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THE SYNTHESES OF NEW NITROGEN–OXYGEN DONOR MACROCYCLES AND LIQUID MEMBRANE TRANSPORT OF ALKALI CATIONS

BIN ZHAO, YANG JIE WU* and JING CHAO TAO

Department of Chemistry, Zhengzhou University, Zhengzhou 450052, P. R. China

and

HAN ZHEN YUAN

Laboratory of Magnetic Resonance and Atomic and Molecular Physics,
Wuhan Institute of Physics, Academic Sinica, Wuhan 430071, P. R. China

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Abstract—Five new nitrogen–oxygen mixed donor macrocycles have been prepared by condensation of *N*,*N*-bis[2-(2-formylphenoxy)ethyl]-4-methylphenylsulphonamide with diamino compounds, followed by a one-pot reduction of the intermediate bis-Schiff base. The transport of alkali metal ions across a liquid membrane using these macrocycles as ion carrier was studied, and the results show that the rates of cation transport are affected by the size of macrocycle.

Oxygen donor macrocycles such as crown ethers are well known to have strong complexation ability for alkali and alkaline earth ions.[1] On the other hand, polyazamacrocycles show a high affinity for transition metal ions. Nitrogen–oxygen mixed donor macrocycles can form stable complexes with both alkali and transition metal ions.[2] Therefore, mixed donor macrocycles have received much attention as receptors for a range of metal ions and other cations.[3,4] It has been clearly documented that the coordination properties of such ligands often span those of the well studied crown polyethers and polyaza categories of macrocycle, and particular attention has been given to mixed donor macrocycles.

In this paper, we report the synthesis of five new nitrogen–oxygen donor macrocycles and the liquid membrane transport of alkali cations (Na^+ and K^+) with these ligands as ion carriers.

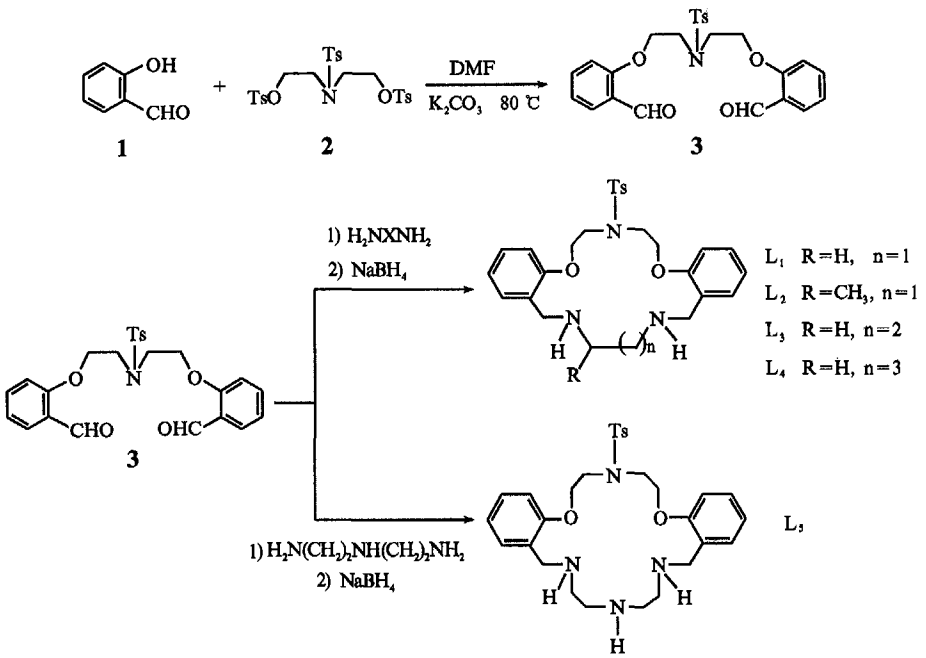
* Author to whom correspondence should be addressed.

RESULTS AND DISCUSSION

Syntheses of macrocycles

The synthetic routes for the new macrocycles are shown in Scheme 1. The dialdehyde, *N*,*N*-bis[2-(2-formylphenoxy)ethyl]-4-methylphenylsulphonamide, was obtained by the reaction of *N*,*N*-bis[2-(4-methylphenylsulphonyloxy)ethyl]-4-methylphenylsulphonamide with salicylaldehyde in the presence of K_2CO_3 in DMF. A little excess of salicylaldehyde was used in order to ensure the formation of the dialdehyde.

