PAPER

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Synthesis and extraction properties of multifunctionalized azocalix[4]arenes containing bipyridyl subunits

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A series of four azocalixarene derivatives bearing bipyridyl units and additional functional groups such as amide, ester and pyridine at the phenolic oxygen atoms were synthesized. The conformational properties of these ligands were obtained by ^{1}H NMR spectroscopy. Moreover, extraction properties towards different metals of **1**, **2**, **4**, **5** and **6** using liquid–liquid extraction by atomic absorption spectrometry have been studied and exhibit Ag^+ selectivity.

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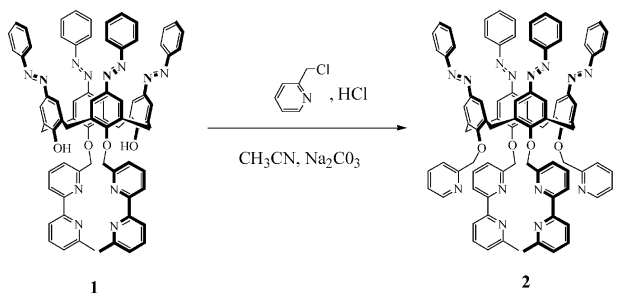
Introduction

Synthetic chromo-ionophores that give rise to specific colour changes on selective complexation with cations have attracted considerable attention as efficient spectrophotometric analytic reagents for the detection of particular species[1] as well as the design of supramolecular devices having recognition and optical sensing functions.[2] Calixarene are useful building blocks in the design of artificial receptors,[3,4] and with the aim of developing new types of optical receptor there has been particular recent emphasis on the synthesis of chromogenic calix[4]arenes.[5] Among these studies azo phenol groups are one of the most frequently employed functions as a signalling device for the design of chromogenic compounds.[6] Moreover, it is now well established that the nature of the substituents both at the upper and lower rims can play an important role in determining the efficiency and the selectivity of cation extraction and complexation by calixarene ligands.[7] For instance, the synthesis and study of the complexation properties of various podands incorporating 2,2′-bipyridyl chelating groups at the lower rim of the *p-tert*-butylcalix[4]arene platform[8,9] show that these groups are good candidates for the selective binding[10,11] and extraction of metal ions.[12] Only few studies, however, have demonstrated the interest of such kinds of complexing structures with the bis(bipyridyl)calixarene displaying in alternate positions two 2,2′-bipyridyl subunits and two opposing chelating groups such as pyridine[9,12,13] or amide.[14] We have recently reported the synthesis of pre-organised azocalixarene–bipyridyl podands for the development of a new class of chromo-ionophore sensors.[15] In order to extend our investigations and to see the additional opportunities offered by the presence of other chelating groups in the azocalixarene bearing bis(bipyridyl) groups, we decided to incorporate two chelating groups such as ester, amide and pyridine in alternate positions with the two bipyridyl groups. This led us to present here the synthesis of four new chromogenic ionophore calixarenes **2**, **4**, **5** and **6** (Scheme 1) which incorporate chelating groups on the lower rim and azophenol as chromophore units on the upper rim with a retention of the cone conformation. The extraction efficiency of these ligands will be discussed.



1 2

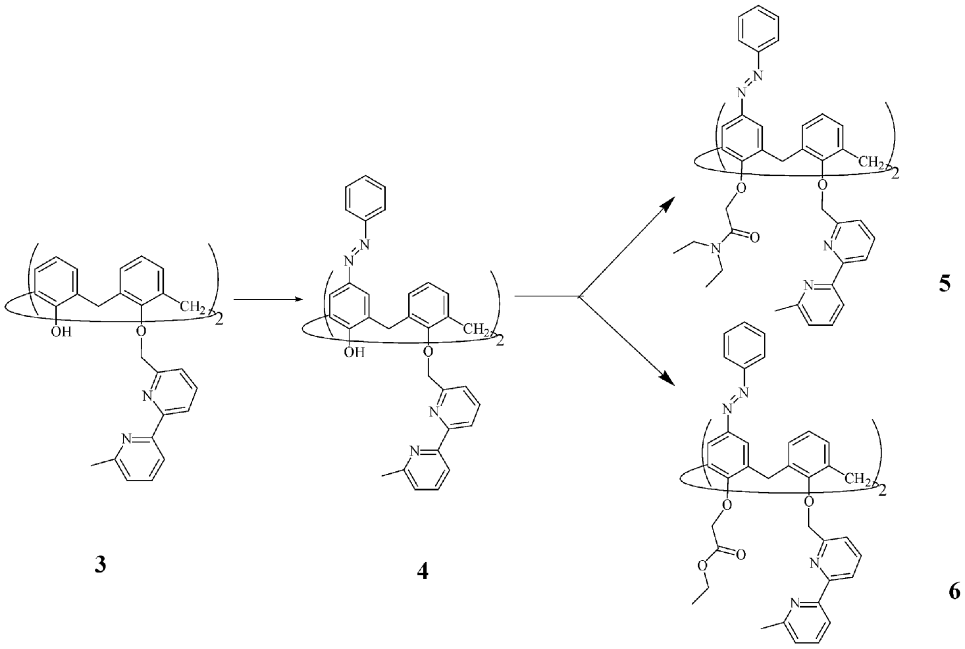
Scheme 1 Synthetic pathway of hetero-functionalized azocalix[4]arene incorporating both bipyridyl and pyridyl groups **2**.

