A simple synthesis of novel extraction reagents. 4-Acyl-5-pyrazolone-substituted crown ethers

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A synthesis of novel 4-acylpyrazol-5-one-substituted crown ethers metal-chelating reagents is described. 4-Acyl-pyrazol-5-one-substituted dibenzo-16-crown-5 **1a**, 4-acylpyrazol-5-one-substituted dibenzo-19-crown-6 **1b**, and bis(4-acylpyrazol-5-one)-substituted diaza-18-crown-6 **1c** were designed and synthesized by simple coupling reactions between α-chloro 4-acylpyrazol-5-one **3** and the corresponding crown ethers **2a–c**. Compound **1a** was found to be an effective and metal ion-selective extraction reagent.

Introduction

4-Acylpyrazol-5-ones are known as powerful chelating reagents and are used for solvent extraction of metal ions.[1] Recently, the combination of 4-acylpyrazol-5-one and a crown ether has shown an improvement in metal-ion selectivity.[2] This is because chelating moieties such as acylpyrazolone prefer metal ions having smaller ionic radii in solvent extraction. On the other hand, crown ethers[3] have preferred sizes of metal ions, depending on the ring size of the macrocycle, and, as a result, a combination of the two units results in higher metal-ion selectivity. In this regard, a molecule which has acylpyrazolone unit(s) and a crown ether unit in the same structure should work even more effectively by complexing *via* species such as **A** or **B** (Chart 1).
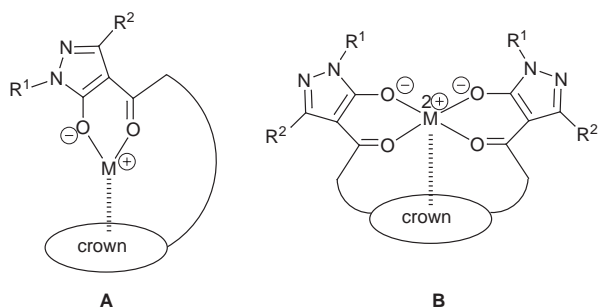

Chart 1 Metal complexes of 4-acylpyrazol-5-one-substituted crown ethers.

In **A**, monovalent metal cations such as alkali metals are expected to bind *via* the β-diketone and crown ether moieties. In **B**, divalent metal cations such as alkaline earth metals and some transition metals are also expected to bind to form 1:1 complexes. Crowns **1a** and **1b** would possibly form unique complexes with tervalent metal ions such as lanthanides.

Although a large number of crown ethers bearing pendant groups have been synthesized,[4] only a few examples of crown ether-bearing chelating reagents have been reported.[5] In order to obtain various metal-selective extraction reagents, the practical synthesis of new crown ethers bearing chelating reagents is desirable. In this report, we disclose the synthesis of novel 4-acylpyrazol-5-one-substituted crown ethers which are highly promising solvent-extraction reagents.

Results and discussion

4-Acylpyrazol-5-one-substituted crown ethers **1a–c** were designed as selective extraction reagents. They have structural variation in the crown ether parts (polyether cavity size, benzo-annulated or not, inclusion of nitrogens or not) and the number of pyrazolone portion(s) (1 for **1a,b**, 2 for **1c**). Compounds **1a** and **1b** are expected to be suitable for monovalent metal cations M$^+$ (corresponding to **A** in Chart 1), and compound **1c** is expected to be suitable for divalent metal cations M^{2+} (corresponding to **B** in Chart 1). Diazacrown **1c** should be potentially useful because there are more metals which exist as divalent cations than as monovalent cations in nature. We planned to synthesize crowns **1a–c** from 4-chloroacetyl-3-methyl-1-phenyl-pyrazol-5-one **3**[6] and readily accessible crown ethers **2a–c**.†[7,8] Hydroxy crown ethers **2a,b** were treated with NaH in THF at room temp. The addition of chloride **3** to the mixture and stirring overnight produced compounds **1a,b** in 48 and 95% yield, respectively [equation (1)]. The smooth nucleophilic substitution reactions are possibly assisted by the capture of Na$^+$ ion by the crown ether moieties.[9] The bis(5-hydroxypyrazol-4-ylcarbonylmethyl)diazacrown **1c** was prepared by the reaction of diazacrown **2c** with chloride **3**, using Et$_3$N as a base in refluxing ethanol overnight, in 51% yield [equation (2)]. Thus, α-chloro carbonyl compound **3** was found to be a versatile reagent for introducing 4-acylpyrazol-5-one units into crown ethers. The structures of products **1a–c** were fully characterized by spectral data and elemental analysis. These compounds are promising chelating reagents for the extraction of metal ions.

