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New macrocycles derived from biphenyl for pH-switched solvent extraction

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Abstract—Four new fluorescent macrocyclic ligands derived from biphenyl are described. The new compounds have been used in liquid–liquid extraction experiments and the influence of pH has been studied in those ligands containing carboxylic groups. The results obtained for the latter ligands have been compared with those observed in the presence of an external acid.

1. Introduction

Solvent extraction belongs to one of the most important processes in water treatment and hydrometallurgical metal winning. The design of the complexing agents plays an important role in such processes. In the solvent extraction of metal ions it is now well established that a variety of ligand types can be employed as the extracting agent and, for example, can form chelate or solvated complexes with metal ions.[1] In particular, macrocyclic ligands, such as certain crown compounds, complex cations selectively and have played an important role in the separation and recovery of toxic metals from waste water.[2] For macrocyclic polyethers, the strong influence of the ligand topology on the extraction efficiency has been well established.[3] On the other hand, the presence of additional functional groups sensitive to the medium pH have been used to regulate complexation and to improve extraction under chosen conditions.[4] In particular, crowns with pendant acidic arms can bind and extract metal ions in the form of their neutral complexes.[5]

For several years our research group has been interested in the preparation of crown ethers derived from biphenyl for use, not only in cation sensing, but also in solvent extraction as well as for use as ionophores for transport experiments across organic membranes.[6] We now report the preparation of five new functionalized ligands of the above type in order to study their efficiency in extraction experiments under different pH conditions (Chart 1).

2. Discussion and results

Ligand **1** has been previously reported. Ligands **3** and **4** were easily prepared by direct reaction of 2-chlorocarbonyl-2′-methoxycarbonyl-4,4′-dinitrobiphenyl with 2-hydroxymethyl-18-crown-6 and 4,13-diaza-18-crown-6, respectively. Hydrolysis of ligands **1** and **4** gave rise to compounds **2** and **5**, respectively, in high yield (Scheme 1).

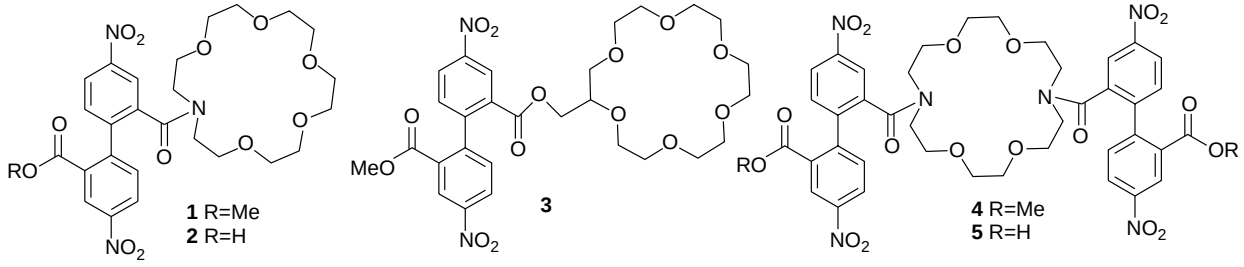

Chart 1.

Keywords: Extraction; pH-switched ligands; Biphenyl; Cations.
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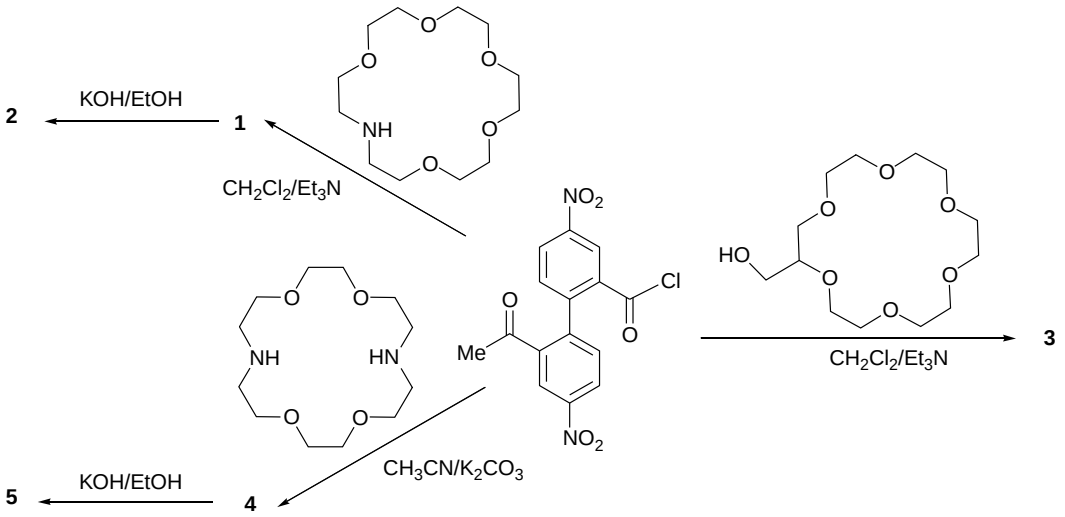