Results and discussion

Synthesis and characterization

First, in order to introduce both pyridyl and bipyridyl groups at the lower rim of the chomogenic calixarene we use the phenylazocalixarene **1** whose synthesis has been described in a previous report.[15] The pre-functionalized calixarene **1** was *O*-substituted at the two residual OH positions using 2-(chloromethyl)pyridine and Na_2CO_3 as base in MeCN at reflux temperature for 48 h (Scheme 1). After purification by column chromatography, the ligand **2** was obtained in 36% yield. We have chosen here the milder base Na_2CO_3 because the use of NaH as base in dry DMF (usually the best conditions to block the calixarene in the cone conformation)[16] gave essentially the starting phenylazocalix[4]arene. The structure of **2** was analysed by ^{1}H and ^{13}C NMR spectroscopy. The ^{1}H NMR spectra show characteristic one single AB system for the bridging methylene groups, a singlet for the OCH_2-*bpy* moieties and a singlet for the OCH_2-*pyridine* moieties. The signal for the bridging methylene groups appears at $\delta = 31.68$ ppm in ^{13}C NMR spectra. These results clearly indicate a cone conformation.[17]

The introduction of ester and amide groups on **1** by the method described above gave very low overall yield. Then this led us to develop a strategy in three steps in order to obtain the ligands **5** and **6**. The intermediate **3** was synthesized for the first time by Beer[18] and was chosen here in order to block the two distal hydroxy groups of calix[4]arene (Scheme 2). Then, diazo-coupling reaction of calix[4]arene **3** with substituted diazonium BF_4^- salt led to **4** in cone conformation (yield: 66%) as described in the literature.[19]

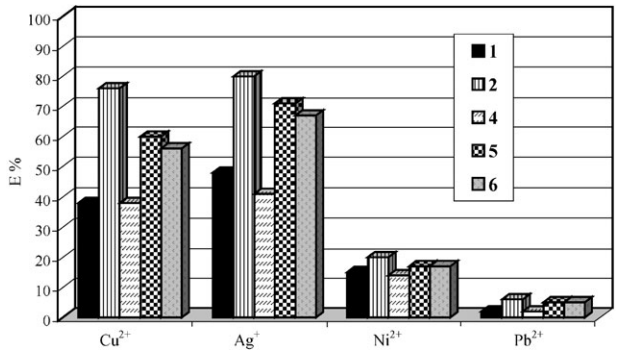


Scheme 2 Synthetic pathway of azocalix[4]arenes incorporating 2,2′-bipyridine units and ester or amide **5**, **6**.

The reaction of **4** with an excess of Na_2CO_3 in dry CH_3CN and then 5 equiv. of α-chloro-*N*,*N*-diethylacetamide at reflux temperature for 48 h afforded ligand **5** in 39% yield. The compound **6** has been obtained from **4** using the same procedure with 5 equiv. of bromoethylester and Na_2CO_3 in acetonitrile (yield: 45%). The cone conformation of these two podands was confirmed by ^{1}H NMR spectra of **5**, **6** that show characteristic one single AB system for the bridging methylene groups, a singlet for the OCH_2-*bpy* moieties. In the corresponding ^{13}C NMR spectra, the signal for the bridging methylene groups appears at $\delta = 32.11$ ppm for **5** and at $\delta = 31.82$ ppm for **6**. These results prove that **5** and **6** are in cone conformation.[17]