For these compounds, examination of the extraction efficacy compared to existing methods and the selectivity for various metal ions in detail is important.[10] As a part of this study, the extraction efficacy of compound **1a** for sodium ion was first examined. Extraction using combinations of a 4-acylpyrazol-5-one and a benzocrown ether was undertaken for comparison with the extraction effectiveness of crown **1a**. As controls, the commercially available benzocrown ethers benzo-15-crown-5 **5a** and benzo-18-crown-6 **5b** were used. The extraction of Na$^+$ into the benzene phase with 0.1 M 4-benzoyl-3-methyl-1-phenyl-1*H*-pyrazol-5-one **4** and 0.1 M **5a** or **5b** is shown in

† Compound **2c** is commercially available.

Scheme 1

2a: X = CH$_2$CH$_2$OCH$_2$CH$_2$
2b: X = CH$_2$CH$_2$OCH$_2$CH$_2$OCH$_2$CH$_2$

1) NaH / THF 2)

(1)

1a: X = CH$_2$CH$_2$OCH$_2$CH$_2$ (48%)
1b: X = CH$_2$CH$_2$OCH$_2$CH$_2$OCH$_2$CH$_2$ (95%)

Scheme 1

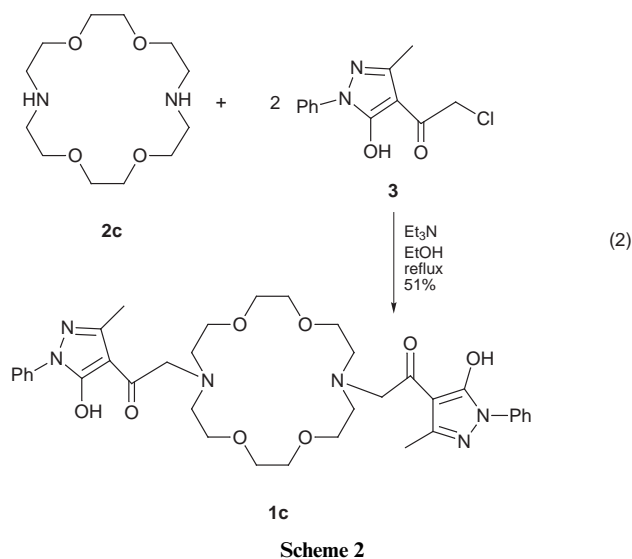2c   +   2   3

(2)

Et$_3$N
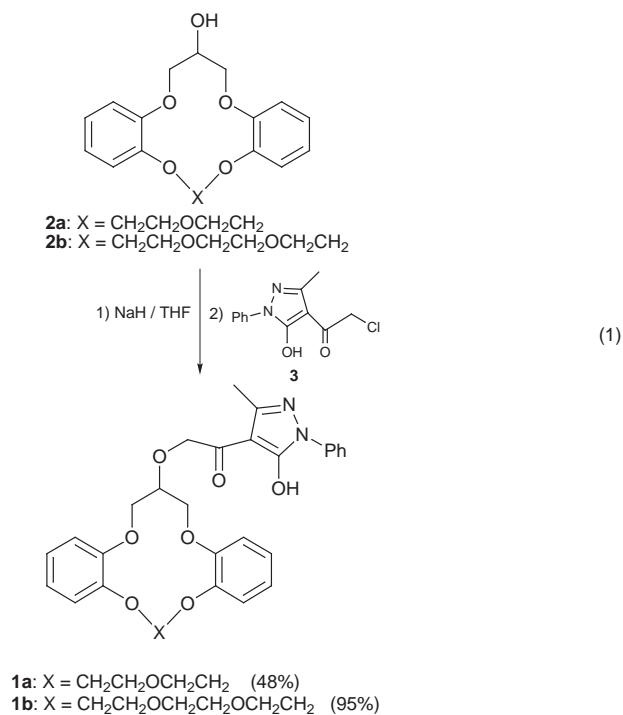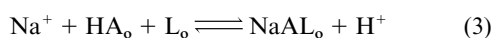EtOH
reflux
51%