Scheme 1.

2.1. Liquid–liquid extraction studies

In order to evaluate the potential of the newly prepared compounds as extracting agents and also the influence of pH on the extraction efficiency, liquid–liquid extraction of several metal cations (Na^+, Cs^+, Ag^+, Zn^{2+}, Eu^{3+}) were conducted using the extraction system metal salt/acid–buffer–H_2O/ligand–chloroform. It is well established that the efficiency of extraction by a lipophilic ligand is influenced by the nature of counter anions, which accompany the cation–ligand complex.[7] To compare the efficiency of the ionophores, experimental conditions need to be carefully controlled as does the nature of the companion anions. The experiments were carried out under different pH conditions in order to determine the influence of the free carboxylic groups on extraction efficiency. Preliminary extraction experiments showed a very poor efficiency for all ligands towards the alkali cations Na^+ and Cs^+. The influence of pH was studied between pH=2.7 and 7.6 and also the effect of different counter anions (picrate, NO_3^-, ClO_4^- and Cl^-) was investigated but no substantial change in extraction were observed. Only ligand **3** was found to extract cesium picrate with an efficiency that was independent of the pH. However, the extraction with this ligand **3** was more than seven times lower than for 18-C-6. The loss of efficiency observed with ligand **3** can be related to the presence of the biphenyl unit that tends to inhibit complexation. The stoichiometry of the complexes formed with both ligands (18-C-6 and **3**) and cesium picrate was in each case 1:1 and the extraction constants were log K_{ex}=4.5 and 3.6, respectively. Experiments carried out with sodium salts demonstrated that the extraction was always negligible even though a range of experimental conditions were used. In addition, experiments for Ag^+ also showed most efficient extraction occurs for **3** to form a 1:1 complexes with silver picrate with a log K_{ex}=3.8.

The results obtained in the experiments involving Zn^{2+} and Eu^{3+} were more interesting. Thus, the extractability showed by ligands **1**–**5** at pH=2.4 (HPic) was negligible; however, clearly different results were observed under basic conditions. Thus, data for extraction of $ZnCl_2$ with ligands **1**–**5**, at pH=8.6–8.7, are presented in Figure 1. Under basic conditions, extractabilities using **2** and **5** were strongly enhanced when compared with the behaviour of **1** and **4**, respectively (from 0.7% for **1** to 75.5% for **2** and from 5.4% for **4** to 90.3% for **5**).

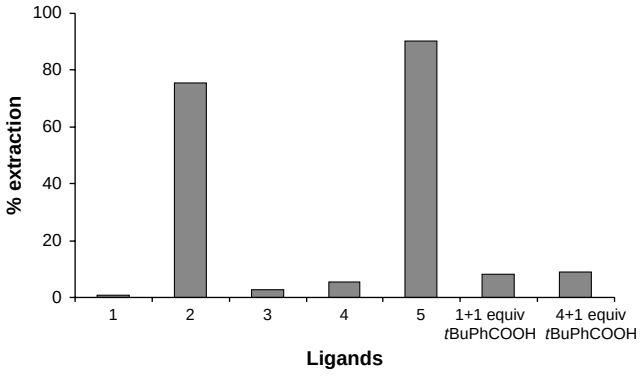

Figure 1. Extraction of Zn^{2+} from aqueous AMP buffer solutions (pH=8.6–8.7) with ligands **1**–**5** in chloroform. $[ZnCl_2]=2.10^{-4}$ M, $[L]=10^{-3}$ M.