Extraction studies

In order to evaluate the ability of azocalixarene derivatives to bind metal ions, liquid–liquid extractions of transition metal ions have been carried out. The percentages of extraction (E%) of Cu^{2+}, Ni^{2+}, Ag^+ and Pb^{2+} at pH 5.3 have been calculated. The results (Scheme 3) indicate some interesting features of the calixarene used. First, we can see that all azocalixarenes **1**, **2**, **4**, **5** and **6** show a selectivity for Cu^{2+} and Ag^+ in comparison with Ni^{2+} and especially Pb^{2+}. Then, the characteristics of the hetero-functionalized compounds **2**, **5** and **6** are dependent on the nature of the groups combined with the bipyridyl groups. If we compare the extraction percentages of Cu^{2+} for podand **1** and **2**, 38% and 76% respectively, it is clear that the presence of the pyridyl groups enhance significantly the extraction ability of the bis(bipyridyl)azocalixarene **1** towards the cations studied. We think that the presence of the nitrogen atom of the pyridyl groups[20] and the basic characteristic of these units increase the affinity of the podand for metal ions as Cu^{2+} and Ag^+. The results for the compounds **5** and **6** indicate that the amide and ester groups improve efficiency the extractability of Ag^+ and Cu^{2+} in comparison with the podand **4**. The amide groups lead to a slightly higher efficiency for Ag^+ (71%) and Cu^{2+} (60%) than the ester groups, as is predictable from the behaviour of the homo-substituted calixarene.[7] Moreover, if we compare the compounds **1** and **4** which are substituted on the lower rim of the calixarene by only two bipyridyl groups, we can observe that they have same affinity for all metals ions studied except for Ag^+. Indeed the podand incorporating four phenylazo groups on the upper rim of calixarene extracts Ag^+ more efficiency in comparison with the podand containing only two phenylazo groups. Therefore, we can suppose by analogy with Nomura's report[21] that the phenylazo groups have a slight binding ability towards only Ag^+ and thus enhanced the extraction ability of the podand **1**.



Scheme 3 Extraction percentages of cations as a function of the nature of the ligands.

These new podants exhibit superior or equal extractabilities for Cu^{2+} and Ag^+ (>50%) than other ionophores calixarenes.[12,22] Moreover, chromo-ionophores based upon calix[4]-arene diamide or diester and bearing two distal azophenol units exhibits mainly a high selectivity towards alkaline earth metal (Li^+, Na^+ and Ca^{2+}).[23]

Conclusion

We have synthesized three "hybrid" phenylazocalix[4]arenes incorporating two bipyridyl subunits on the lower rim of the macrocycle. These compounds extract Cu^{2+} and Ag^+ efficiently. But the most efficient among the five studied compounds is the azocalixarene incorporating both bipyridyl and pyridyl groups. Their extraction properties towards some other metal ions are under investigation.

Experimental

General

Solvents were purified and dried by standard methods prior to use. All reactions were carried out under nitrogen. Column chromatography was performed with silica gel 60 (0.040–0.063

mm) from Merck. Melting points were recorded on an Electrothermal 9100 capillary apparatus and were uncorrected. UV measurements were recorded on a Shimadzu UV-2401 PC spectrophotometer, λ_{max} in nm. Infrared measurements were performed on a Mattson 5000 FT apparatus (ν in cm^{-1}). ^1H and ^{13}C NMR spectra were recorded on a Brucker AM 300 (300.13 and 75 MHz), (chemical shifts in ppm, J in Hertz). Mass spectra were obtained by electrospray technique (positive mode).