In the syntheses of the macrocycles L_1–L_5, the dialdehyde was condensed with different diamines in hot methanol. The corresponding Schiff base derivatives were not isolated, but instead reduction was carried out *in situ* by slow addition of sodium borohydride to the reaction solution. The condensation reaction can be performed at room temperature over a long period of time, but the yields are usually low. The reduction step can also be carried out at room temperature without lowering the yields of macrocycles. It is not necessary to



Scheme 1. The synthetic routes of L_1–L_5.

carry out the ring closure step under high dilution conditions.

The structures proposed for the new macrocycles are consistent with data obtained from their elemental analyses, IR, ^1H NMR and mass spectra (Tables 1–3).

Transport of cations across a liquid membrane

Ligands L_1–L_5 can form 1 : 1 type complexes with NaPic and KPic (Pic = picrate), so, they can be used as cation carriers. As an extension of the ability of these macrocycles to extract or release alkali metal cations, their role as transport agents across a liquid membrane was studied. The apparatus used is shown in Fig. 1. These experiments were performed through a dichloromethane membrane separating two aqueous solutions. The alkali metal picrates were transported with the aid of the ligands from an aqueous phase (phase 1) to another aqueous phase (phase 2). The picrate concentration was found to increase in phase 2, detected by a UV–vis spectrophotometer. The ligands function as cation carriers by dissolving the alkali metal picrate into the organic phase and releasing it through the liquid membrane to phase 2.

The transport of Na^+ and K^+ cations was studied individually from an aqueous solution which contained a mixture of metal picrate and nitrate. The transport co-anion will be the picrate because of its lipophilic properties.[5,6] This allows a good incorporation in the organic phase containing the macrocycle. There was no transport of picrate ion across the membrane in the absence of the macrocycle. For the transport by cryptates possessing tertiary amines, Kirch and Lehn[5] have demonstrated that

Table 1. Melting points and elemental analysis data for L_1–L_5

Ligand	Formula	M.p. (°C)	Elemental analysis: Found (Calc.) C	H	N
L_1	$C_{27}H_{33}N_3SO_4 \cdot 1.5H_2O$	146–148	62.0 (62.0)	6.9 (6.9)	7.9 (8.0)
L_2	$C_{28}H_{35}N_3SO_4$	138–139	65.7 (66.0)	7.0 (6.9)	8.5 (8.3)
L_3	$C_{28}H_{35}N_3SO_4$	140–142	66.0 (66.0)	6.9 (6.9)	8.1 (8.3)
L_4	$C_{29}H_{37}N_3SO_4$	137–138	66.4 (66.5)	7.2 (7.1)	7.8 (8.0)
L_5	$C_{29}H_{38}N_4SO_4$	122–124	64.4 (64.7)	7.2 (7.1)	10.2 (10.4)

Table 2. IR, UV and mass spectral data for L_1–L_5

Ligand	IR (KBr), cm^{-1}	UV ($CHCl_3$), (log ε) nm	MS (*m/z*)
L_1	3310 (NH); 1599, 1495 (Ar); 1324, 1159 (SO_2); 1240, 1011 (Ar—O—CH_2); 812 (1,4-Ar); 755 (1,2-Ar)	271 (3.62) 244 (3.74)	495 (M^+)
L_2	3320, 3250 (NH); 1599, 1492 (Ar); 1326, 1151 (SO_2); 1240, 1018 (Ar—O—CH_2); 814 (1,4-Ar); 755 (1,2-Ar)	271 (3.61) 247 (3.59)	509 (M^+)
L_3	3310 (NH); 1599, 1495 (Ar); 1324, 1150 (SO_2); 1238, 1018 (Ar—O—CH_2); 811 (1,4-Ar); 755 (1,2-Ar)	271 (3.64) 243 (3.79)	509 (M^+)
L_4	3310 (NH); 1598, 1495 (Ar); 1325, 1157 ($ArSO_2$); 1238, 1016 (Ar—O—CH_2); 813 (1,4-Ar); 756 (1,2-Ar)	271 (3.60) 242 (3.77)	523 (M^+)
L_5	3305 (NH); 1598, 1495 (Ar); 1325, 1152 ($ArSO_2$); 1238, 1020 (Ar—O—CH_2); 811 (1,4-Ar); 754 (1,2-Ar)	271 (3.59) 243 (3.76)	538 (M^+)

