Liquid -liquid extraction of copper (II), cadmium (II) and lead (II) using tripodal N-donor pyrazole ligands

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Abstract

Two different series of N-donor pyrazole ligands have been used in the liquid-liquid extraction of Cu(II), Cd(II) and Pb(II) ions from aqueous solution using methylene chloride as a solvent. The percentage of extracted metal ion determined by atomic absorption measurements has been analyzed as a function of the ligand structure. It is shown that the ligand capacity to extraction is affected by the nature of the bridge between the central nitrogen atom and the pyrazole rings. The tridentate ligand exhibits a good extractive affinity for copper (II) and lead (II).

Keywords: N-Donor, tripod, extraction, copper (II), lead (II), cadmium (II) and pyrazole

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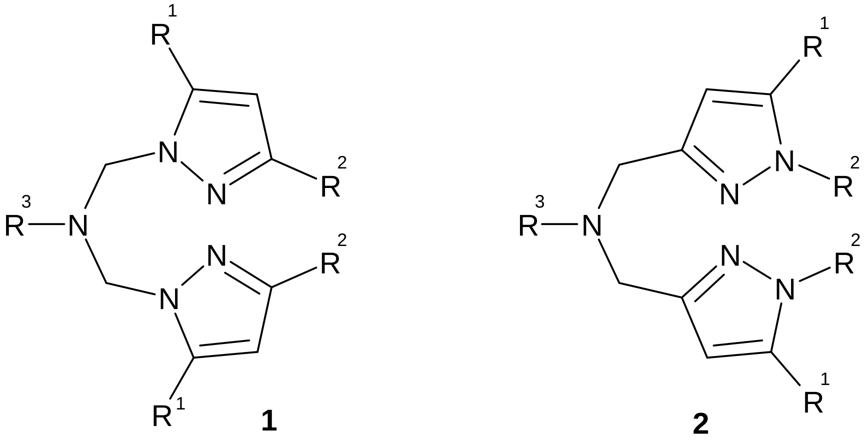
Introduction

Copper (II), cadmium (II) and lead (II) ions are known to be toxic to human health. Selective signaling of heavy metal ions is a very important topic for the detection of toxic metal ions in various chemical systems including living systems. In this field, pyrazole derivatives are currently the subjects of several studies.[1-6] For instance, the N,N-bis[(3,5-dimethylpyrazol-1-yl)methyl]-amines **1** and N,N-bis[(1,5-dimethylpyrazol-3-yl)methyl]-amines **2** are very interesting ligands as potentially donating six electrons in two types of nitrogen donor groups as reported for metal-containing complexes with a benzyl[7] group as R^3 (**Figure 1**).



