SHORT PAPER

J. Chem. Research (S),
2003, 356–357

Synthesis and characterisation of a series of new aza-crown ethers[†]

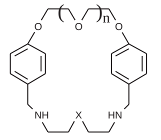
Xiao Li Hu, Guang Nong Lu, Lei Chen and Ru Dong Yang*

College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, 730000 China

A series of aza-crown ethers were synthesised by the *in situ* reduction of Schiff base crown ethers that were obtained by the condensation of a dialdehyde with a diamine in methanol solution. The aza-crown ethers were characterised by elemental analysis, FAB-MS, IR, and ^{1}H NMR. They were obtained in good yields.

Keywords: aza-crown ethers

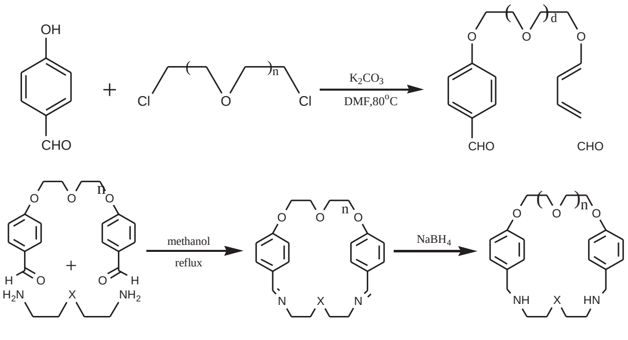
Aza-crown ethers show good coordination properties to transition metal and heavy metal ions,[1, 2] and their complexes have great importance in host-guest chemistry and as membrane transportation ionophores,[3,4] while oxa-crown ethers show strong recognition properties to alkaline ions, alkaline earth ions and rare earth ions. This paper reports a series of new aza-crown ethers compounds 5: **1** (1, 16, 19-triaza-3, 6: 11, 14-dibenzo-7, 10 – dioxa - cycloheneicosane); **2** (1, 19, 22-triaza-3, 6: 14, 17-dibenzo-7, 10, 13-trioxa-cyclotetracosane); **3** (1, 22, 25-triaza-3, 6: 17, 20-dibenzo-7, 10, 13, 16-tetraoxa-cycloheptacosane) and **4** (1, 22-diaza-3, 6: 17, 20-dibenzo-7, 10, 13, 16, 25-pentaoxa-cycloheptacosane). Each of them has these two types of functional groups in one molecule that are separated by benzenoid ring see fig. 1.



1 n=0, X=NH **2** n=1, X=NH **3** n=2, X=NH **4** n=2, X=O

Fig.1 Aza-crown ethers with two kinds of functional groups.

The synthetic route is outlined in Scheme 1. The starting materials, ethylenedioxybis (4-formylbenzene), 3-oxa-1,5-dichloropentane, 3,6-dioxa-1,8-dichlorooctane and oxybis (2-aminoethylene) were prepared according to literature methods.[5,6,7] Di (2-aminoethyl) amine was bought as chemical reagent.



Scheme 1 Preparation of aza-crown ethers **1, 2, 3, 4**.

Experimental

Carbon, hydrogen and nitrogen analyses were performed by a Carlo Erba-1106 elemental analyzer. IR spectra in the region 4000–400cm^{-1} were recorded on a Nicolet Model FT-170SX IR spectrophotometer using KBr pellets. ^{1}H NMR spectra were recorded in $CDCl_3$ in a Bruker AC80 spectrometer with TMS as an internal standard.

Mass spectra were recorded on a VG.ZAB-HS mass spectrophotometer.

General procedure: The synthetic scheme for dialdehydes is outlined in Scheme 1: 4-hydroxylbenzoaldehyde (12g, 0.1mol), potassium carbonate (13.8g, 0.1mol) and 3-oxa-1,5-dichloropentane (3,6-dioxa-1,8-dichlorooctane) (0.05mol) were stirred in DMF (100ml, 80°C) under dinitrogen for *ca* 24h. The resulting mixture was cooled and poured into 400ml ice water, the solid obtained was filtered and washed thoroughly with water. Crystallised from ethanol/water give the products as white needles.

The synthesis for the compounds **1, 2, 3** and **4**, was as in the to literature,[8] we used high dilution methods to synthesise the Schiff base precursors, then reduced with $NaBH_4$ *in situ* to obtain the final products. A solution of diamine (0.01mol) in anhydrous methanol (50ml) was added dropwise to a solution of dialdehyde (0.01mol) into boiling anhydrous methanol (800ml) in about 1 hour. The solution was refluxed for 4 hours, the precursor Schiff base was formed, cooled down to room temperature, then reduced with $NaBH_4$ (3.0g) in situ. The solvent was evaporated; 50ml of distilled water was added to the residue, which was then extracted with dichloromethane (30ml) twice. The organic layer was dried with anhydrous Na_2SO_4, distillation removed dichloromethane and left the crude product as a viscous oil, which was purified through an alkaline Al_2O_3 column, ethyl acetate/methanol (1/1) was used as eluent, the final product was obtained as a white powder. The structures of **1, 2, 3** and **4** were confirmed by ^{1}H NMR, IR, FAB-MS spectra and elemental analysis.

