DALTON
FULL PAPER

Substituted diazacrown ethers. Synthesis, spectral characterization and single-crystal structures of $C_{20}H_{42}N_2O_8(NaI)_2\cdot H_2O$ and $C_{20}H_{42}N_2O_8(KI)_2\cdot H_2O$

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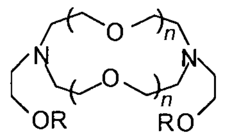
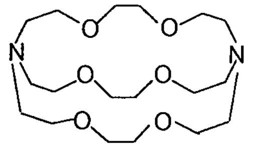
Two *N*,*N′*-bis(2-hydroxyethyl) diaza-24-crown-8 potassium and sodium complexes have been prepared by a one-step reaction of ethanolamine with 1,11-dichloro-3,6,9-trioxaundecane. Their structures are ascertained by elemental analyses, ^{1}H, ^{13}C NMR and FTIR spectra. To corroborate further the structure assignments single-crystal structures of the complexes 10,22-bis(2-hydroxyethyl)-1,4,7,13,16,19-hexaoxa-10,22-diazacyclotetracosane-bis(sodium iodide) monohydrate and -bis(potassium iodide) monohydrate were determined. The structural features of the complexes are compared with each other and those of diazacrown ethers and cryptates.

Owing to the recognition of the complexation properties of macrocyclic polyethers with alkali-, alkaline-earth-metal cations and uncharged organic molecules,[1,2] considerable work has been done in the macrocyclic polyethers area.[3–14] There are several kinds of macrocyclic polyethers, *e.g.* monocyclic crowns (coronands),[1,2,7,9,10,14] bicyclic polyethers (cryptands),[15–18] tricyclic polyethers (spherands),[6,19,20] cavitands,[6,20] and lariat ethers.[4,6,8,21–27] The particular ligation behaviour of polyethers depends on different parameters including the number of donor atoms, the nature of the ring size as well as topological and conformational parameters. It has been shown that ligation properties of lariat ethers are enhanced relative to the simple monocyclic polyethers and the donor group bearing side-arm of polyethers participates intramolecularly in the complexation process both in solution and in the solid states.[25,26,28,29] In lariat ethers, cation selectivity is increased because the ethers are designed to mimic naturally occurring ionophors like valinomycin by surrounding a cation with a three-dimensional, intramolecular array including the additional two binding arms attached to the ring nitrogen atoms, as do the cryptands or spherands.[6,27] Functional groups in lariat crown ethers are useful to attach additional complexation sites or lipophilic side groups to bind the crowns to the polymer backbone, to tie together two or more crown compounds (bis- or tris-crown ethers) or to form new host topologies.[6,21–29] General formulae of the lariat crown ethers and cryptands are illustrated below.

In this study, we report: (i) the first binuclear complexes (**2a** and **2b**) of the bibrachial lariat ether (BiBLE) **2** with NaI or KI, respectively; (ii) the characterization of the new complexes, $[(2M^+ \subset H1\text{-}33\text{-}1H)\ 2I^-\cdot H_2O]$ (M = Na **2a** or K **2b**), with respect to the analytical, physical, spectroscopic and crystal structure data; (iii) the structural comparison of **2a** and **2b** with the lariat ether complexes (**1a**, **1b** and **3b**),[25] and cryptates (**4a** and **4b**).[30,31] In describing the BiBLEs (**2** and **3**) and their complexes (**1a**, **1b**, **2a**, **2b** and **3b**), a shorthand (analogous to that used for cryptates[16,17]) has been adopted.[25] For example, BiBLEs **2** and **3** have been designated as H1-22-1H and H1-33-H1, respectively, where H1 refers to a hydroxyl oxygen rather than an ether.



	n	R	Notation[25]
1	2	H	[H1-22-1H]
2	3	H	[H1-33-1H]
3	2	Me	[1-22-1]
1a	$[(Na^+\subset H1\text{-}22\text{-}1H)I^-]$		
1b	$[(K^+\subset H1\text{-}22\text{-}1H)I^-]$		
2a	$[(2Na^+\subset H1\text{-}33\text{-}1H)2I^-]$		
2b	$[(2K^+\subset H1\text{-}33\text{-}1H)2I^-]$		
3b	$[(K^+\subset 1\text{-}22\text{-}1)I^-]$		



