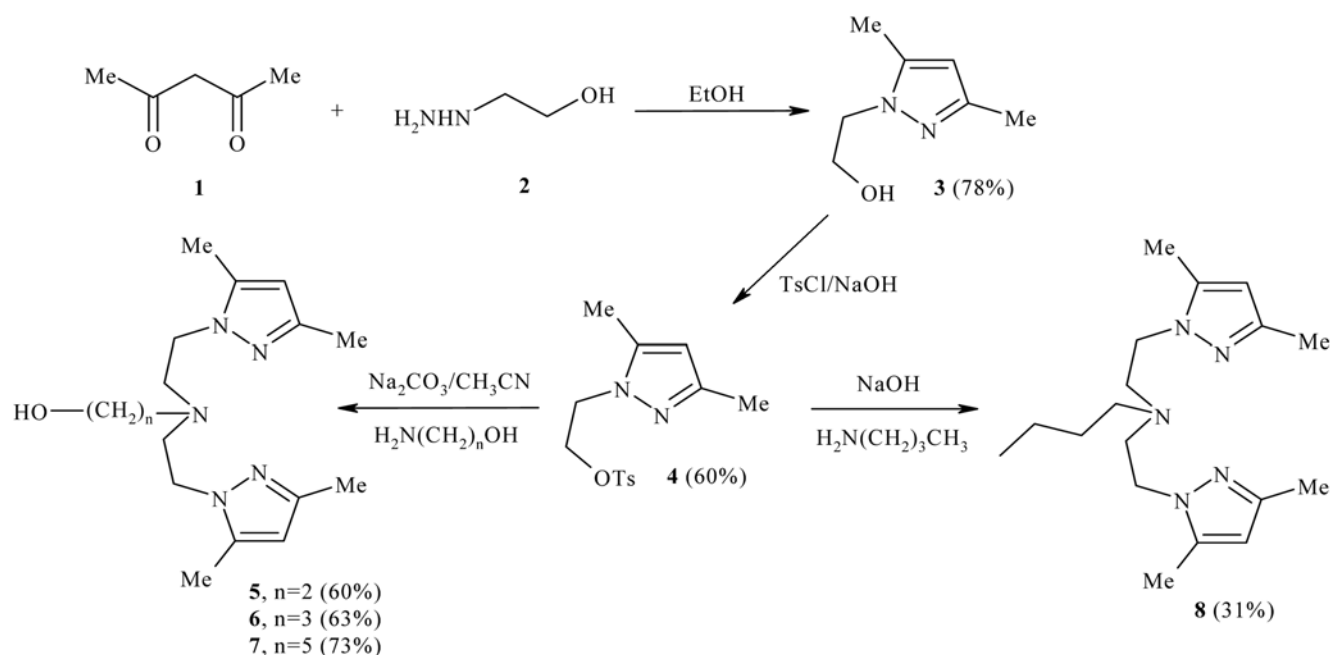
Liquid-liquid extraction of individual cations. Liquid-liquid extraction was used as process to evaluate the relative complexing capabilities of synthesized tripods towards bivalent metal ions (Hg^{2+} , Cd^{2+} , Pb^{2+} , Cu^{2+} and Zn^{2+}) and alkaline metal cations (K^+ , Na^+ and Li^+). Metal nitrates have been extracted into the organic layer by complex formation with tripodal receptors. The percentage limits of extraction have been determined by atomic absorption and the results are given in Table 1.

The results in Table 1 show that in analogy to our previous work¹⁸⁻²⁶ in which acyclic pyrazoles extract only the transition metal cations when the macrocyclic pyrazolic compounds are expected to form stable complexes both with transition and alkali metals, we demonstrate also here an affinity of these new acyclic tripods only with the transition metal cations, with no complexation being observed toward alkali cations.

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

We also notice an affinity toward Cu^{2+} and a zero or a very weak affinity towards all others metals. We can thus suggest an important selectivity for these ligands towards mercury and copper.

Contrary to the literature in which a donor atom in a side chain of a lariat ethers increases the binding ability of the macrocycles,³⁰⁻³² the comparison between tripodal ligands **5-7** with a donor atom in a side chain and **8** without a donor

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

	Hg ²⁺	Cd ²⁺	Pb ²⁺	Cu ²⁺	Zn ²⁺	K ⁺	Na ⁺	Li ⁺
5	26	7	5	30	0	0	0	0
6	25	4	8	20	0	0	0	0
7	27	7	9	22	0	0	0	0
8	28	0	4	17	0	0	0	0

heteroatom shows that there is practically no change in the percentage of complexation of Hg²⁺. Indeed, we can conclude here that the complexation of this cation was due to the tripod nitrogen without contribution of a side arm.