1 **2**

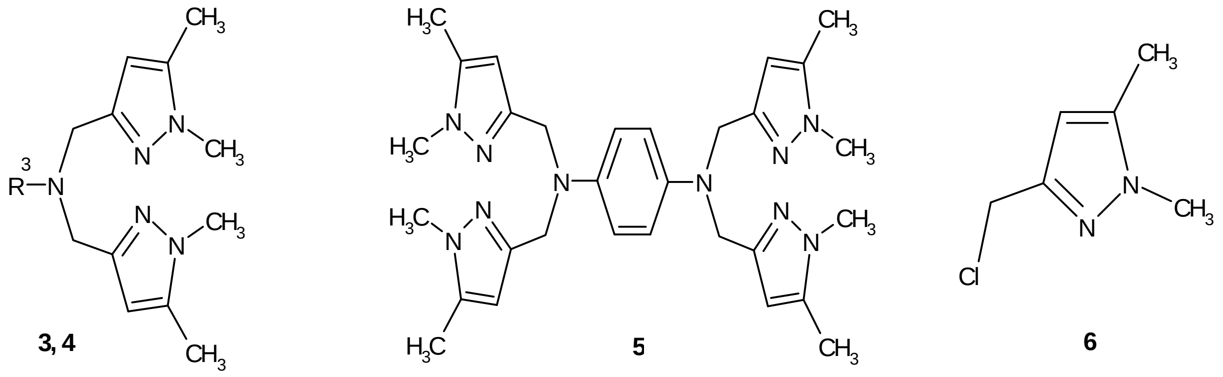
Figure 1

For example, ligand **1** with $R^1 = R^2 = H$ and $R^3 = PhCH_2$ can coordinate Cu(II) cations via the central nitrogen atom and two nitrogen atoms, each from another pyrazole ring, thus acting as six-electron-donating ligands.[7] Interestingly, the same ligand coordinates Zn(II) in a four electron-donating mode via two nitrogen atoms of pyrazole rings.[7] Furthermore, polydentate pyrazolic receptors are well known for their ability not only to complex alkali cations,[8] but also to form stable complexes with transition metal ions.[9] Ligand **2** with $R^1 = R^2 = CH_3$ and $R^3 = HO(CH_2)_3$ can be bonded to a silica gel and presents a good extractive affinity for mercury (II).[10] In our group, the synthesis and the study of extractive properties of a series of N-donor pyrazole compounds containing one, two, three or four pyrazole rings[11-13] has shown that the coordination behavior and the reactivity of the corresponding metal ion complexes can strongly depend on both the electron density on the nitrogen atoms and steric hindrances of substituents R^1, R^2 and R^3. It was therefore interesting to increase the diversity of tridentate ligands **1** and **2** with a view to studying their extractive affinity for metal ions.

In this paper we report the studies of liquid-liquid extraction of heavy metal ions (Cu^{2+}, Pb^{2+} and Cd^{2+}) using eight N-donor tripodal bis(pyrazolyl)amines containing diverse bulky groups linked to the central nitrogen atom, which is attached to the pyrazole rings by two different types of bridges [**C**-C-**N** or **N**-C-**N**].

Results and Discussion

N-Donor tripod ligands (**3-5**) were prepared as previously reported[15] via the condensation of 3-chloromethyl-1,5-dimethylpyrazol (**6**)[14] with aniline, *p*-toluidine in a 2:1 ratio or *p*-phenylenediamine in a 4:1 ratio, using sodium carbonate in refluxing acetonitrile during three hours. **Figure 2** shows the resulting compounds.