4	cryptand 222
4a	$[(Na^+\subset 222)I^-]$
4b	$[(K^+\subset 222)I^-]$

Experimental

General

Melting points were measured on a Thomas Hoover apparatus using a capillary tube. FTIR spectra were obtained from a Mattson 1000 FTIR spectrometer as KBr discs and are reported in cm^{-1}. Proton (200 MHz) NMR spectra were recorded with a Bruker AC-200 FT-NMR spectrometer (Me_4Si as internal standard); ^{13}C (50 MHz) NMR were also obtained with the Bruker instrument. Microanalyses were carried out by the microanalytical service of TÜBİTAK-MAE Gebze-Kocaeli (Turkey).

Chemicals

Silica gel used for column chromatography was 70–230 mesh

Table 1 Experimental data and structure-refinement parameters

Compound	**2a**	**2b**
Formula	$C_{20}H_{44}N_2O_9Na_2I_2$	$C_{20}H_{44}N_2O_9K_2I_2$
M	772.37	788.6
Crystal system	Monoclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$
T/K	298	298
a/Å	15.798(1)	9.678(2)
b/Å	11.148(1)	9.680(1)
c/Å	17.643(2)	17.648(2)
α/°		81.22(2)
β/°	100.79(1)	81.20(2)
γ/°		70.46(2)
U/Å^3	3052.3(4)	1530.6(2)
Z	4	2
μ_{calc}/mm^{-1}	2.01	2.38
Reflections measured	3354	5478
Unique reflections	3085	4777
Number of reflections with $I > 3\sigma(I)$	2187	3904
R_{int}	0.021	0.035
R	0.032	0.050
R'	0.047	0.065

Table 2 Selected geometric parameters (Å, °) for compound **2a**

Na1–O1	2.459(4)	O4–C10	1.409(6)
Na1–O2	2.400(4)	O3–C7	1.409(5)
Na1–O3	2.474(4)	N1–C3	1.479(7)
Na1–O4	2.558(3)	O3–C8	1.444(6)
Na1–O5	2.575(4)	N1–C4	1.475(6)
Na1–N1	2.573(4)	N1–C6	1.472(6)
O1–C1	1.416(5)	C2–C3	1.486(7)
O1–C2	1.433(6)	C4–C5	1.491(7)
O2–C5	1.405(6)	C6–C7	1.489(8)
O4–C9	1.426(6)	C8–C9	1.493(7)
O1–Na1–O2	119.6(1)	Na1–O4–C10	113.9(3)
O1–Na1–O4	147.6(1)	C9–O4–C10	113.9(3)
O1–Na1–O3	109.9(1)	Na1–O3–C7	112.8(3)
O1–Na1–O5	98.9(1)	Na1–O3–C8	114.4(3)
O1–Na1–N1	69.0(1)	C7–O3–C8	110.9(4)
O2–Na1–O4	92.6(1)	Na1–N1–C3	108.2(2)
O2–Na1–O3	94.6(1)	Na1–N1–C4	109.3(3)
O2–Na1–O5	87.4(1)	Na1–N1–C6	105.6(3)
O2–Na1–N1	69.4(1)	C3–N1–C4	110.2(4)
O4–Na1–O3	67.9(1)	C3–N1–C6	111.5(4)
O4–Na1–O5	77.4(1)	C4–N1–C6	111.8(4)
O4–Na1–N1	132.6(1)	O1–C2–C3	109.4(4)
O3–Na1–O5	145.2(1)	N1–C3–C2	113.3(4)
O3–Na1–N1	70.3(1)	N1–C4–C5	111.8(4)
O5–Na1–N1	140.8(1)	O2–C5–C4	110.0(4)
Na1–O1–C1	118.5(3)	N1–C6–C7	112.1(4)
Na1–O1–C2	116.6(3)	O3–C7–C6	111.2(4)
C1–O1–C2	110.9(4)	O3–C8–C9	108.5(4)
Na1–O2–C5	111.6(3)	O4–C9–C8	111.6(4)
Na1–O4–C9	111.2(3)		
O2–Na1–O1–C1	95.8(1)	O3–Na1–O1–C1	163.8(1)
O4–Na1–O1–C1	−20.3(1)	O5–Na1–O1–C1	−119.0(1)
N1–Na1–O1–C1	28.8(1)	O1–Na1–O2–C4	−54.3(1)
O1–Na1–O2–C5	73.7(1)	O3–Na1–O2–C4	−145.2(1)
O3–Na1–O2–C5	−17.2(1)	O4–Na1–O2–C4	69.5(1)
O4–Na1–O2–C5	−162.5(1)	O5–Na1–O2–C4	−146.4(1)
O5–Na1–O2–C5	−18.4(1)	N1–Na1–O2–C4	11.8(1)
N1–Na1–O2–C5	139.9(1)	O1–Na1–O3–C6	−107.7(1)
O1–Na1–O3–C7	22.6(1)	O2–Na1–O3–C6	−13.7(1)
O2–Na1–O3–C7	116.6(1)	O4–Na1–O3–C6	78.9(1)
O4–Na1–O3–C7	−150.8(1)	O5–Na1–O3–C6	165.6(1)
O5–Na1–O3–C7	−64.1(1)	N1–Na1–O3–C6	−43.6(1)
N1–Na1–O3–C7	86.7(1)	O1–Na1–O4–C8	−161.7(1)
O1–Na1–O4–C9	61.7(1)	O2–Na1–O4–C8	90.6(1)
O2–Na1–O4–C9	−46.1(1)	O3–Na1–O4–C8	10.7(1)
O3–Na1–O4–C9	−125.9(1)	O5–Na1–O4–C8	−69.7(1)
O5–Na1–O4–C9	153.7(1)	N1–Na1–O4–C8	149.0(1)