1c

Scheme 2

Fig. 1. No extraction took place in the absence of benzocrown ethers. The extraction equilibrium can be written as equation (3) where the extractant HA denotes **4** and the ligand L denotes

$$Na^+ + HA_o + L_o \rightleftharpoons NaAL_o + H^+ \quad (3)$$

5a or **5b**. The subscript o denotes the species in the organic phase. The extraction constant, K_{ex}, is defined as $[NaAL]_o[H^+]/[Na^+][HA]_o[L]_o$. The logarithm of the distribution ratio of Na$^+$, D (= $[NaAL]_o/[Na^+]$), was plotted against the pH in the aqueous phase in Fig. 1. As expected from equation (3), the plots fall on a straight line with a slope of one in the lower pH region. The values of log K_{ex} were calculated on the basis of equation (3) to be -4.80 for the benzo-15-crown-5 system and -6.18 for the benzo-18-crown-6 system, respectively.

The extraction of Na$^+$ with crown **1a** (0.01 M) is also shown in Fig. 1. The extraction equilibrium for **1a** can be written as equation (4) where the extractant HA denotes **1a**. K_{ex} for the

$$Na^+ + HA_o \rightleftharpoons NaA_o + H^+ \quad (4)$$

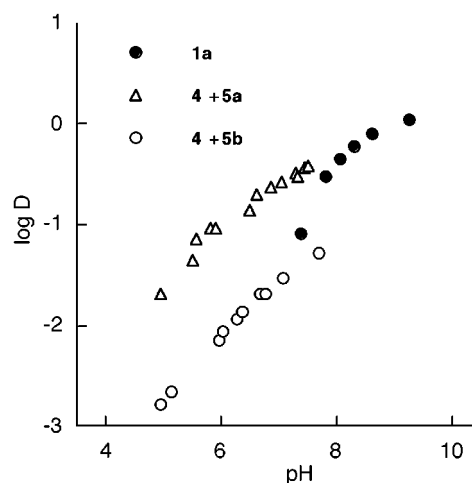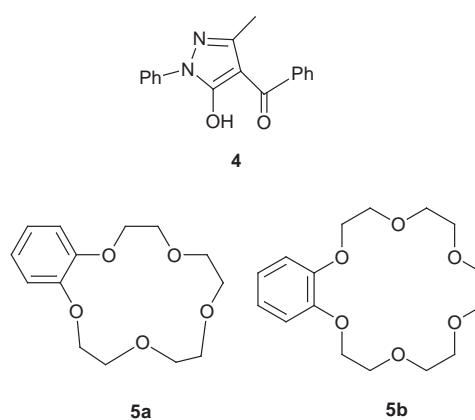extraction with crown **1a** is defined as $[NaA]_o[H^+]/[Na^+][HA]_o$

Fig. 1 Extraction of Na$^+$ into benzene with crown **1a** or the combination of chloride **4** and the benzocrown ether. $[1a]_o = 0.01$ M, $[4]_o = [5a]_o = [5b]_o = 0.1$ M in benzene.

4

5a   **5b**

and the value of log K_{ex} is calculated on the basis of equation (4) to be -6.41.