5,11,17,23-Tetra(azophenyl)-25,27-di[(6-(6′-methyl-2,2′-bipyridine)-yl)methoxy]-26,28-di[pyridine-2-yl)methoxy]calix[4]arene (2). 5,11,17,23-Tetra(phenylazo)-25,27-di[(6-(6′-methyl-2,2′-bipyridine)-yl)methoxy]-26,28-di(hydroxy)calix[4]arene[18] **1** (0.1 g, 0.83 10^{-4} mol) and Na_2CO_3 (0.132 g, 1.2 mmol) were stirred in refluxing CH_3CN (25 ml) under nitrogen for 1 h. The resulting mixture was then cooled to room temperature and 2-chloromethylpyridine hydrochloride (0.068 g, 0.41 mmol) was added in one portion. The mixture was then heated under reflux for 48 h. After evaporation to dryness, the residue was dissolved in CH_2Cl_2 (40 ml) and washed with water (3 × 30 ml). The organic phase was dried over Na_2SO_4 and removed by evaporation. The product was purified by chromatography column on silica gel (AcOEt/hexane; 8/2) to give **2** as a red powder (0.042 g, 36%). Mp: 183–184 °C.^1H NMR (CD_2Cl_2): 2.64 (s, 6H, CH_3-*bpy*); 3.81, 4.70 ('q', AB, J_{AB} = 13.3, 8H, Ar–CH_2–Ar); 5.05 (s, 4H, OCH_2-py); 5.65 (s, 4H, OCH_2-*bpy*); 7.16 (d, J = 7.5, 2H, H-*bpy*); 7.24 (d, J = 7.7, 2H, H-*bpy*); 7.48-7.59 (m, 12H, H–Ar(azo)); 7,69 (s, 4H, H–Ar); 7.71–7.74 (m, 4H, H-*bpy*); 7.76–7.90 (m, 8H, H–Ar(azo)); 7.96 (s, 4H, H–Ar); 8.10 (m, 4H, H-py); 8.25 (d, J = 7.8, 2H, H-*bpy*); 8.35 (m, 2H, H-py); 8.45 (d, J = 7.8, 2H, H-*bpy*); 8.52 (m, 2H, H-py). ^{13}C NMR (DMSO): 25.24 (CH_3-*bpy*); 31.68 (Ar–CH_2–Ar); 72.72 (OCH_2-*bpy*); 73.75 (OCH_2-py); 122.94, 124.25, 124.98 , 129.54, 129.63, 129.69, 130.12, 131.27, (C(H), bpy and py); 131.60, 131.93, 132.05, 133.07, 133.21 (C(H)–Ar); 128.49, 131.73, 131.92, 132.35, 134.10, 134.40, 145.92 (C–Ar); 148.0, 152.99, 155.90, 155.60, 156.43 (C-py, C-bpy). ES-MS m/z: 1388.5 $[M + H]^+$; 1410.4 $[M + Na]^+$ (calcd. 1388.2 $[M + H]^+$; 1410.2 $[M + Na]^+$). UV: 269 (58320); 289 (62380), 317 (48500); 432 (7360). IR: 3103 (Csp^2-H); 2922 (Csp^3-H); 1507, 1472, 1445 (C═C); 1591 (C═N); 1116 (C–O–C).

5,17-Di(phenylazo)-25,27-di[(6-(6′-methyl-2,2′-bipyridine)-yl) methoxy]-26,28-di(hydroxy)calix[4]arene (4). A mixture of 25,27-[(4-methyl-2,2′-bithiazolyl-4′-yl)methoxy] 26,28-bis (hydroxy)calix[4]arene **3** (0.22 g, 0.28 mmol) and the benzenediazonium BF_4^- salt (0.84 mmol) were dissolved in THF (30 ml). The reaction was initiated by the addition of pyridine (1 ml) to the cooled THF solution at 0 °C. After 48 h, the orange precipitate was recovered by filtration and washed with methanol. The product was recrystallised with CH_2Cl_2/MeOH (98/2) affording **4** as an orange powder (0.187 g, 66%). Mp: 197-198 °C. ^1H NMR ($CDCl_3$): 2.66 (s, 6H, CH_3-*bpy*); 3.46, 4.48 ('q', AB, J_{AB} = 13.2, 8H, Ar–CH_2–Ar); 5.28 (s, 4H, OCH_2-*bpy*); 6.71-6.85 (m, 2H, H-*bpy*); 6.93-7.06 (m, 6H, H–Ar); 7.11-7.16 (m, 6H, H–Ar(azo)); 7.49-7.52 (m, 2H, H-*bpy*); 7.61-7.69 (m, 4H, H–Ar(azo)); 7.81 (m, 4H, H–Ar); 7.87 (d, J = 7.7, 2H, H- *bpy*); 8.07-8.15 (m, 2H, H-*bpy*); 8.23 (d, J = 7.6, 2H, H-*bpy*); 8.36 (d, J = 7.6, 2H, H-*bpy*); 8.65 (s, 2H, OH).^{13}C NMR (CD_2Cl_2): 24.68 (CH_3-*bpy*); 32.13 (Ar–CH_2–Ar); 79.71 (OCH_2-*bpy*); 118.71, 121.44, 122.82, 122.88, 122.94, 123.78 (C(H)-*bpy*); 124.62, 129.40, 129.49, 130.70, 130.99, 138.57 (C(H)–Ar); 128.68, 128.97, 134.08, 137.44, 147.16, 148.05, 152.25, 152.97, 153.13, 154.63 (C–Ar, C-*bpy*). ES-MS m/z: 1003.3 $[M + H]^+$ (calcd. 1003.15). UV: 291 (31600), 300 (30954); 333 (29478); 440 (5176). IR: 3330 (OH); 3176 (Csp^2-H); 2925 (Csp^3-H); 1593 (C═N); 1523, 1471, 1444 (C═C); 1114 (C–O–C).