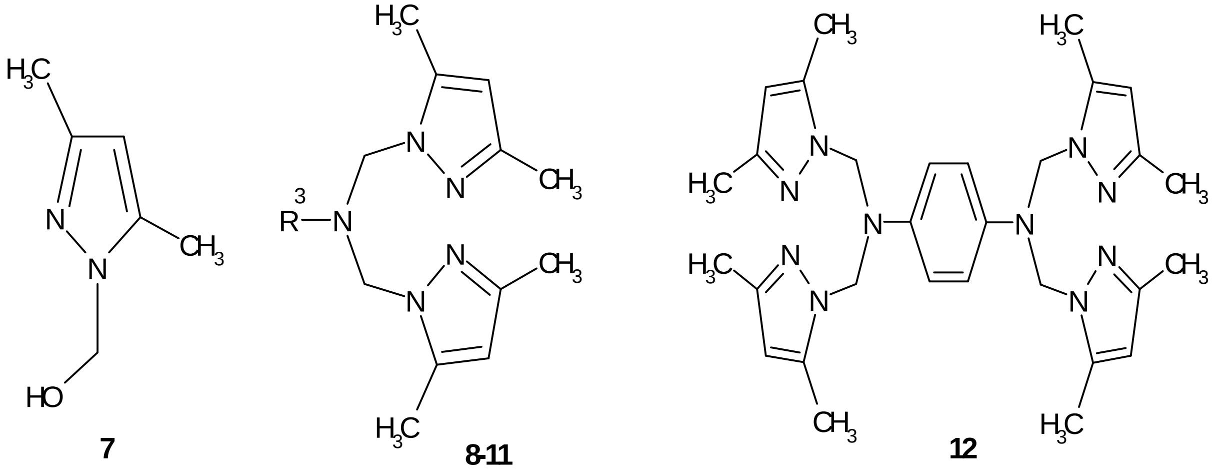
3, 4 **5** **6**

3 : R^3 = C$_6$H$_5$- ; **4** : R^3 = p-H$_3$C-C$_6$H$_5$-

Figure 2

These products are characterized by the presence of **N**-C-**C** junction bond between the central nitrogen atom and the pyrazole rings.

Furthermore, other pyrazolyl derivatives **N**-C-**N** junction ligands **8-12** were prepared by condensation of 1-(hydroxymethyl)-3,5-dimethylpyrazole (**7**)[16] with a series of primary amines as cyclohexylamine,[7] ethanolamine,[17,18] N,N-dimethyl-p-phenylenediamine,[19] benzylamine[20] in 2:1 ratio or p-phenylenediamine[21] in 4:1 ratio (**Figure 3**).



7 **8-11** **12**

8 : R^3 = C$_6$H$_{11}$; **9** : R^3 = HOC$_2$H$_4$; **10** : R^3 = p-(CH$_3$)$_2$NC$_6$H$_4$; **11** : R^3 = C$_6$H$_5$CH$_2$

Figure 3

The influence of different R^3 groups is visible on the chemical shift in ^{1}H NMR of the hydrogen atoms of pyrazolyl groups and of the two hydrogen atoms of the methylene bridges between the central nitrogen atom and the pyrazole rings. As expected, the hydrogen atoms of the pyrazole rings are more strongly influenced by the nature of the R^3 group and the **N**-C-**N** bridge (5.65 ppm for **12** and 5.80 ppm for **8**) than by the nature of the R^3 group and the **N**-C-**C** bridge (5.85 ppm for **4** and 5.90 ppm for **5**). Protons of the methylene groups are affected by both R^3 group and the nature of the bridge as follows from the observed values for **8** (4.85 ppm) and **10** (5.30 ppm; influence of R^3) and **5** (4.35 ppm) versus **12** (5.34 ppm; influence of R^3 and the nature of the bridges between the central atom and the two pyrazole rings) (**Table 1**).

Table 1. Comparison of the ^{1}H NMR chemical shifts between the different products

Product	M. p. (°C)	$^a\delta$ (C4-$\underline{H}$) ppm	$^a\delta$ (pz-C$\underline{H}_2$-N) ppm	$^a\delta$ (C5-C$\underline{H}_3$) ppm
3	132 – 134 [15]	5.86	4.49	2.16
4	98 – 100 [15]	5.85	4.46	2.16
5	184 – 185 [15]	5.90	4.35	2.15
8	96-97 [7]	5.80	4.85	2.30
9	78-80 [17]	5.75	4.93	2.25
10	88-90 [19]	5.68	5.30	1.85
11	71-72 [20]	5.76	4.90	1.96
12	174-175 [21]	5.65	5.34	1.87

[a] Chemical shifts are listed in ppm and are reported relative to tetramethylsilane.

The observed changes in chemical shifts of pyrazole-ring protons (from 5.65 to 5.90 ppm) and of methylene groups (from 4.35 to 5.35 ppm) prove that the introduction of various electron-acceptor and / or bulky substituents to pyrazole rings can be used for tuning the electron density on nitrogen atoms of this potential ligands. Besides, the change of the nature of the bridges between the central nitrogen atom and the two pyrazole rings brings about potentially different coordination behavior in the liquid-liquid extractions of Cu(II), Pb(II) and Cd(II).