In the extraction of sodium, it was found that benzocrown ethers work as a synergist ‡ like trioctylphosphine oxide, enhancing the extraction into the benzene phase. The synergistic effects displayed by the benzocrown ethers are equal to that of trioctylphosphine oxide [12] which is known as one of the most powerful synergists. Dibenzocrown **1a** is a β-diketone type extractant and is also likely to work as a synergist with the crown ether moiety. It is not possible to simply compare the extraction constants obtained from equations (3) and (4), however, considering that if extraction occurs at $[HA]_o = [L]_o = 0.01$ M, the extraction curve would move to the alkaline region by 2 pH units. Therefore, one can conclude that compound **1a** is obviously a more powerful extractant.

Next, as a basic study for ion selectivity, the extractions of Li$^+$, Na$^+$ and K$^+$ with dibenzocrown **1a** were examined and are shown in Fig. 2. As shown, Na$^+$ is the most extractable, followed by K$^+$ and Li$^+$. The values of log K_{ex} were calculated on the basis of equation (4) to be -7.35 for K$^+$ and -8.24 for Li$^+$, respectively. Multidentate chelating reagents, such as

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‡ It has been shown that alkali metal ions (M$^+$) are not extractable into the organic phase with β-diketone-type extractants (HA). Alkali metal ions react with extractants to form 1:1 chelate complexes (MA) with vacant coordination sites, which are usually occupied by water molecules. Therefore, the chelate complexes have low hydrophobicity and, as a result, the distribution ratio of metal ions is low. It is known that when Lewis bases (L) such as trioctylphosphine oxide are added to the organic phase, they replace water molecules and increase the distribution ratio. The co-use of the extractant and Lewis base is known as a "synergistic effect".[11]
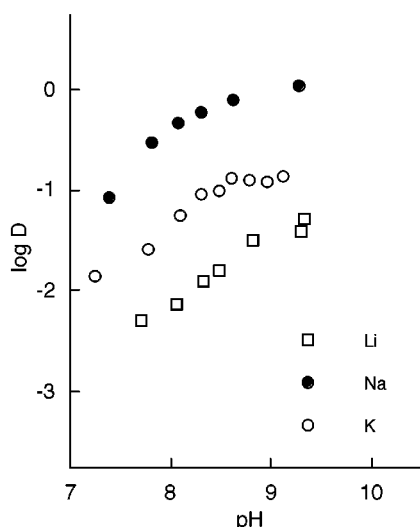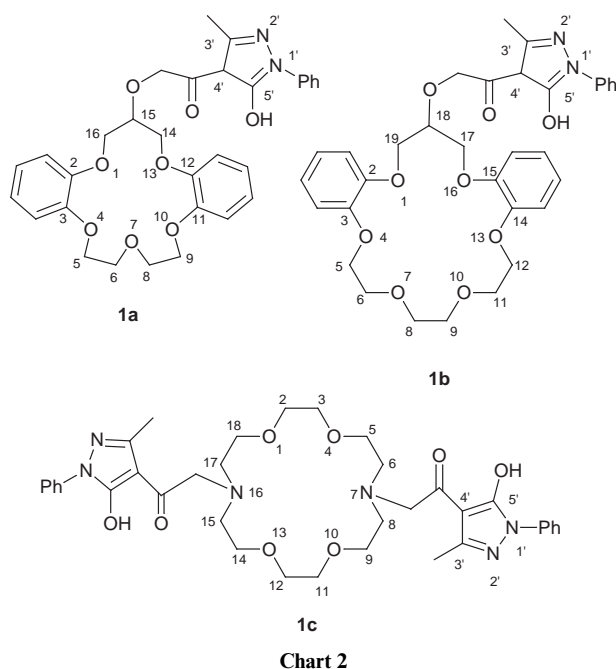
Fig. 2 Extraction of Li$^+$, Na$^+$ and K$^+$ into benzene with crown **1a**. [**1a**]$_o$ = 0.01 M in benzene.