(Merck), and all reactions were monitored by using Kieselgel 60 F 254 (silica gel) precoated TLC plates. Standard procedures were employed in drying the solvents. Ethanolamine (98%, Merck) was distilled from Zn(dust)–KOH. The other chemicals were used as supplied. 1,11-Dichloro-3,6,9-trioxaundecane was prepared by the known literature procedure.[32]

Synthetic procedures

10,22-Bis(2-hydroxyethyl)-1,4,7,13,16,19-hexaoxa-10,22-diazacyclotetracosane bis(sodium iodide) monohydrate, [(Na$^+$$\subset$H1-33-1H)2I$^-$·H$_2$O] 2a. A solution of ethanolamine (6.10 g, 0.10 mol), 1,11-dichloro-3,6,9-trioxaundecane (23.10 g, 0.10 mol), NaI (34.45 g, 0.23 mol) and anhydrous Na_2CO_3 (12.72 g, 0.12 mol) was stirred vigorously and refluxed in 0.5 L of MeCN for 72 h. The solution was cooled, filtered and evaporated under reduced pressure. The residue was chromatographed on silica gel using $CHCl_3$–THF (3 : 1) as eluent. The appropriate product was recrystallized from $CHCl_3$–Me_2CO (1 : 3) to give 3.4 g (9.0%) of **2a** as a white crystalline solid (mp 175 °C). IR (KBr): 3412s, 3310s ($\nu_{O\text{–}H}$), 2978, 2902, 2851s ($\nu_{C\text{–}H}$), 1651, 1483, 1451, 1348s, 1343, 1115, 1089s, 1052s (ν_{COC} asym.), 930 cm^{-1}. ^{1}H NMR (D_2O): δ 2.76 and 2.84 (t and t, 12H, $^3J_{HH}$ = 6.24 and 5.76 Hz, CH_2N), 3.71 (m, 28H, CH_2O). ^{13}C NMR (D_2O): δ 53.73, 56.23, 59.22, 68.84, 70.11, 70.23 (Found: C, 31.91; H, 5.63; N, 3.94. Calc. for $C_{20}H_{44}N_2O_9Na_2I_2$: C, 31.74; H, 5.55; N, 3.70%).