6,9,12-trioxa-2,5:13,16-dibenzo-1,17-hept-dialdehyde: Yield 80%, m.p. 143–144°C. ^{1}H NMR ($CDCl_3$, δppm): 4.13–4.90(dt, 8H, $–CH_2–O–$), 7.10–8.06(dd, 8H, Ar), 10.03(s, 2H, –CHO).

6,9,12,15-tetraoxa-2,5:16,9-dibenzo-1, 20-cosa-dialdehyde: Yield 78%, m.p. 70–72°C. ^{1}H NMR ($CDCl_3$, δppm): 3.90–4.27 (dt, 12H, $–CH_2–O–$), 6.86–7.86(dd, 8H, Ar), 9.80(s, 2H, –CHO).

Compound **1**: Yield 47%, m.p. 176–178°C.FAB-MS: required $[M+1]^+$ *m/z* 342.2 . ^{1}H NMR ($CDCl_3$, δppm): 6.78–7.28 (dd, 8H, Ar), 4.28 (t, 4H, $ArO–CH_2–C$), 3.73(s, 4H, $Ar–CH_2–N$), 2.78 (t, 8H, $N–CH_2–C$), 1.59 (s, 3H, –NH–); IR (KBr, cm^{-1}): 3329, 2829, 1610, 1515, 1447, 1243; EA (**1**·H_2O): Calcd. C (66.82), H (8.13), N (11.69), Found: C (66.43), H (8.48), N (11.65).

Compound **2**: Yield 70%, m.p. 56–57°C.FAB-MS: required $[M+1]^+$ *m/z* 386.2. ^{1}H NMR ($CDCl_3$, δppm): 1.77 (s, 3H, –NH–), 2.83 (t, 8H, $C–CH_2–N$), 3.70 (s, 4H, $Ar–CH_2$-N), 3.83 (t, 4H, $C–CH_2–OR$), 4.17 (t, 4H, $ArO–CH_2–C$), 6.63–7.16 (dd, 8H, Ar); IR (KBr, cm^{-1}): 3444(OH), 3317, 2803, 1608, 1511, 1444, 1247, 1113; EA (**2**·H_2O): Calcd. C (65.48), H (8.24), N (10.41), Found: C (65.63), H (8.63), N (10.48).

Compound **3**: Yield 53%, m.p. 54–55°C.FAB-MS: required $[M+1]^+$ *m/z* 430.2. ^{1}H NMR ($CDCl_3$, δppm): 6.76–7.30 (dd, 8H, Ar), 4.23 (t, 4H, $ArO–CH_2–C$), 4.01 (t, 8H, $C–CH_2–O$), 3.83 (s, 4H, $Ar–CH_2–N$), 2.93 (t, 8H, $N–CH_2–C$), 2.16 (s, 3H, –NH–); IR (KBr, cm^{-1}): 3412(OH), 3313, 2809, 1611, 1512, 1455, 1249, 1109; EA (**3**·1/2H_2O): Calcd. C (65.75), H (8.22), N (9.59), Found: C (65.60), H (7.99), N (9.59).

Compound **4**: Yield 74%, m.p. 74–75°C.FAB-MS: required $[M+1]^+$ *m/z* 431.2. ^{1}H NMR ($CDCl_3$, δppm): 6.70–7.20 (dd, 8H, Ar), 4.16

---

* To receive any correspondence. E-mail: foxhxl@hotmail.com

[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

(t, 4H, ArO–CH_2–C), 4.00 (t, 8H, O–CH_2–C), 3.80 (s, 4H, Ar–CH_2–N), 3.66 (t, 4H, O–CH_2–C–N), 2.93 (t, 4H, C–CH_2–N), 1.96 (s, 2H, –NH–); IR (KBr, cm^{-1}): 3311, 2823, 1611, 1513, 1459, 1247, 1113; EA: Calcd. C (66.98), H (7.91), N (6.51), Found: C (66.88), H (7.66), N (6.70).

The ions' recognition experiments and their rare earths complexes' preparation are in progress in our laboratory.

We are grateful to the National Science Foundation of China for financial support (No. 9573005).

Received 15 September 2002; accepted 12 March 2003
Paper 02/1554

References

1 C.T. WU, *Crown Ether Chemistry*, 1st edn., Science Press, Beijing, 1992, p.117.
2 F. Nicolò, D. Plancherel and G. Chapuis, *Inorg. Chem.*, 1988, **27**, 3518.
3 K.R. Adam, M. Antolovich and D.S. Baldwin, *J. Chem. Soc. Dalton Trans.*, 1993, (7), 1013.
4 J. Kim, A.J. Leong and L.F. Lindoy, *Dalton*, 2000, (19), 3453.
5 Z. Ma, R.D. Yang and L. Yan, *Chin. Chem. Lett.*, 1999, **10**, 995.
6 C.T. Wu, *Crown Ether Chemistry*, 1st ed., Science Press, Beijing, 1992, p.63.
7 O.A. Gansow, A. Rashid Kausar and K.B. Triplett, *J. Heterocyclic Chem.*, 1981, **18**, 297.
8 K.R. Adam, L.F. Lindoy and H.C. Lip, *J. Chem. Soc. Dalton Trans.*, 1981, (1), 74.