Chart 2

β-diketones, and monodentate ligands with oxygen as a donating atom, such as trioctylphosphine oxide, are known to exhibit more stable complexation with metal ions having smaller ionic radii. Consequently, Li$^+$ was more extractable than Na$^+$ in the synergistic extraction with acylpyrazolone derivatives and trioctylphosphine oxide.[12] The ion size selectivity of an acylpyrazolone with crown ethers towards alkali metal ions is quite different from acylpyrazolones with trioctylphosphine oxide. The extraction selectivity with compound **1a** depends on both chelation with the acylpyrazolone moiety and adduct formation with the crown ether moiety. It is clear that the present unique extractability (Na$^+$ > K$^+$ > Li$^+$) is brought about by the effect of the adduct formation reaction with the crown ether moiety.

16-Crown-5 ethers such as the starting alcohol **2a** are supposed to have Na$^+$ preferability from the estimated diameter of the crown cavity[13] and by the effective synthesis using the suggested template effect[6] in the literature. However, the selectivity of compound **1a** to various metal ions may not be the same as that of the co-use of the acylpyrazolone and 16-crown-5 ethers such as compound **2a**, since the other side of the metal ion is already occupied by the acylpyrazolone moiety and the degree of freedom of the crown ether moiety is restricted by the methylene chain linkage in **1a**. The ring size of the crown and

length of the linkage as well as the chelating moiety should all be significant factors in the extractability.

Conclusions

In summary, the practical synthesis of structurally novel crown ether-bearing chelating reagents **1a**–**c** has been presented. The effective and unique extractability of alkali metal ions with compound **1a** has been shown. Further studies on the selectivity of metal-ion extractions by these novel chelating molecules, and the design and synthesis of new structure systems as extraction reagents, are in progress.

Experimental

General methods

Mps were measured on a Yamato MP-21 melting point apparatus and are uncorrected. IR spectra were recorded with a JASCO FT-IR 5000 spectrophotometer. NMR spectra were recorded on a JEOL JNM-AL400 or Varian INOVA 400 spectrometer. Chemical shifts are reported in ppm relative to Me$_4$Si or residual nondeuterated solvent. J-Values are given in Hz. Mass spectra were recorded on a JEOL JMS700 spectrometer at an ionizing voltage of 70 eV by EI or FAB. All reactions were carried out under nitrogen.

15-[(5′-Hydroxy-3′-methyl-1′-phenylpyrazol-4′-yl)carbonyl-methoxy]-5,6,8,9,15,16-hexahydro-14H-2,3;11,12-dibenzo-1,4,7,10,13-pentaoxacyclohexadecapentaene § 1a

After removal of the mineral oil from sodium hydride (63% dispersion in oil; 684 mg, 18.0 mmol) by washing twice with n-pentane, a THF (54.0 cm^3) solution of the alcohol **2a** (1.384 g, 4.0 mmol) was added. After the reaction mixture had been stirred for 30 min, a solution of chloride **3** (1.50 g, 6.0 mmol) in THF (10.0 cm^3) was added dropwise over a period of 30 min. After the addition, the mixture was stirred overnight. Water was then added and the THF was evaporated *in vacuo*. The residue was extracted with CH$_2$Cl$_2$. The organic phase was washed with 1 M HCl, dried (MgSO$_4$), and the solvent was evaporated *in vacuo*. The crude residue was crystallized from acetone. The obtained crude solid was dissolved in CH$_2$Cl$_2$ and filtered to remove insoluble material. The CH$_2$Cl$_2$ solution was concentrated *in vacuo* and the residue was recrystallized from acetone to give *title compound* as crystals **1a** (1.074 g, 48%); mp 125–126 °C (from acetone); δ_H NMR (400 MHz; CDCl$_3$) 2.47 (3H, s, Me), 3.86–3.97 (4H, m, OCH$_2$CH$_2$O), 4.11–4.18 (4H, m, OCH$_2$CH$_2$O), 4.32–4.38 (3H, m, H-14, -15, -16), 4.41–4.46 (2H, m, H-14, -16), 4.96 (2H, s, OCH$_2$C=O), 6.81–6.88 (4H, m, ArH of crown ether), 6.94–6.98 (4H, m, ArH of crown ether), 7.27–7.31 (1H, m, *p*-H of NPh), 7.41–7.45 (2H, m, *m*-H of NPh) and 7.78 (2H, d, J 8.0, *o*-H of NPh); δ_C(99.45 MHz, CDCl$_3$) 15.9 (Me), 67.5 (OCH$_2$CH$_2$O), 69.6 (OCH$_2$CH$_2$O), 71.8 (C-14, -16), 74.2 (OCH$_2$C=O), 78.7 (C-15), 102.4, 113.1, 118.6, 121.3, 121.3 (*o*-C of NPh), 123.2, 126.8 (*p*-C of NPh), 129.0 (*m*-C of NPh), 137.2, 148.0, 148.2, 150.3, 158.7 (pyrazolone C-5′) and 193.6 (OCH$_2$C=O) (for atom numbering, see Chart 2). NMR assignment was made by C–H COSY spectra; ν_{max}(KBr)/cm^{-1} 2990, 2880, 1650 (CO) and 1597; *m/z* (EI) 560 (M$^+$, 21%), 346 (30), 281 (34), 243 (100) and 231 (69) (Found: M$^+$, 560.2181. C$_{31}$H$_{32}$N$_2$O$_8$ requires M, 560.2159) (Found: C, 66.4; H, 5.75; N, 5.0. Calc. for C$_{31}$H$_{32}$N$_2$O$_8$: C, 66.42; H, 5.75; N, 5.00%).