10,22-Bis(2-hydroxyethyl)-1,4,7,13,16,19-hexaoxa-10,22-diazacyclotetracosane bis(potassium iodide) monohydrate [(K$^+$$\subset$H1-33-1H)2I$^-$·H$_2$O] 2b. This compound was synthesized by following the procedure for complex **2a**, starting from ethanolamine (6.10 g, 0.10 mol), 1,11-dichloro-3,6,9-trioxaundecane (23.10 g, 0.10 mol), K_2CO_3 (16.56 g, 0.12 mol) and KI (38.18 g, 0.23 mol) in 0.5 L MeCN. The residue was chromatographed on silica gel using MeOH–Me_2CO (1 : 3) as eluent. The complex was crystallized from MeOH–Me_2CO (1 : 3) to give 9.6 g (12.5%) of **2b** as a white crystalline solid (mp 165 °C). IR (KBr): 3392s, 3299s ($\nu_{O\text{–}H}$), 2980, 2949, 2908s, 2846 ($\nu_{C\text{–}H}$), 1651, 1483, 1451, 1348s, 1343, 1119s, 1075s, 1049s ($\nu_{COC\ asym.}$), 930 cm^{-1}. ^{1}H NMR (D_2O): δ 3.11 and 3.19 (t and t, 12H, $^3J_{HH}$ = 6.33 and 5.84 Hz, CH_2N), 4.05 (br s, 28H, CH_2O). ^{13}C NMR (D_2O): δ 56.03, 58.57, 61.58, 71.16, 72.40 (Found: C, 31.77; H, 5.79; N, 3.62. Calc. for $C_{20}H_{44}N_2O_9K_2I_2$: C, 32.05; H, 5.92; N, 3.74%).

10,22-Bis(2-hydroxyethyl)-1,4,7,13,16,19-hexaoxa-10,22-diazacyclotetracosane 2. Complex **2b** (8.0 g, 1.06, 10^{-2} mol) was dissolved in H_2O (50 mL) and the solution was continuously extracted with chloroform (250 mL) for 48 h. The organic phase was dried over Na_2SO_4. Evaporation of the chloroform gave the free lariat ether **2** as a hygroscopic liquid, yield 2.4 g (53.5%). IR (KBr): 3361 (br) ($\nu_{O\text{–}H\,+\,H_2O}$), 2927, 2876s ($\nu_{C\text{–}H}$), 1114s ($\nu_{COC}$). ^{1}H NMR ($CDCl_3$): δ 2.57 (m, 12H, CH_2N), 3.47 (m, 28H, CH_2O), 3.72 (s, 4H, OH and H_2O) (Found: C, 52.35; H, 9.33; N, 6.24. Calc. for $C_{20}H_{44}N_2O_9$: C, 52.61; H, 9.71; N, 6.14%).

X-Ray crystallography

Experimental data, methods and procedures used to elucidate the structures of **2a** and **2b** and other related parameters are given in Table 1. Since the difference syntheses did not clarify the positions of the H atoms they were placed in calculated positions at a distance of 0.95 Å from the corresponding atoms. Non-H atoms were refined anisotropically. A riding model was used in refinement processes of the geometrically calculated H positions. Calculations were carried out using SHELXS86[33] and MolEN[34] packages on the Microvax 3100 computer. The atomic scattering factors were taken from ref. 35. The selected geometric parameters for the structures **2a** and **2b** are given in Tables 2 and 3.

CCDC reference number 186/1143.