5,17-Di(phenylazo)-25,27-di[(6-(6′-methyl-2,2′-bipyridine)-yl)methoxy]-26,28-di[[(*N*,*N*-diethylaminocarbonyl) methoxy])-calix[4]arene (5). A solution of **4** (0.08 g, 0.8 10^{-4} mol) in dry CH_3CN (20 ml) was heated under nitrogen for 1 h at 80 °C with Na_2CO_3 (0.127 g, 1.2 mmol). α-chloro-*N*,*N*-diéthylacetamide (0.054 g, 0.36 mmol) was then added and reflux continued for 28 h. After evaporation to dryness, the residue was dissolved in CH_2Cl_2 (40 ml) and washed with 2 × 10 ml HCl (1 M) and with water (2 × 20 ml). The organic phase was dried over $MgSO_4$ and removed by evaporation. The residue was dissolved in low amount of CH_2Cl_2 and MeOH was then added. The resulting precipitate was purified by chromatography column on silica gel (AcOEt/Hexane: 7/3) to give 5 as a red powder (0.038 g, 39%). Mp: 194–195 °C. ^1H NMR ($CDCl_3$): 1.12 (t, 12H, NCH_2CH_3); 2.64 (s, 6H, CH_3-*bpy*); 3.38, 4.24 ('q', AB, J_{AB} = 13.2, 8H, Ar–CH_2–Ar); 3.84 (q, J = 6.4, 4H, NCH_2CH_3); 4,07 (q, J = 6.2, 4H, NCH_2CH_3); 4.42 (s, 4H, OCH_2–CO); 5.29 (s, 4H, OCH_2-*bpy*); 6.56-6.67 (m, 6H, H–Ar, 2H, H-*bpy*); 6.78-6.82 (m, 4H, H-*bpy*); 6.98-7.14 (m, 6H, H–Ar(azo), 4H, H–Ar); 7.44 (t large, 2H, H-*bpy*); 7.56 (m, 4H, H-Ar(azo)); 7.61 (d, J = 7.7, 2H, H-*bpy*); 7.76 (d, J = 7.7, 2H, H-*bpy*).^{13}C NMR (CD_2Cl_2): 13.25 (NCH_2CH_3); 14.47 (NCH_2CH_3); 25.16 (CH_3-*bpy*); 32.11 (Ar–CH_2–Ar); 40.70 (NCH_2CH_3); 41.35 (NCH_2CH_3); 72.91 (OCH_2–CO); 73.81 (OCH_2-*bpy*); 122.96, 123.57, 124.36, 124.48, 130.75, 131.06 (C–H *bpy*); 122.72, 122.90, 129.35 (C(H), Ar); 128.86, 130.95, 134.70, 146.03, 150.06, 152.92 (C–Ar); 153.32, 156.86, 159.92, 162.41 (C-*bpy*); 167.40 (CO). ES-MS m/z: 1223.3 $[M + H]^+$ (calcd. 1223.4). UV: 285 (130380); 301 (112720); 334 (98620); 432 (10480). IR: 3069 (Csp^2-H); 2970 (Csp^3-H); 1738 (C═O); 1567, 1468, 1447 (N═N, C═C); 1584 (C═N).