18-[(5′-Hydroxy-3′-methyl-1′-phenylpyrazol-4′-yl)carbonyl-methoxy]-5,6,8,9,11,12,18,19-octahydro-17H-2,3;14,15-dibenzo-1,4,7,10,13,16-hexaoxacyclononadecahexaene § 1b

The crude compound was purified by column chromatography over silica gel and elution with CH$_2$Cl$_2$–MeOH (15:1) (yield

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§ The non-systematic numbering scheme shown in Chart 2 for the dibenzo-fused crown ether systems **1a**, **1b** is used.

95%) [$R_f = 0.3$ (CH$_2$Cl$_2$–MeOH 15 : 1)] to afford *crystals*; mp 48–51 °C; δ_H(400 MHz, CDCl$_3$) 2.44 (3H, s, Me), 3.77–3.80 (4H, m, OCH$_2$CH$_2$O), 3.84–3.86 (4H, m, OCH$_2$CH$_2$O), 4.08–4.19 (4H, m, OCH$_2$CH$_2$O), 4.32–4.37 (5H, m, H-17, -18, -19), 4.91 (2H, s, OCH$_2$C=O), 6.86–7.00 (8H, m, ArH of crown ether), 7.27–7.30 (1H, m, *p*-H of NPh), 7.41–7.45 (2H, m, *m*-H of NPh) and 7.76 (2H, d, *J* 7.7, *o*-H of NPh); δ_C(100.6 MHz, CDCl$_3$) 15.9 (q, Me), 69.4 (t, OCH$_2$CH$_2$O), 69.8 (t, OCH$_2$-CH$_2$O), 71.1 (t, OCH$_2$CH$_2$O), 71.4 (t, C-17, -19), 74.0 (t, OCH$_2$C=O), 79.2 (d, C-18), 102.4 (s, pyrazolone C-4′), 114.4 (d, arom CH of crown ether), 117.7 (d, arom CH of crown ether), 121.3 (d, *o*-C of NPh), 121.7 (d, arom CH of crown ether), 122.9 (d, arom CH of crown ether), 126.9 (d, *p*-C of NPh), 129.1 (d, *m*-C of NPh), 137.3 (s, N1′-C of Ph), 148.2 (s, *C*-CH$_3$), 148.9 (s, arom C of crown ether), 149.9 (s, arom C of crown ether), 158.8 (s, pyrazolone C-5′) and 193.8 (s, OCH$_2$C=O). NMR assignment was made by COSY, DEPT, HMQC and HMBC spectra; ν_{max}(KBr)/cm^{-1} 2920, 2872, 1650 (CO) and 1595; *m/z* (EI) 604 (M$^+$, 1.0%), 390 (2.2), 250 (31) and 201 (100) (Found: M$^+$, 604.2434. C$_{33}$H$_{36}$N$_2$O$_9$ requires *M*, 604.2421) (Found: C, 65.7; H, 6.0; N, 4.9. Calc. for C$_{33}$H$_{36}$N$_2$O$_9$: C, 65.55; H, 6.00; N, 4.63%).