To confirm that the presence of additional carboxylic groups in the ligands is responsible of the observed strong extraction increments, additional experiments for **1** and **4** in the presence of external acid were carried out.[8] The results obtained (shown in Fig. 1) demonstrate that the effect of the carboxylic groups is only important when they are included as part of the ligand structure and complex through intramolecular interactions.

Similar studies were carried out with $Eu(ClO_4)_3$ under different pH conditions and the results obtained are illustrated in Figure 2.

As was expected, the influence of the pH on extraction with ligands **1** and **4** is essentially negligible, with only a small increment being observed at higher pH. In contrast, the ligands incorporating carboxylic groups in their structures are more sensitive to pH. Thus, **2** leads to a clear increase in

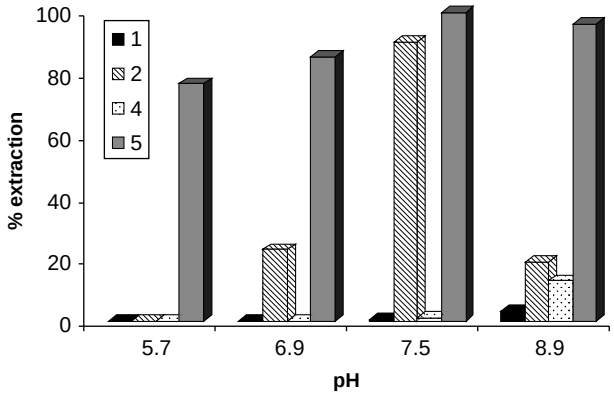

Figure 2. Extraction of $Eu(ClO_4)_3$ from aqueous solution with ligands **1**, **2**, **4** and **5** in chloroform at different pH values. $[Eu(ClO_4)_3]=10^{-4}$ M, $[L]=10^{-3}$ M.

extraction when the pH was higher than 7. Similar behaviour was observed with ligand **5**; this gives rise to high extraction values even at pH=5.7. This behaviour is in accord with pK_a values for **2** ($pK_a=5.28\pm0.3$) and **5** ($pK_a1=4.76\pm0.2$ and $pK_a2=6.06\pm0.3$) determined by potentiometry in dioxane/water 70:30.

Additional experiments were carried out to investigate the type of complexes formed by **2** and **5** under different conditions and the results are summarised in Table 1.[9] Thus, it was determined that the complex formed by **2** had a L_2M stoichiometry with $\log K_{ex}=8.7$ when the buffer was HEPES (Fig. 3). By contrast, when the buffer was AMP no extraction was observed even though the pH of the solution was the same.

Table 1. $Eu(ClO_4)_3$ extraction studies with ligands **2** and **4**

Ligand	Acid	Buffer	pH	Extraction (%)	Stoichiometry	Log K_{ex}
2	$HClO_4$	AMP	5.3	0	—	—
2	$HClO_4$	HEPES	5.2	3.96	2:1	8.7
4	$HClO_4$	AMP	4.6	8.99	2:1	4.7
4	$HClO_4$	HEPES	5.3	99.34	1:1	11.2

Complex stoichiometry and log K determinations under different experimental conditions.

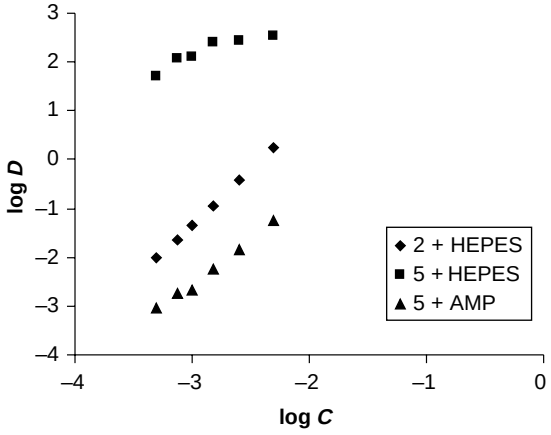

Figure 3. Plot of log D versus log c_L for $Eu(ClO_4)_3$ extraction for ligands **2** and **4** at different pH values.

In the case of **4**, more interesting behaviour was observed since the stoichiometry appears to be a function of pH. Thus, a 2:1 stoichiometry was assigned at pH=4.6, changing to 1:1 at pH=5.3.