Table 3. ^1H NMR spectral data for L_1–L_5

Ligand	^1H NMR ($CDCl_3$, δ, ppm)
L_1	1.93 (br, 2H, NH), 2.41 (s, 3H, $ArCH_2$), 2.74 (s, 4H, NCH_2CH_2N), 3.71 (s, 4H, $ArCH_2$), 3.80 (t, 4H, $TsNCH_2$), 4.19 (t, 4H, OCH_2), 6.74–7.72 (m, 12H, ArH)
L_2	1.03 (d, 3H, CH_3), 1.92 (br, 2H, NH), 2.41 (s, 3H, $ArCH_3$), 2.55 (d, 2H, CH_2CH), 2.69 (m, 1H, CH), 3.55 (s, 4H, $ArCH_2$), 3.79 (t, 4H, $TsCH_2$), 4.25 (t, 4H, OCH_2), 6.73–7.74 (m, 12H, ArH)
L_3	1.72 (q, 2H, CCH_2C), 1.87 (br, 2H, NH), 2.35 (s, 3H, $ArCH_3$), 2.69 (t, 4H, NCH_2), 3.69 (s, 4H, $ArCH_2$), 3.86 (t, 4H, $TsNCH_2$), 4.17 (t, 4H, OCH_2), 6.76–7.70 (m, 12H, ArH)
L_4	1.67 (s, 4H, CH_2), 2.34 (s, 3H, $ArCH_3$), 2.60 (s, 4H, NCH_2), 3.64 (s, 4H, $ArCH_2$), 3.79 (t, 4H, $TsCH_2$), 4.17 (t, 4H, OCH_2), 6.75–7.74 (m, 12H, ArH)
L_5	2.25 (br, 3H, NH), 2.30 (s, 3H, $ArCH_3$), 2.67 (s, 8H, NCH_2CH_2), 3.69 (s, 4H, $ArCH_2$), 3.87 (t, 4H, $TsNCH_2$), 4.21 (t, 4H, OCH_2), 6.74–7.68 (m, 12H, ArH)

the protonation of these ligands occurs to a significant extent. Ligands L_1–L_5 are bases; therefore, the deionized water used in the experiments was adjusted to pH 8 with NaOH or KOH to avoid the protonation of these ligands.

As an example, the transport curves of Na^+ and K^+ by L_3 are shown in Fig. 2. The transport rates can be calculated from the linear part of the curves. The transport rates and selectivity ratios are given in Table 4. Several conclusions can be drawn as follows:

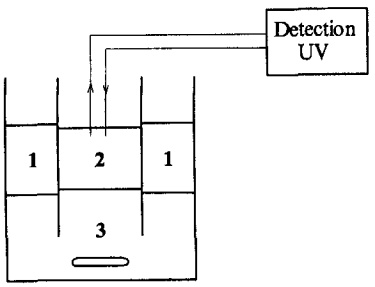


Fig. 1. Cell for liquid membrane transport.

(a) The observed transport rates of Na^+ by L_1–L_5 have the following order: $L_1 > L_3 > L_2 > L_4 > L_5$. The transport rate decreases approximately with the increase of the ring size of the ligand.

(b) The transport rates of K^+ by L_1–L_5 have the order as follows: $L_5 > L_3 \sim L_4 > L_1 > L_2$. The transport rate increases approximately with decreasing ring size.

(c) The ring size has an important effect on cation transport. The transport rate of Na^+ by L_1 is superior to that by the others, and the transport rate of K^+ by L_5 is the greatest.

(d) The methyl group in L_2 affects the transport of cations owing to the steric effect, so that L_2 has lower transport rates than L_1.

(e) L_1 and L_2 show high Na^+/K^+ selectivity ratios and L_5 has the lowest Na^+/K^+ selectivity ratio. This result indicates that L_1 and L_2 are well

Table 4. Transport rates and selectivity ratios

Ligand	Cation	Transport rate (mol $h^{-1} \times 10^7$)	Transport selectivity (v_{Na^+}/v_{K^+})
L_1	Na^+	6.60	8.92
	K^+	0.74	
L_2	Na^+	5.10	8.95
	K^+	0.57	
L_3	Na^+	5.25	1.48
	K^+	3.54	
L_4	Na^+	4.42	1.42
	K^+	3.11	
L_5	Na^+	3.23	0.54
	K^+	6.02	

adapted to complex Na^+ and L_5 is well adapted to complex K^+.

EXPERIMENTAL

Melting points were determined using a WC-1 microscopic apparatus and are uncorrected. Elemental analyses were determined on a Carlo Erba 1106 Elemental Analyser. IR spectra were recorded on a Shimadzu 435 Spectrophotometer as KBr pellets. ^{1}H NMR spectra were recorded on a Bruker ARX-500 spectrometer in $CDCl_3$. Chemical shifts (δ) are given in ppm relative to that of $CHCl_3$ (δ 7.24 ppm). UV–vis spectra were measured on a Shimadzu 2100 spectraphotometer. Mass spectra were obtained on a JMS-D100 spectrometer by the electron impact method.

All solvents were of analytical grade and were used without further purification. Ethylene diamine, 1,2-diaminopropane, 1,3-diaminopropane, 1,4-diaminobutane, diethylenetriamine and salicylaldehyde were purified by normal distillation or by distillation under reduced pressure before use.