Table 3 Selected geometric parameters (Å, °) for compound **2b**

K2–O3	2.514(7)	K2–O4	2.464(9)
K2–O5	2.399(9)	K2–O6	2.476(7)
K2–O7	2.563(9)	K2–N2	2.56(1)
K2–O9	2.585(7)	K1–O9	2.602(7)
O1–C1	1.40(2)	O2–C4	1.43(1)
O2–C5	1.43(2)	O3–C6	1.44(1)
O3–C7	1.44(1)	O4–C8	1.43(1)
K1–O1	2.402(9)	O5–C12	1.40(2)
K1–O2	2.472(7)	O6–C14	1.42(1)
K1–O3	2.557(9)	O6–C15	1.43(2)
K1–O7	2.513(7)	O7–C16	1.43(1)
K1–O8	2.466(9)	O7–C17	1.44(1)
K1–N1	2.57(1)	O8–C18	1.42(1)
O8–C19	1.42(2)	C5–C6	1.49(2)
N2–C10	1.47(2)	C7–C8	1.48(2)
N2–C11	1.47(1)	C9–C10	1.50(2)
N2–C13	1.47(1)	C11–C12	1.48(2)
N1–C2	1.48(1)	C13–C14	1.50(2)
N1–C3	1.46(1)	C15–C16	1.49(2)
N1–C20	1.47(2)	C17–C18	1.50(2)
C1–C2	1.49(2)	C19–C20	1.50(2)
C3–C4	1.49(2)	O4–C9	1.42(2)
O4–K2–O5	119.0(3)	O4–K2–O6	109.7(3)
O4–K2–O7	147.6(3)	O4–K2–N2	68.8(3)
O5–K2–O6	95.4(3)	O3–K2–O4	68.1(3)
O5–K2–O7	93.2(3)	O3–K2–O5	164.8(3)
O5–K2–N2	69.1(3)	O3–K2–O6	94.4(2)
O3–K2–O7	79.8(3)	O3–K2–N2	125.3(3)
O6–K2–O7	67.7(3)	O6–K2–N2	70.7(3)
O7–K2–N2	132.7(3)	O3–K1–O7	79.9(3)
O1–K1–O2	95.3(3)	O3–K1–O8	147.6(3)
O1–K1–O3	93.2(3)	O3–K1–N1	132.8(3)
O1–K1–O7	165.0(3)	O1–K1–O8	118.9(3)
O1–K1–N1	69.3(3)	O7–K1–O8	68.0(3)
O7–K1–N1	125.0(3)	O2–K1–O3	67.8(3)
O2–K1–O7	94.4(2)	O2–K1–O8	109.7(3)
O2–K1–N1	70.6(3)	O8–K1–N1	68.6(3)
K1–O1–C1	111.8(8)	N1–K1–C1	49.0(3)
K1–O2–C4	112.6(6)	K1–O2–C5	115.2(6)
C4–O2–C5	110.4(8)	K2–O3–K1	86.9(3)
K2–O3–C6	122.3(6)	K2–O3–C7	105.4(5)
K1–O3–C6	111.0(7)	K1–O3–C7	115.4(6)
C6–O3–C7	113.5(8)	K2–O4–C8	117.3(7)
K2–O4–C9	116.8(7)	C8–O4–C9	112.4(9)
K2–O5–C12	111.7(8)	K2–O6–C14	112.6(6)
K2–O6–C15	115.2(6)	C14–O6–C15	110.4(8)
K2–O7–K1	86.8(3)	K2–O7–C16	110.9(7)
K2–O7–C17	115.2(6)	K1–O7–C16	122.3(6)
K1–O7–C17	105.6(5)	C16–O7–C17	113.6(8)
N1–C3–C4	113.1(1)	K1–O8–C18	117.6(7)
K1–O8–C19	116.7(7)	C18–O8–C19	112.0(9)
K1–O9–K2	84.5(8)	O9–K2–O7	77.6(7)
O9–K2–O6	145.4(9)	O9–K2–O5	87.0(7)
O9–K2–N2	140.4(8)	O9–K2–O4	99.0(9)
O9–K2–O3	78.4(8)	O9–K1–O3	77.3(7)
O9–K1–O1	87.3(7)	O9–K1–O2	145.1(8)
O9–K1–N1	140.8(9)	O9–K1–O8	99.1(9)
O9–K1–O7	78.2(8)	N1–C20–C19	113.0(1)
O2–C4–C3	110.0(9)	K2–N2–C10	108.4(6)
K2–N2–C11	109.0(7)	K2–N2–C13	105.2(7)
O2–C5–C6	108.5(9)	C10–N2–C11	110.3(9)
O3–C6–C5	111.8(8)	C10–N2–C13	111.6(9)
C11–N2–C13	112.2(8)	K1–N1–C2	108.8(7)
O3–C7–C8	112.2(8)	K1–N1–C3	105.3(7)
O4–C8–C7	109.0(1)	K1–N1–C20	108.6(6)
O4–C9–C10	109.0(1)	C2–N1–C3	111.9(8)
C2–N1–C20	110.0(9)	C3–N1–C20	112.2(9)
N2–C10–C9	113.0(1)	N2–C11–C12	111.8(9)
O1–C1–C2	109.1(9)	N1–C2–C1	112.0(1)
O5–C12–C11	109.3(9)	O7–C16–C15	112.1(9)
N2–C13–C14	113.0(1)	O7–C17–C18	111.7(8)
O8–C18–C17	109.0(1)	O6–C14–C13	109.9(9)
O8–C19–C20	109.0(1)	O6–C15–C16	108.5(9)
O4–K2–O3–K1	146.8(3)	O6–K2–O3–K1	−103.7(3)
O7–K2–O3–K1	−37.3(2)	N2–K2–O3–K1	−173.1(3)
O3–K2–O7–K1	38.0(2)	O4–K2–O7–K1	45.1(6)
O5–K2–O7–K1	−128.4(3)	O6–K2–O7–K1	137.1(3)
N2–K2–O7–K1	167.3(4)	O1–K1–O3–K2	−128.4(3)
O2–K1–O3–K2	137.1(3)	O7–K1–O3–K2	38.1(2)
O8–K1–O3–K2	45.1(6)	N1–K1–O3–K2	167.1(4)
O2–K1–O7–K2	−103.8(3)	O3–K1–O7–K2	−37.3(2)
O8–K1–O7–K2	146.8(3)	N1–K1–O7–K2	−173.1(3)