2.2. Spectroscopic studies

In order to obtain additional information about the structure of these ligands a number of spectroscopic measurements were carried out. ^{1}H NMR spectra in CD_3CN were obtained for the complexes formed by **2** and **5** with $Eu(ClO_4)_3$. Figure 4 shows the ^{1}H NMR spectra of free **5** and this ligand after addition of 0.5 equiv of Eu^{3+} in CD_3CN. Significant upfield shifts were observed for the protons on the crown moiety suggesting that the complexation involves the crown cavity. In addition, a broadening on the signals corresponding to one of the aromatic rings in the biphenyl systems was also observed. The other aromatic protons are less affected (Table 2). Similar proton NMR shifts and line broadening have been reported for the complexation of Eu^{3+} with a crown ether.[10]

The IR absorption spectral data of the free ligands **2** and **5** and their Eu^{3+} complexes are summarized in Table 3. The shift of the CC–O stretching frequencies arising from the polyether ring, 1115 cm^{-1} in **2** and 1110 cm^{-1} in **5** to 1096 and 1098 cm^{-1}, respectively, for their corresponding complexes, is in keeping with complexation of Eu^{3+} with the cavity oxygens. On the other hand, the amide band I in the 2:1 complexes compared to the bands for the free ligands shows a displacement to lower frequencies, suggesting some coordination by the carbonyl oxygen atom.[11] In comparison, almost no change was observed in the frequency of the acid carbonyl group under the above conditions.

Finally, a clearly different situation was observed for the 1:1 complex formed between **5** and $Eu(ClO_4)_3$. In this complex, the most affected carbonyl frequency is that of the acid group (1728 cm^{-1} in the free ligand and 1714 cm^{-1} in the complex). Also clear shifts were observed in the amide II band; this appears to be related more to a conformational change of the ligand rather than arising from a contribution of the amide nitrogen atom to complex formation.

3. Conclusions

The extraction experiments carried out with ligands **1**–**5** clearly demonstrate that these systems are not useful for alkali cation extraction. In contrast, high extraction was observed for **2** and **5** towards Zn^{2+} and Eu^{3+}. In addition, the presence of carboxylic groups in these systems allows pH control of extraction. This effect is undoubtedly influenced by the pK_a value for the carboxylic groups. On the other hand, ligand **5** forms two types of complexes depending on the pH. Thus, when only one carboxylic group is deprotonated a L_2M complex is formed but at higher pH values deprotonation of both acid groups occurs to yield a LM complex.

Structural modelling suggests interactions between the crown cavity and the different carbonyl groups present in

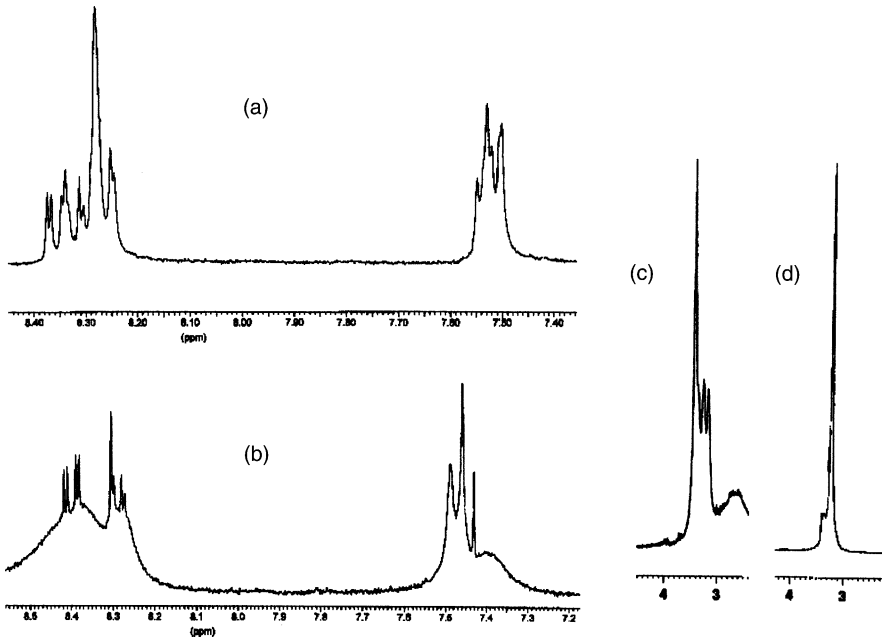

Figure 4. ^{1}H NMR spectra in CD_3CN (a) aromatic region for free **5**, (b) aromatic region for **5** plus 0.5 equiv of $Eu(ClO_4)_3$, (c) crown ether region for free **5**, (d) crown ether region for **5** plus 0.5 equiv of $Eu(ClO_4)_3$.