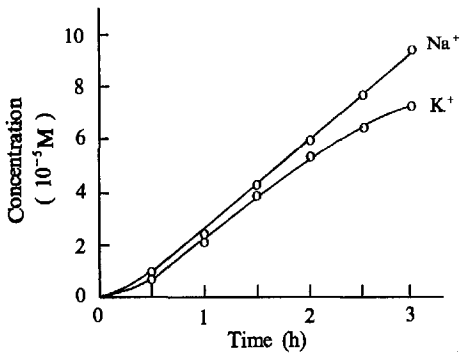


Fig. 2. The transport curves of L_3.

Preparation of N,N-*bis*[2-(4-*methylphenylsulphonyloxy*)*ethyl*]-4-*methylphenylsulphonamide* (**2**)

Diethanolamine (5.2 g, 0.05 mol) was slowly added to a stirred solution of *p*-toluenesulphonyl chloride (38.2 g, 0.2 mol) in pyridine (60 cm^3) over a period of 30 min at room temperature. The solution was stirred for 3.5 h and then water (200 cm^3) was added. Stirring was continued for an additional 1 h. The pale yellow precipitate was filtered, washed with water and dried at 60°C for 8 h to afford 24.5 g (90%) crude product. Recrystallization from methanol three times gave colourless microcrystals, m.p. 78–79°C (lit.[7] 65–67°C, lit.[8] 78–79°C).

Preparation of N,N-*bis*[2-(2-*formylphenoxy*)*ethyl*]-4-*methylphenylsulfonamide* (**3**)

Salicylaldehyde (8.5 g, 0.07 mol), potassium carbonate (11 g) and DMF (80 cm^3) were placed in a three-necked, N_2-flushed flask. The mixture was held at *ca* 80°C while **2** (18.6 g, 0.03 mol) was added. The reaction mixture was stirred vigorously at 80°C for 10 h. After cooling, the reaction mixture was poured into ice-water (200 cm^3). The pale yellow solid was filtered, washed with water and dried. Recrystallization three times from chloroform–ethanol (1 : 1) gave white crystals of the dialdehyde (12 g, 78%), m.p. 135.5–136.5°C. Found: C, 64.2; H, 5.5; N, 2.8. Calc. for $C_{25}H_{25}NO_6S$: C, 64.2; H, 5.4; N, 3.0%. IR: 2758, 1685 cm^{-1} (CHO). UV: 256 (log $\varepsilon = 4.12$), 317 (log $\varepsilon = 3.89$). ^{1}H NMR: 2.36 (s, 3H, $ArCH_3$), 3.78 (t, 4H, NCH_2), 4.31 (t, 4H, OCH_2), 6.86–7.81 (m, 12H, ArH), 10.28 (s, 2H, CHO). MS: *m/z* 467 (M^+).

Preparation of ligands

To a refluxing solution of dialdehyde **3** (1.17 g, 0.0025 mol) in methanol (150 cm^3) was added ethylenediamine (0.15 g, 0.0025 mol) in methanol (20 cm^3). After the addition, the reaction solution was stirred for 5 min, and then a small amount of borax followed by sodium borohydride (0.8 g) was added slowly to the stirred solution. The reaction solution was filtered and reduced to a small volume (*ca* 20 cm^3) by using a rotary evaporator. The residue was dissolved in water (60 cm^3) and extracted with chloroform (3×50 cm^3). The chloroform extracts were mixed and washed with water, dried over anhydrous sodium sulphate and then evaporated to dryness to afford a crude oily product, which eventually crystallized to form a white solid. Recrystallization from CH_2Cl_2–ether (1 : 2) gave 0.93 g of L_1 (75%) as white crystals.

L_2–L_5 were prepared in a manner similar to the procedure described above for ligand L_1. Recrystallization from dichloromethane–petroleum gave the desired products as white crystals; yields: L_2 71%, L_3 80%, L_4 79%, L_5 71%.

Cation transport through a liquid membrane

The apparatus with a magnetic bar (2.6 mm long and 0.7 mm in diameter, 1.5 turns s^{-1}), as shown in Fig. 1, was used.

Phase 1 : aqueous solution (15 cm^3) of alkali picrate (1×10^{-3} M) and nitrate (0.1 M).

Phase 2 : distilled water (15 cm^3).

Phase 3 : dichloromethane solution (45 cm^3) of the macrocycle to be studied (5×10^{-5}M).

The transport was performed at 25.0 ± 0.5°C. The appearance of the picrate anion in phase 2 was detected by UV–vis spectrophotometry at 355 nm for KPic and 345.5 nm for NaPic. Standard curves were obtained from the solutions with known concentrations. The absorption changes were recorded as a function of time.

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