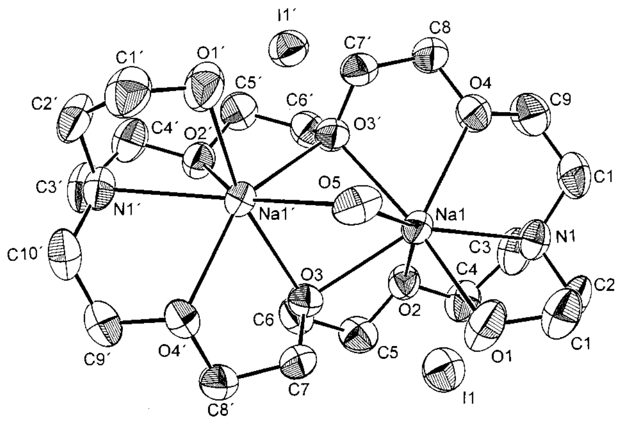
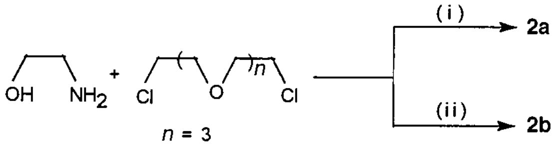


Fig. 1 An ORTEP drawing of molecule **2a** with the atom-numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

See http://www.rsc.org/suppdata/dt/1998/3635/ for crystallographic files in .cif format.

Results and discussion

Bibrachial lariat ethers (BiBLEs) may be prepared by either single or multi-step reactions.[36–39] In the present study, *N*,*N*′-bis(2-hydroxyethyl) diaza-24-crown-8 types of lariat ether complexes have been synthesized by a one-step reaction of ethanolamine with 1,11-dichloro-3,6,9-trioxaundecane. As shown in Scheme 1, compounds **2a** and **2b** are obtained from the reactions of ethanolamine and 1,11-dichloro-3,6,9-trioxaundecane in MeCN using Na_2CO_3–NaI and K_2CO_3–KI, respectively. Compounds **2a** and **2b** are binuclear complexes of diaza-24-crown-8 type lariat ether bridged by a water molecule. To the best of our knowledge, there are no other binuclear lariat ether complexes of this type. Free lariat ether **2** is obtained in good yield from the chloroform extraction of complex **2b** in water. The structures of these compounds (**2a**, **2b** and **2**) are determined by elemental analyses, ^1H, ^{13}C NMR and FTIR spectra (see Experimental section). The obtained results are in good agreement with the expected ones. According to the ^{13}C NMR spectra, **2a** and **2b** have six ^{13}C NMR signals, which show that the structures in solution are symmetrical. The lariat ethers (**1** and **3**) and their complexes (**1a**, **1b** and **3b**)[25] and the cryptand complexes (**4a** and **4b**)[30,31] have been reported previously. The crystal structures of **2a** and **2b** are determined and they are compared with the structural results of **1a**, **1b**, **3b**, **4a** and **4b**.



Scheme 1 Synthesis of the lariat ether complexes, (i) Na_2CO_3–NaI in MeCN; (ii) K_2CO_3–KI in MeCN.