N,N′-Bis[(5′-hydroxy-3′-methyl-1′-phenylpyrazol-4′-yl)carb-onylmethyl]-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane 1c

A solution of diazacrown **2c** (266 mg, 1.01 mmol), chloride **3** (758 mg, 3.01 mmol) and triethylamine (0.55 cm^3, 3.97 mmol) in ethanol (2.0 cm^3) was refluxed overnight. The reaction mixture was poured into water (50 cm^3) and extracted with chloroform (100 cm^3). The organic layer was dried (Na$_2$SO$_4$) and evaporated *in vacuo*. Acetone was added to the residue to give a solid. The solid was separated, and was then recrystallized from MeOH to give the title compound as crystals **1c** (0.354 g, 51%); mp 213–215 °C; δ_H(400 MHz, DMSO-d$_6$) 2.25 (6H, s, Me), 3.45 (8H, br s, NCH$_2$CH$_2$O), 3.54 (8H, s, OCH$_2$CH$_2$O), 3.76 (8H, br m, NCH$_2$CH$_2$O), 4.41 (4H, br m, NCH$_2$C=O), 7.01 (2H, t, *J* 7.1, *p*-H of NPh), 7.31 (4H, t, *J* 7.9, *m*-H of NPh) and 8.01 (4H, d, *J* 7.9, *o*-H of NPh); δ_C(100.6 MHz, DMSO-d$_6$) 16.3 (q, Me), 53.7 (t, NCH$_2$CH$_2$O), 61.0 (t, NCH$_2$C=O), 64.7 (t, NCH$_2$-CH$_2$O), 69.5 (t, OCH$_2$CH$_2$O), 101.6 (s, pyrazolone C-4′), 117.9 (d, *o*-C of NPh), 122.6 (d, *p*-C of NPh), 128.3 (d, *m*-C of NPh), 140.4 (s, N1′-C of Ph), 148.8 (s, pyrazolone C-3′), 165.5 (s, pyrazolone C-5′) and 180.2 (s, CH$_2$C=O). NMR assignment was made by COSY, DEPT, HSQC (H–C) and HMBC spectra; ν_{max}(KBr)/cm^{-1} 3038, 2884, 1632 (CO) and 1597; *m/z* (FAB) (M$^+$) 690.3355 (C$_{36}$H$_{46}$N$_6$O$_8$ requires *M*, 690.3377) (Found: C, 62.3; H, 6.8; N, 12.2. Calc. for C$_{36}$H$_{46}$N$_6$O$_8$: C, 62.59; H, 6.71; N, 12.17%).

Extraction of alkali metal ions

A 10 cm^3 aliquot of an aqueous phase containing 1×10^{-4} M of alkali metal ion, 0.1 M tetramethylammonium chloride to keep the ionic strength at 0.1, and 0.01 M 2-morpholinoethane-sulfonic acid as buffering component was adjusted to the desired pH with hydrochloric acid or tetramethylammonium hydroxide solution. The aqueous phase was shaken with an equal volume of benzene containing the required amount of ligand at 25 °C for 1 h. A shaking time of 1 h was found to be long enough for the mixture to reach equilibrium. After centri-fugation, the pH of the aqueous phase was measured and taken as the equilibrium value. The metal concentration in the aque-ous phase was determined by atomic absorption spectrometry. That in the organic phase was measured in the same way after back-extraction by stripping with hydrochloric acid. The sum of the metal concentrations in the two phases agrees well with the initial concentration.

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