Table 2. ^{1}H NMR shifts for **2** and **5** and their complexes with $Eu(ClO_4)_3$ in CD_3CN

	$H_a/H_{a'}$	$H_b/H_{b'}$	$H_c/H_{c'}$	Crown	$H_d/H_{d'}$
2	8.62/8.34	8.28/8.37	7.57/7.53	3.51	3.24/3.30
2·$Eu(ClO_4)_3$ 1:1	—/—	—/—	7.53/—	3.40	3.07/3.29
5	8.63/8.28	8.38/8.30	7.54/7.51	3.41	3.27/3.26
5·$Eu(ClO_4)_3$ 2:1	8.29/—	8.39/—	7.47/—	2.94	3.45
5·$Eu(ClO_4)_3$ 1:1	8.29/—	8.40/—	7.47/7.41	3.24	3.42

Table 3. Assignments in the IR absorptions for the free ligands **2** and **5** and their $Eu(ClO_4)_3$ complexes

	Acid (C=O)	Amide I	Amide II	NO_2 as	NO_2 *si*	CC–O	δ (C=C)
2	1723	1633	1606	1523	1348	1115	658
2·$Eu(ClO_4)_3$ 2:1	1724	1610	1606	1524	1349	1096	652
5	1728	1635	1604	1524	1349	1110	652
5·$Eu(ClO_4)_3$ 2:1	1724	1610	1606	1524	1349	1098	627
5·$Eu(ClO_4)_3$ 1:1	1714	1644	1598	1518	1348	1084	626

ligands **2** and **5**. This fact is in agreement with the information obtained by ^{1}H NMR and IR spectroscopic measurements.

4. Experimental

4.1. General methods

All commercially available reagents were used without further purification. Water sensitive reactions were performed under argon. Column chromatography was carried out on SDS activated neutral aluminium oxide (0.05–0.2 mm; activity degree 1). IR spectra were recorded on a Perkin-Elmer 1750 FT-IR and a Bruker Equinox 55 FT-IR. NMR spectra were recorded with Bruker Avance 300/400/500 spectrometers. Chemical shifts are reported in parts per million downfield from TMS. Spectra were referenced to residual undeuterated solvent. High-resolution mass spectra were taken with a Fisons VG-AUTOSPEC.

4.1.1. Synthesis of 2. To a stirred suspension of KOH/EtOH (10%) heated at 60 °C was added a solution of **1**[3] (0.423 g, 0.715 mmol) in absolute EtOH (10 ml). When the addition was finished, the heating was continued until the completion of the reaction (TLC, 25 min). Then the reaction was quenched with a solution of HCl (10%) until pH=1. A white powder appeared in the solution and it was removed by filtration. After that, the solution was concentrated under reduced pressure and redissolved in a CH_2Cl_2/H_2O mixture. The organic phase was washed with three portions of H_2O (3×25 ml) and dried over anhydrous Na_2SO_4. The organic solvent was distilled to give a yellow solid. (0.396 g, 0.686 mmol). (96% yield). ^{1}H NMR (300 MHz, CD_3COCD_3) δ_H 8.77 (1H, s, Ar-H), 8.49 (1H, dd, J_1= 2.3 Hz, J_2=8.5 Hz, Ar-H), 8.40 (1H, d, J=2.3 Hz, Ar-H), 8.33 (1H, dd, J_1=2.3 Hz, J_2=8.5 Hz, Ar-H), 7.74 (1H, d, J=8.5 Hz, Ar-H), 7.66 (1H, d, J=8.5 Hz, Ar-H), 3.65–3.45 (20H, m, $-CH_2O-$), 3.41 (2H, m, $-NCH_2-$), 3.34 (2H, m, $-NCH_2-$). ^{13}C NMR (75 MHz, CD_3COCD_3) δ_C 169.15 ($-CON(CH_2)_2-$), 166.53 ($-COOCH_3-$), 149.09 (C_{Ar}),