Crystal structure of $C_{20}H_{44}N_2O_9Na_2I_2$ 2a

Colourless crystals of the sodium iodide complex of 10,22-bis(2-hydroxyethyl)-1,4,7,13,16,19-hexaoxa-10,22-diazacyclotetracosane suitable for X-ray structural investigations were obtained from $CHCl_3$–EtOH (3 : 1). Fig. 1 shows an ORTEP[40] drawing of the structure with atom numbering. Compound **2a** is a crystallographically centrosymmetric binuclear sodium complex. The asymmetric unit contains only one half molecule. Sodium is seven-coordinate bonding to five oxygen atoms from the macroring, one oxygen from the bridging water molecule and one nitrogen. The side arms are arranged in a *syn* fashion

Table 4 Comparison of selected structural parameters of compounds **2a** and **2b** with lariat ether (**1a**, **1b** and **3b**) and cryptand (**4a** and **4b**) complexes

	Sodium complex			Potassium complex				
					2b			
Interaction	**1a**[a]	**2a**	**4a**[b]	**1b**[a]	K1	K2	**3b**[c]	**4b**[d]
M–O/Å	2.611	2.400(4)	2.582	2.834	2.472(7)	2.514(7)	2.848	2.776
Ring	2.437	2.558(3)	2.582	2.834	2.557(9)	2.464(9)	2.848	2.776
	2.590	2.474(4)	2.582	2.848	2.513(7)	2.476(7)	2.803	2.789
	2.564	2.575(4)	2.566	2.848	2.466(9)	2.563(9)	2.803	2.789
	—	—	2.566	—	2.602(7)	2.585(7)	—	2.790
	—	—	2.566	—	—	—		2.790
Sidearm	2.426	2.459(4)	—	2.721	2.402(9)	2.399(1)	2.860	—
	2.588	—	—	2.721	—	—	2.860	—
M–N/Å	2.630	2.573(4)	2.782	3.128	2.57(1)	2.56(1)	2.941	2.874
	2.637	—	2.722	3.128	—	—	—	2.874
R/Å	1.14	1.136	1.19	1.46	1.094	1.094	1.438	1.38
N–M–O (bridged)/°	—	140.8(1)	—	—	140.8(9)	140.4(9)	—	—
N–M–N/°	159.5	—	180	176.4	—	—	180	180
N···N/Å	5.183	8.569	5.504	6.253	8.558	8.558	5.882	5.748
Coordination number	8	7	8	8	7	7	8	8

[a] Ref. 25. [b] Ref. 30. [c] Refs. 25 and 26. [d] Ref. 31.

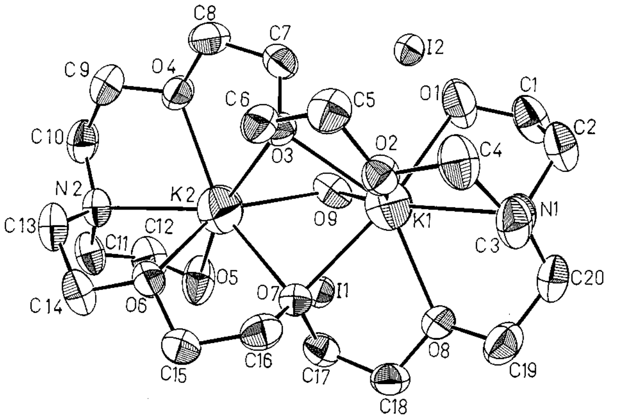


Fig. 2 An ORTEP drawing of molecule **2b** with the atom-numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

as in the monodentate sodium and potassium complexes of **1**. The bridging water oxygen atom coordinates to symmetry related Na^+ ions. Besides that, the two symmetry related oxygen atoms contribute to the bridging between two Na^+ ions. The Na–O_{water} bond length is the longest Na–O bond in the structure, as in compound **2b**. In **2a**, the bridging Na–O–Na′ bond angles [Na1–O3–Na′ 86.4(1), Na1–O5–Na1′ 85.2(1)°] are smaller than the O3–Na1–O5 [145.2(1)°] angle, which is different from O–K–O [average 78.5(6)°] angle in **2b**.