5,17-Tetra(phenylazo)-25,27-di[(6-(6′-methyl-2,2′-bipyridine)-yl)methoxy]-26,28-di[(ethoxycarbonyl)methoxy] calix[4]arene (6). A solution of **4** (0.08 g, 0.8 10^{-4} mol) and Na_2CO_3 (0.126 g, 0.12 mmol) were stirred for 2 h under nitrogen in dry acetonitrile (20 ml) at room temperature. After the addition of ethyl bromoacetate (0.066 g, 0.4 mmol), the mixture was heated at 60 °C for 48 h. After evaporation to dryness, the residue was dissolved in CH_2Cl_2 (40 ml) and washed with a saturated aqueous ammonium chloride solution (10 ml) and water (2 × 20 ml). The organic phase was dried over Na_2SO_4 and removed by evaporation. The product was purified by chromatography column on silica gel (AcOEt/hexane: 8/2) to give 6 as an orange powder (0.042 g, 45%). Mp: 205–206 °C. ^1H NMR ($CDCl_3$): 1.24 (t, J = 7, 6H, OCH_2CH_3); 2.63 (s, 6H, CH_3-*bpy*); 3.29 4.53 ('q', AB, J_{AB} = 13.1, 8H, $ArCH_2Ar$); 4.12 (q, 4H, OCH_2CH_3); 4.35 (s, 4H, OCH_2CO_2Et); 5.70 (s, 4H, OCH_2-*bpy*); 6.48-6.50 (m, 6H, H–Ar); 7.07-7.09 (m, 4H, H-*bpy*); 7.44-7.51 (m, 6H, H–Ar(azo)); 7.60 (s, 4H, H–Ar); 7.76 (m, 4H, H-*bpy*); 7.85 (m, 4H, H–Ar(azo)); 7.98 (d, J = 7.7, 2H, H-*bpy*); 8.42 (d, J = 7.7, 2H, H-*bpy*). ^{13}C NMR (C_5D_5N): 14.29 (OCH_2CH_3); 23.68 (CH_3-*bpy*); 31.82 ($ArCH_2Ar$); 61.48 (OCH_2CH_3); 73.72 (OCH_2CO_2Et); 75.02 (OCH_2-*bpy*); 123.17, 123.67, 124.96, 126.43, 129.36, 130.24 (C–H *bpy*); 123.95, 132.97, 129.81, 130.94, 150.39, 151.56 (C(H)–Ar); 129.36, 132.97, 135.35, 136.00, 146.88, 149.70, 150.42, 152.34, 153.59, 157.11 (C–Ar and C-*bpy*); 170.51 (CO_2Et). ES-MS m/z: 1169.2 $[M + H]^+$ (calcd. 1169.3). UV: 290 (37032); 303 (34256); 333 (34216); 431 (2776). IR: 3062 (Csp^2-H); 2931 (Csp^3-H); 1736 (C═O); 1544, 1472, 1437 (C═C); 1584 (C═N); 1117 (C–O–C). ES-MS m/z: 1570.7 $[M + H]^+$ (calcd. 1570.8). UV: 286 (159200); 302 (shoulder 129320); 334 (111080). IR: 3058 (C–H), 1469, 1440 (N═N,C═C). 1584 (C═N).

Spectrocopic measurements

The extractions of metal ions (Ag^+, Cu^{2+}, Ni^{2+}, Pb^{2+}) by the compounds **2**, **4**, **5** and **6** were investigated using acetate and

nitrate salts. The organic solutions were made by dissolving a weighed amount of the ligand in dichoromethane. The aqueous solution was buffered to pH 5.3 with CH_3COOH (99%, Acros) (1.8×10^{-3} M) and CH_3COONa (99%, Fluka) (8.2×10^{-3} M) and the ionic strength was maintained at $\mu = 0.1$ with KCl (98%, Acros). Liquid–liquid extraction experiments were carried out in a flask by shaking for 12 h in a thermostated bath (30 °C), 25 ml of an aqueous phase containing metal salt (1.06×10^{-4} M) and 5 ml of organic phase containing **2**, **4**, **5** and **6** (5.3×10^{-4} M). The aqueous phase was separated, centrifuged, then 1% of HNO_3 was added to these solutions and analysed by atomic absorption spectrometry (Perkin Elmer 3110) with an air–acetylene flame, the measurements being carried out using standard conditions calibration. The percentages of extraction (E%) were determinated from eqn. (1).

$$E\% = ([M]_{blank} - [M]_{final})*100/[M]_{blank} \quad (1)$$

Where $[M]_{blank}$ and $[M]_{final}$ represent the metal concentration in the aqueous phase extracted with pure dochloromethane and with the dichloromethane solutions containing ligands respectively.

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