148.64 (C_{Ar}), 146.11 (C_{Ar}), 145.05 (C_{Ar}), 138.43 (C_{Ar}), 133.98 (2C_{Ar}), 132.42 (C_{Ar}), 127.03 (C_{Ar}), 126.21 (C_{Ar}), 124.24 (C_{Ar}), 123.49 (C_{Ar}), 73.76 (–OCH_2–), 72.12 (–OCH_2–), 71.79 (–OCH_2–), 71.70 (–OCH_2–), 71.68 (–OCH_2–), 71.62 (–OCH_2–), 71.31 (–OCH_2–), 71.28 (–OCH_2–), 69.80 (–OCH_2–), 69.72 (–OCH_2–), 50.78 (–NCH_2–), 45.92 (–NCH_2–). IR ν_{max} (KBr) 3088 (Ar-H), 2871 (–(C=O)–*OH*), 1724 (–(*C*=*O*)–OH), 1633 (amide I), 1606 (amide II), 1523 (–NO_{2asym}), 1349 (–NO_{2sym}). EM (EI^+): M^+ found 577.19077. $C_{26}H_{31}N_3O_{12}$ required 577.19077. Mp: 65–67°.

4.1.2. Synthesis of 3. 2-Chlorocarbonyl-2′-methoxycarbonyl-4,4′-dinitrobiphenyl (0.307 g, 0.886 mmol) was added to an excess of thionyl chloride (30 ml). The suspension was refluxed with magnetic stirring until a clear solution had formed (2 h). Then the excess of thionyl chloride was distilled, dry benzene was added and the solution was redistilled. The solid obtained was dissolved in dry CH_2Cl_2 (25 ml) and added dropwise to a stirred mixture of 2-(hydroxymethyl)-18-crown-6 (0.261 g, 0.886 mmol) and dry triethylamine (99%) (0.0897 g, 0.886 mmol) in dry CH_2Cl_2 (20 ml) at 0 °C, under an inert atmosphere of Ar. When the addition was finished, the stirring was continued at room temperature. After completion of the reaction (TLC, 12 h), the solution was washed with three portions of HCl (10%) (3×15 ml) and dried over anhydrous Na_2SO_4. Then the organic phase was concentrated under reduced pressure and the crude reaction product was purified by chromatography through an alumina neutral column using CH_2Cl_2–AcOEt (7/3) as eluent to give the desired compound as a yellow oil. (0.358 g, 0.575 mmol). (65% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 8.94 (2H, d, J=2.5 Hz, Ar-H), 8.43 (2H, dd, J_1=2.5 Hz, J_2=8.5 Hz, Ar-H), 7.38 (1H, d, J=8.5 Hz, Ar-H), 7.37 (1H, d, J=8.5 Hz, Ar-H), 4.31 (1H, m, –CH_2–), 4.17 (1H, m, –CH_2–), 3.75 (3H, s, –$COOCH_3$), 3.68–3.57 (23H, m, crown). ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 164.96 (–*CO*OCH_3), 164.48 (–*CO*OCH_2–), 148.45 (2C_{Ar}), 147.83 (2C_{Ar}), 131.18 (2C_{Ar}), 130.76 (C_{Ar}), 130.66 (C_{Ar}), 126.81 (2C_{Ar}), 125.86 (2C_{Ar}), 71.39 (–$(OCH_2)_2$–*CH*–OCH_2–), 71.27 (–OCH_2–), 71.22 (–OCH_2–), 71.09 (–OCH_2–), 71.05 (–OCH_2–), 71.01 (–OCH_2–), 70.19 (–OCH_2–), 69.00 (–OCH_2–), 67.06 (–OCH_2–), 65.82 (–OCH_2–), 65.77 (–$COOCH_2$–), 65.27 (–OCH_2–), 62.30 (–OCH_2–), 53.09 (–$COOCH_3$). IR ν_{max} (KBr) 3401 (Ar-H), 1731 (–(*C*=*O*)–OCH_3), 1524 (–NO_{2asym}), 1349 (–NO_{2sym}), 1106 (–(O=*C*)–*O*CH_3). EM (FAB^+): M+1 found 623.208829. $C_{28}H_{35}N_2O_{14}$ required 623.20882.