On the other hand, we notice an increase of complexation toward Cu²⁺ for the compound **5** with two carbons in a side chain, compared to the structures **6-8**. This is probably due to the possible contribution of the oxygen in a side arm in the stability of the formed complex, forming thus a five-membered chelating ring which is part of several rings when the whole ligand is considered. It is well known³³ that five-membered ring chelates are more stable than six-membered and four-membered ones. This stable chelates was observed with ZnCl₂ and ligand **5** after being converted to its alkoxide derivative using NaH.²⁸

In conclusion, metal cations and macrocyclic pyrazolic compounds are expected to form stable complexes both with transition and alkali metals, while the new acyclic tripod ligands reported here only form complexes with transition metal cations. They do not complex alkali metal cations at all. Moreover, we can suggest an important selectivity for these ligands towards mercury and copper.

Experimental Section

General procedure for the synthesis of 5-7. To a mixture

of the tosylated product **4** (2 g, 6.80 × 10⁻³ mol) and anhydrous sodium carbonate (2.88 g, 27.21 × 10⁻³ mol) in acetonitrile (40 mL), was slowly added *n*-aminoalkanol (*n* = 2, 3 and 5) (3.40 × 10⁻³ mol) in acetonitrile (10 mL). The mixture was, then, stirred under reflux for 4 days. After filtration and elimination of the solvent under reduced pressure, the obtained residue was purified on silica using the ternary mixture (Ethanol/Ether/CH₂Cl₂: 5/47.5/47.5) as eluant to give a 60%, 63% and 73% yield of **5**, **6** and **7** respectively.

Synthesis of ligand 8. To a solution of sodium hydroxide (0.45 g, 1.25 × 10⁻³ mol) in distilled water (15 mL), was added butyl amine (0.24 g, 3.28 × 10⁻³ mol) then tosylated product **4** (1.94 g, 10.18 × 10⁻³ mol). The mixture was refluxed for 24 h. After cooling, the resulting solution was neutralized with acetic acid and extracted with chloroform. Then, the organic phase was dried on sodium sulfate and the solvent was removed under reduced pressure. The obtained residue was purified on silica using the ternary mixture (Ethanol/Ether/Hexane: 5/47.5/47.5) as eluant to give a 31% yield of **8**.

Supporting information available. The detail of experimental procedures for the synthesis of the ligands and their analytical and spectroscopic data was available in supporting information (www.kcsnet.or.kr/bkcs).

References

1. Trofimenko, S. *Prog. Inorg. Chem.* **1986**, *34*, 115-210.
2. Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943-980.
3. Driessen, W. L.; Wiesmeijer, W. G. R.; Schipper-Zablotskaja, M.; De Graaff, R. A. G.; Reedijk, J. *Inorg. Chim. Acta* **1989**, *162*, 233-238.
4. Veldhuis, J. B.; Driessen, W. L.; Reedijk, J. *J. Chem. Soc. Dalton*