Liquid-liquid extractions of individual cations

The tripodal compounds were purified and characterized by NMR, IR, MS spectroscopies and elemental analysis before use. The results given in **Table 2** correspond to the percentages (E%) of extracted cations from solutions using tripodal N-donor pyrazole derivatives. The extraction data with **C**-C-**N** bond compounds **3-5** have been investigated for various cations. The extraction yield for Cu(II) was observed between 12-34%, while for Pb(II) and Cd(II) the E% was lower than 8%. Among these compounds, bis-tripod **5** presents the best efficiency for the extraction of Cu(II) with 34%. This result is probably due to the presence of two coordination units. For the other cations, this phenomenon was not observed. It is clear from these results that our compounds have no affinity for Cd(II) and Pb(II), thus these **C**-C-**N** bond compounds are not efficient for the extraction of these metal ions. These results are probably due to the electrostatic interaction between the cations and the cavity enlarged by the junctions between the pyrazole rings and nitrogen atom.

Table 2. Liquid-liquid extraction percentages of cations by **C**-C-**N** and **N**-C-**N** bond tripods

Metal Ion / Ligand	**3**	**4**	**5**	**8**	**9**	**10**	**11**	**12**
Cu^{2+}	22	12	34	62	25	40	24	44
Pb^{2+}	7	8	6	64	37	4	45	9
Cd^{2+}	4	4	3	1	0	1	3	5

In order to increase the extraction percentage, we have used other N,N-bis(pyrazolyl-1-ylmethyl)amine derivatives (**8-12**). Concerning Cd(II), no extraction of the tested compounds was observed (less than 5%, **Table 2**). These results show an affinity only with Cu(II) and Pb(II) metal ions. In this case, three groups will be distinguished.

- *Case where the central nitrogen atom is linked to the CH_2 moiety* [R-CH_2-N(CH_2pz)$_2$](**9,11**) : The extraction percentages are the same (25%, 24%) for Cu^{2+}. The efficiency was probably controlled by the tripodal cavity. The product **11** is the most efficient for the extraction of lead (45%).
- *Case where the central nitrogen atom is linked to the benzene ring* [R-C_6H_4-N(CH_2pz)$_2$] (**10 ,12**) : Our data show that compound **12** presents a very good extractive affinity for Cu^{2+} (44%) in comparison with Pb^{2+} (9%).
- *Case where the central nitrogen atom is linked to the C_6H_{11} group* [H-C_6H_{10}-N(CH_2pz)$_2$] **8** : This compound extracts separately copper(II) and lead(II) with 62% and 64%, respectively, which indicates a good affinity for these two metal ions.

We also notice an increased complexation of ligand **12** with Cu^{2+} then for its isomer **5** in which the pyrazoles are linked to the benzene ring by **N**-C-**C** junctions. This is consistent with a flexibility induced by **N**-C-**N** junctions. For Pb^{2+}, very high extraction percentages are noted with three tripodal compounds in the order **8** > **11** > **9**. The extraction percentages were influenced by the nature of the R^3 group. With ligand **9**, Pb^{2+} is extracted better than Cu^{2+}, probably due to the partial hydrolysis of the ligand in the presence of the copper(II) salt in solution.[17]

From this screening study, it is possible to draw the following conclusions:

- the ligands having a **N**-C-**N** bridge are more efficient than the tripodes having a **C**-C-**N** bridge;
- copper(II) and lead(II) show the higher extractive affinity for these compounds;
- in the present conditions (25°C and pH = 7.00) cadmium(II) is poorly extracted from aqueous solution by tripode and bis-tripode derivatives;
- For these metal-ligand systems, despite the lack of data for individual complexes, the Irving-Williams[22] stability order of copper (II) > lead (II) > cadmium (II) appears to apply.

Experimental Section

General Procedures. 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[13, 23]. 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 tripod or bis-tripod in 25 mL of CH_2Cl_2 was stirred for 2h 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).