4.1.3. Synthesis of 4. 2-Chlorocarbonyl-2′-methoxycarbonyl-4,4′-dinitrobiphenyl (0.504 g, 1.45 mmol) was added to an excess of thionyl chloride (30 ml). The suspension was refluxed under magnetic stirring until it became a clear solution (2 h). The excess of thionyl chloride was removed by distillation, dry benzene was added and the solution was redistilled. The solid obtained was dissolved in dry CH_2Cl_2 (25 ml) and this solution was added dropwise to a stirred mixture of 4,13-diaza-18-crown-6 (0.190 g, 0.725 mmol) and dry triethylamine (99%) (0.147 g, 1.45 mmol) in dry CH_2Cl_2 (20 ml) at 0 °C under an inert atmosphere of Ar. When the addition was finished, the stirring was continued at a room temperature. After completion of the reaction (TLC, 12 h) the solution was washed with three portions of HCl (10%) (3×15 ml) and dried over anhydrous Na_2SO_4. Then the organic phase was concentrated under reduced pressure and the crude reaction product was purified by chromatography using an alumina neutral column and CH_2Cl_2–AcOEt (8/2) as eluent to give the desired compound as a white solid. (0.445 g, 0.484 mmol). (67% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 8.85 (1H, d, J=2.3 Hz, Ar-H), 8.84 (1H, d, J=2.3 Hz, Ar-H), 8.39 (1H, dd, J_1=2.3 Hz, J_2=8.0 Hz, Ar-H), 8.37 (1H, dd, J_1=2.3 Hz, J_2=8.0 Hz, Ar-H), 8.31–8.26 (4H, m, Ar-H), 7.62 (2H, d, J=8.0 Hz, Ar-H), 7.40 (2H, d, J=8.0 Hz, Ar-H), 3.80 (3H, s, –$COOCH_3$), 3.79 (3H, s, –$COOCH_3$), 3.51–3.36 (24H, m, crown). ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 168.24 (2-*CO*$N(CH_2)_2$–), 165.25 (2-*CO*OCH_3–), 148.13 (2C_{Ar}), 147.72 (C_{Ar}), 145.38 (C_{Ar}), 145.33 (C_{Ar}), 143.54 (C_{Ar}), 137.16 (C_{Ar}), 130.99 (C_{Ar}), 126.42 (C_{Ar}), 125.96 (C_{Ar}), 123.72 (C_{Ar}), 122.75 (C_{Ar}), 70.92 (2-O*CH*$_2$*CH*$_2$O–), 69.86 (4-NCH$_2$*CH*$_2$O–), 53.33 (2-COO*CH*$_3$), 49.96 (2-N*CH*$_2$CH$_2$O–), 46.05 (2-N*CH*$_2$CH$_2$O–). IR ν_{max} (KBr) 3090 (Ar-H), 1731 (–(*C*=*O*)–OCH_3), 1635 (amide I), 1608 (amide II), 1524 (–NO_{2asym}), 1349 (–NO_{2sym}), 1123 cm^{-1} (–(O=*C*)–*O*CH_3). EM (FAB^+): M+1 found 919.263384. $C_{42}H_{43}N_6O_{18}$ required 919.26338. Mp: 179–180 °C.