- Trans.* **1986**, 537-541.
5. Pennings, Y. C. M.; Driessen, W. L.; Reedijk, J. *Polyhedron* **1988**, 7, 2583-2589.
6. Blonk, H. L.; Driessen, W. L.; Reedijk, J. *J. Chem. Soc. Dalton Trans.* **1985**, 1699-1705.
7. Dowling, C.; Murphy, V. J.; Parkin, G. *Inorg. Chem.* **1996**, 35, 2415-2420.
8. Haanstra, W. G.; Driessen, W. L.; van Roon, M.; Stoffels, A. L. E.; Reedijk, J. *J. Chem. Soc. Dalton Trans.* **1992**, 481-486.
9. Lupo, B.; Tarrago, G. *Bull. Soc. Chim. Fr.* **1984**, 2, 473-480.
10. Ramdani, A.; Tarrago, G. *Tetrahedron* **1981**, 37, 987-990.
11. Gal, M.; Tarrago, G.; Steel, P.; Marzin, C. *New J. Chem.* **1985**, 9, 617-620.
12. Boudouche, S.; Coquelet, C.; Jacquet, L.; Marzin, C.; Sandeaux, R.; Tarrago, G. *J. Inclusion Phenom.* **1993**, 16, 69-80.
13. Malek, F.; Persin, M.; Ramdani, A.; Sarrazin, J.; Zidane, I. *New J. Chem.* **2002**, 26, 876-882.
14. Elguero, J.; Espada, M.; Ramdani, A.; Tarrago, G. *J. Heterocycl. Chem.* **1980**, 17, 137-142.
15. Marzin, C.; Tarrago, G.; Gal, G.; Zidane, I.; Hours, T.; Lerner, D.; Andrieux, C.; Camp, H.; Saveant, J. M. *Inorg. Chem.* **1986**, 25, 1775-1778.
16. Bol, J. E.; Mars, B.; Gonesh, G.; Driessen, W. L.; Goubitz, K.; Reedijk, J. *Heterocycles* **1997**, 45, 1477-1491.
17. Mary, F.; Marzin, C.; Salhi, S.; Tarrago, G. *Supramol. Chem.* **1993**, 3, 57-61.
18. Attayibat, A.; Radi, S.; Ramdani, A.; Lekchiri, A.; Hacht, B.; Bacquet, M.; Willai, S.; Morcellet, M. *Bull. Korean Chem. Soc.* **2006**, 27, 1648-1650.
19. Attayibat, A.; Radi, S.; Lekchiri, A.; Ramdani, A.; Hacht, B.; Bacquet, M.; Willai, S.; Morcellet, M. *J. Chem. Res.* **2006**, 10, 655-657.
20. Malek, F.; Ramdani, A.; Zidane, I.; Yahyi, A.; Radi, S. *Tetrahedron* **2005**, 61, 2995-2998.
21. Malek, F.; Ramdani, A.; Radi, S. *J. Chem. Res.* **2004**, 9, 640-641.
22. Radi, S.; Ramdani, A.; Lekchiri, Y.; Morcellet, M.; Crini, G.; Janus, L.; Bacquet, M. *New J. Chem.* **2003**, 27, 1224-1227.
23. Radi, S.; Ramdani, A.; Lekchiri, A.; Morcellet, M.; Crini, G.; Morcellet, J.; Janus, L. *Eur. Polym. J.* **2000**, 36, 1885-1892.
24. Radi, S.; Ramdani, A.; Lekchiri, A.; Morcellet, M.; Crini, G.; Morcellet, J.; Janus, L. *J. Chem. Res.* **2003**, 11, 712-714.
25. Radi, S.; Ramdani, A.; Lekchiri, A.; Morcellet, M.; Crini, G.; Janus, L. *Tetrahedron* **2004**, 60, 939-942.
26. Radi, S.; Yahyi, A.; Ramdani, A.; Zidane, I.; Hacht, B. *Tetrahedron* **2006**, 62, 9153-9155.
27. Haanstra, W. G.; Driessen, W. L.; Reedijk, J.; Turpeinen, U.; Hämäläinen, R. *J. Chem. Soc. Dalton Trans.* **1989**, 2309-2314.
28. Jeong, J. H.; Park, Y. D.; Roh, S.-G. *Bull. Korean Chem. Soc.* **2003**, 24, 521-523.
29. Driessen, W. L.; de Graaff, R. A. G.; Parlevliet, F. J.; Reedijk, J.; De Vos, R. M. *Inorg. Chim. Acta* **1994**, 216, 43-49.
30. Schultz, R. A.; Dishong, D. M.; Gokel, G. W. *Tetrahedron Lett.* **1981**, 22, 2623-2626.
31. Davidson, R. B.; Izatt, R. M.; Christensen, J. J.; Schultz, R. A.; Dishong, D. M.; Gokel, G. W. *J. Org. Chem.* **1984**, 49, 5080-5084.
32. Kaifer, A.; Gustowski, D. A.; Echegoyen, L. A.; Gatto, V. J.; Schultz, R. A.; Cleary, T. P.; Morgan, C. R.; Goli, D. M.; Rios, A. M.; Gokel, G. W. *J. Am. Chem. Soc.* **1985**, 107, 1958-1965.
33. Lehn, J. M.; Sauvage, J. P. *J. Am. Chem. Soc.* **1975**, 97, 6700-6707.
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