Crystal structure of $C_{20}H_{44}N_2O_9K_2I_2$, 2b

Colourless crystals of potassium iodide complex of 10,22-bis(2-hydroxyethyl)-1,4,7,13,16,19-hexaoxa-10,22-diazacyclotetracosane suitable for X-ray structural investigations were obtained from MeOH–Me_2CO (1 : 3). Fig. 2 shows an ORTEP drawing of the structure with atom numbering. Compound **2b** is a binuclear potassium complex. Potassium is seven-coordinate bonding to five oxygen atoms from the macroring, one oxygen from the water molecule and one nitrogen. Two O atoms of the macroring contribute to the bridging between the two K^+ ions, as well as the oxygen of the bridging water molecule. The interatomic distances $O9_{water}$–H9 ··· O1 [2.566(2) Å] and $O9_{water}$–H9′ ··· O7 [2.390(2) Å] indicate the close contacts leading to the interactions between the atoms. The macroring is highly twisted probably to accommodate the two K^+ ions. Therefore, the side arms are neither in *syn* nor *anti* fashion. In this respect binuclear K^+ complex **2b** seems to be different from the mononuclear K^+ and Na^+ complexes of **1**.[6,25,26] The water oxygen atom contributing to the bridging is so positioned that the K1–O9 [2.602(7) Å] and K2–O9 [2.585(7) Å] bond distances are almost the same; the corresponding bond lengths between the two K^+ ions and the coordinated N or O atoms are also nearly the same, as can be seen from Table 4. The side arm O atom–K^+ ion bond lengths are the shortest K–O bond distances in the structure. The bridging K–O–K bond angles [K1–O9–K2 84.5(8), K1–O3–K2 86.9(3), K1–O7–K2 86.8(3)°] are larger than the O–K–O [average 78.5(6)°] angles. The arrangement of the donor atoms in complex **2b** seems to be different from the cryptand 222 complexes of Na^+ and K^+ (**4a** and **4b**). So, the M–O bond lengths found are shorter than those reported for the cryptate complexes.[31] There is no significant difference between the M–O_{water} bond lengths [K1–O9 2.602(7), K2–O9 2.585(7) Å and Na1–O5 = 2.575(4) Å] and M–O_{water}–M bond angles [K1–O9-K2 84.5(8) and Na1–O5–Na1′ 85.2(1)°] in the structures of compounds **2a** and **2b**. However, the M–O_{water}–M bond angles have smaller values than the other M–$O_{bridging}$–M bond angles, while the M–O_{water} bond lengths are longer than the M–$O_{bridging}$ ones. Generally, the corresponding intramolecular N–N distances, bond lengths and angles for compounds **2a** and **2b** (binuclear complexes) are in good agreement, regardless of the metal type, as can be seen from Table 4. In the mononuclear complexes, generally, the M–O and M–N bond lengths and the mean cavity radius values, *R*,[41] are larger than in the binuclear complexes. Thus, in mononuclear lariat ether and cryptand 222 complexes, the fitting between the cavity and the part of the cation located inside it is better than that between the cavity and the whole cation in binuclear lariat ether complexes. In bibrachial lariat ether complexes, BiBLEs, generally, when two side arms are attached to a macroring, complexation may be enhanced by ligation from the same or opposite sides of the macroring. It is pointed out in the literature that the complexes are expected to resemble cryptate complexes, when complexation occurs from the same side.[25,26] Characteristic structural data for K^+ and Na^+ complexes **2a** and **2b** are presented in Table 4 along with comparable data for cryptand 222 complexes, **4a** and **4b**, and *anti* fashioned complexes **3b**. The large N–K distance in [(K^+ ⊂1-22-1)I^-] **3b**[25] (2.941 Å) suggests that nitrogen may not be involved as a donor atom. The *R* value in binuclear Na^+ complexes is in good agreement with Shannon's value[42] and cryptate and lariat ether complexes of sodium. However, the *R* values in the binuclear lariat ether K^+ complex **2b** are not in agreement with the *R* values given for the cryptate complexes and the values given in

Shannon's table.[42] In the binuclear Na^+ lariat ether complex **2a** the mean cavity radius values, *R*, are larger than in the binuclear K^+ lariat ether complex, as can be seen from Table 4. The structural data suggest that the binuclear K^+ and Na^+ lariat ether (BiBLE) complexes do not encapsulate K^+ and Na^+ metal ions as well as the cryptands.

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