4.1.4. Synthesis of 5. This product was prepared following the same method used to obtain **2**, but in this case starting from **4** (0.384 g, 0.379 mmol). The compound was isolated as a yellow solid (0.360 g, 0.405 mmol). (97% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 8.91 (2H, d, J=2.3 Hz, Ar-H), 8.45 (2H, dd, J_1=2.3 Hz, J_2=8.5 Hz, Ar-H), 8.35 (2H, dd, J_1=2.3 Hz, J_2=8.5 Hz, Ar-H), 8.21 (2H, d, J=2.3 Hz, Ar-H), 7.66 (2H, d, J=8.5 Hz, Ar-H), 7.49 (2H, d, J=8.5 Hz, Ar-H), 3.59–3.23 (24H, m, crown). ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 176.11 (–*CO*OH), 171.71 (–*CO*OH), 169.92 (–*CO*$N(CH_2)_2$–), 168.08 (–*CO*$N(CH_2)_2$–), 148.18 (C_{Ar}), 147.69 (C_{Ar}), 146.23 (C_{Ar}), 144.26 (C_{Ar}), 136.73 (C_{Ar}), 134.37 (C_{Ar}), 131.26 (C_{Ar}), 127.47 (C_{Ar}), 126.52 (C_{Ar}), 126.10 (C_{Ar}), 124.04 (C_{Ar}), 121.81 (C_{Ar}), 70.71 (2-O*CH*$_2$-CH$_2$O–), 70.22 (2-OCH$_2$*CH*$_2$O–), 67.64 (4-NCH$_2$*CH*$_2$O–), 48.46 (4-N*CH*$_2$CH$_2$O–). IR ν_{max} (KBr) 3089 (Ar-H), 2870 (–(C=O)–*OH*), 1728 (–(*C*=*O*)–OH), 1636 (amide I), 1605 (amide II), 1524 (–NO_{2asym}), 1349 (–NO_{2sym}). EM (FAB^+): M+1 found 891.232084. $C_{40}H_{39}N_6O_{18}$ required 891.23207. Mp: 142–143 °C.

4.2. Potentiometric titrations

They were carried out under nitrogen in dioxane–water (70/30 v/v) using a reaction vessel water-thermostatted at 25.0±0.1 °C (0.1 mol dm^{-3} tetrabutylammonium perchlorate). The titrant was added by means of a Crison microburete 2031. The potentiometric measurements were made using a Crison 2002 pH-meter and a combined glass electrode. The titration system was automatically controlled by a PC computer using a program that monitors the e.m.f. values and the volume of titrant added. The electrode was dipped in dioxane–water (70/30 v/v) for half an hour before use. It was calibrated for hydrogen concentration by titration of a known amount of HCl with CO_2 free LiOH solution and determining the equivalent point by the Gran's method; this gives the standard potential E'° and the ionic product of water (K'_w=[H+][OH–], pK=

15.9±0.1).[12] The computer program SUPERQUAD[13] was used to calculate the protonation constants.

4.3. Liquid–liquid extraction experiments

The liquid–liquid extraction experiments were carried out at 22±2 °C in polypropylene microcentrifuge tubes (2 ml) with a phase ratio $V_{(w)}$:$V_{(org)}$ of 1:1 (each phase 0.5 ml). The aqueous phase contained the metal ion (at 10^{-4} M), a supporting anion, HPic, HNO_3, $HClO_4$ or HCl, at different concentrations and a selected buffer (HEPES or AMP, used to maintain the chosen pH). The organic phase contained a known concentration of ligand in $CHCl_3$ (normally 10^{-3} M except variable concentration experiments were employed). All experiments involved mechanical shaking of the vials for 30 min. At the end of these periods, the phases were separated, centrifuged (to ensure full phase separation) and then duplicate 100 μl samples of both phases were removed for analysis.

The metal concentration in both phase was determined radiometrically by means of γ-counting using a NaI(Tl) scintillation counter (Cobra II, Canberra-Packard). The following radioisotopes were employed: ^{22}Na, ^{137}Cs, ^{65}Zn, ^{110m}Ag and ^{152}Eu.

The distribution ratio D_M for each metal was calculated by the following equation:

$$D_M = \frac{[M^{n+}]_{(org)}}{[M^{n+}]_{(w)}}$$

With this parameter it was possible to calculate the extractability E using the equation:

$$E(\%) = \frac{D_M}{D_M + 1} 100$$

All the extraction reactions are described by the following two equilibria:

$$M^{n+}(w) + nA^-(w) + sL(org) \overset{K_{ex}}{\rightleftharpoons} ML_sA_n(w),(org)$$

$$M^{n+}_{(w)} + sH_nL_{(org)} \rightleftarrows ML_{s(org)} + nsH^+_{(w)}$$

$$K_{ex} = \frac{[ML_sA_n]_{(org)}}{[M^{n+}]_{(w)}[A^-]^n_{(w)}[L]^s_{(org)}}$$

$$\log D_M = \log K_{ex} + n \log[A^-]_{(w)} + s \log[L]_{(org)}$$

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