References

1. Roqai, M. C.; Grandmont, G. J. G.; Brunette, J. P. *Analusis* **1998**, *26*, 74.
2. Tsuyoshi, K.; Yoshiki, S.; Yasuo, H.; Hiroshi, M.; Hiroki, W.; Kazumasa, U. *Polyhedron* **2004**, *23*, 283.
3. Claudio, L.; Patricio, P.; Aurora, M.; Alfonso, O. *Bol. Soc. Chil. Quim.* **2001**, *46*, 1.
4. Alfonso, O.; Aurora, M.; Francisco, Z.; Patricion, P. *Microchimica Acta* **2002**, *140*, 201.
5. Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943.
6. Kitajima, N.; Moro-oka, Y. *Chem. Rev.* **1994**, *94*, 737.
7. (a) Driessen, W. L. *J. R. Neth. Chem. Soc.* **1982**, *101*, 441. (b) Touzani, R.; Ramdani, A.; Ben-Hadda, T.; El Kadiri, S; Maury, O.; Le Bozec, H. ; Dixneuf, P. H. *Synth. Commun.* **2001**, *31(9)*, 39.; Sheu S. C.; Tien M. J.; Cheng M. C.; Ho T. I.; Peng S. M.; Lin Y. C. *J. Chem. Soc., Dalton Trans.* **1995**, 3503.
8. Lupo, B.; Tarrago, G. *Bull. Soc. Chim. Fr.* **1984**, *2*, 473.
9. Elguero, J.; Espada, M.; Ramdani, A.; Tarrago, G. *J. Heterocycl. Chem.* **1980**, *17*, 137.
10. Radi, S.; Ramdani, A.; Lekchiri, Y.; Morcellet, M.; Morcellet, J.; Crini, G.; Janus, L.; Bacquet, M. *New J. Chem.* **2003**, *27*, 1224.
11. Radi, S.; Ramdani, A.; Lekchiri, Y.; Morcellet, M.; Crini, G.; Morcellet, J.; Janus, L. *Eur. Polym. J.* **2000**, *36*, 1885.
12. Malek, F.; Ramdani, A.; Zidane, I.; Yahyi, A.; Radi, S., *Tetrahedron* **2005**, *61*, 2995.
13. Radi, S.; Ramdani, A.; Lekchiri, Y.; Morcellet, M.; Crini, G. ; Janus, L. *Tetrahedron* **2004**, *60*, 939.
14. Fifani, J.; Ramdani, A.; Tarrago, G. *Nouv. J. Chem.* **1977**, *1*, 521.

15. (a) Bouabdallah, I.; Ramdani, A.; Zidane, I.; Touzani, R.; Eddike, D.; Radi, S.; Haidoux, A. *J. Chem. Res.*, **2005**, *April*, 242. (b) Bouabdallah, I.; Ramdani, A.; Zidane, I. and Touzani, R. *Molbank*, **2005**, M 397. (c) Bouabdallah, I.; Ramdani, A.; Zidane, I. and Touzani, R. *Molbank*, **2005**, submitted.
16. Dvoretzky I.; Richte G. H. *J. Org. Chem*. **1950**, *15*, 1285.
17. El Kodadi, M.; Malek, F.; Touzani, R.; Ramdani, A.; El Kadiri, S.; Eddike, D. *Molecules* **2003**, *8 (11)*, 780.
18. Malachowski, M. R.; Davidson, M. G.; Hoffman, J. N. *Inorg. Chim. Acta* **1989**, *157*, 91.
19. Bouabdallah, I.; Ramdani, A.; Zidane, I.; Touzani, R. *Molbank*, **2005**, M398.
20. Malachowski, M. R.; Davidson, M. G. *Inorg. Chim. Acta* **1989**, *162*, 199.
21. Bouabdallah, I. *Rapport de DESA* **2001**, Faculté des Sciences, Oujda, Maroc.
22. Irwing, H.; Williams, D.R. J. Chem. Soc. **1953**, *3192*
23. Bouabdallah, I.; Zidane, I.; Touzani, R.; Hacht, B.; Ramdani, A. *Arkivoc*, **2006** (x), 77