FULL PAPER

Synthesis and Characterization of New Bis(crown ether)s of Schiff Base Type Containing Recognition Sites for Sodium and Nickel Guest Cations [1])

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Abstract. New bis(crown ether) ligands of Schiff base type (**2**–**4**) containing recognition sites for sodium and nickel guest cations have been synthesized by the condensations of two equivalents of 4'-formyl-5'-hydroxy(benzo-15-crown-5) (**1**) with diamines, $H_2N-(CH_2)_n-NH_2$ (n = 2–4). Homonuclear ditopic crystalline 2 : 1 (Na$^+$: ligand) complexes (**2a**–**4a**, **2b**–**4b**) of the ligands with NaSCN and NaClO$_4$ have been prepared. The NaClO$_4$ complexes of **3** and **4** (**3b** and **4b**) form heteronuclear tritopic crystalline complexes with Ni$^{2\oplus}$ cations of stoichiometry 2 : 1 : 1 (Na$^\oplus$: Ni$^{2\oplus}$: Ligand). A homonuclear monotopic Ni$^{2\oplus}$ complex has also been prepared by the reaction with Ni(CH$_3$COO)$_2 \cdot$ 6H$_2$O. The UV-VIS spectra of **2**–**4** and their NaClO$_4$ complexes (**2b**–**4b**) are studied in different solvents including acidic and basic media. In polar solvents, tautomeric equilibria (phenol–imine, O–H···N and ketoamine, O···H–N forms) are present, as supported by the UV-VIS data.
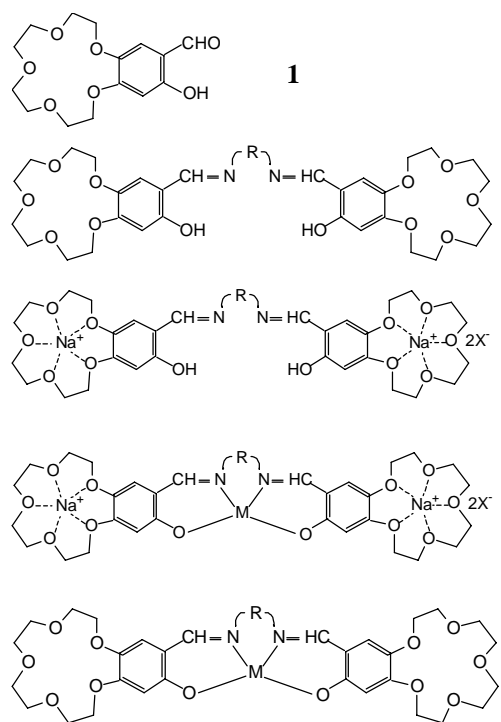
The study of bis(crown ether)s has attracted great interest in the last two decades, not only from the synthetic and selective alkali and alkaline earth cation complexation properties point of view, but also with respect to their unusual structural characteristics [1, 2]. For the linkage of two crown ether units by means of aliphatic or aromatic chains, ester [3, 4, 5], amide [6, 7] and Schiff base type [8, 9] precursors are commonly used. It is a well-known fact that monocyclic crown and also bis(crown ether)s yield complexes with alkali [10, 11] and alkaline earth metal ions [11, 12]. If the diameter of the metal ion is larger than the hole size of the crown ether ring, sandwich type complexes (clams) are formed, giving rise to a stabilizing "bis(crown ether) effect" [12, 13, 14] in case of the intramolecular bis(crown) sandwich complexes. And, derived from this, bis(crown ether)s are more selective than the corresponding crown ether components (coronands) with reference to particular cations, *e.g.* K$^+$ against Na$^+$ [8]. In addition to the homonuclear mono- and ditopic complexes of bis(crown ether)s with alkali and alkaline earth metal ions, heteroatoms of the linkage unit between the two crown ether rings can form complexes with some transition metal cations [15] to yield interesting heteronuclear (heteropolymetallic) oligotopic complexes of bis(crown ether)s in solution and in the solid state [1]. Complexes of this type may be used as simple models for biological systems, such as metalloenzymes [16].

In this paper, we describe the synthesis of new tritopic bis(crown ether)s **3** and **4** (Scheme 1) characteristic of a double Schiff base structure connecting two salicylidene modified benzo-15-crown-5 rings *via* alkyl chains of different length that are homologues of **2**. Homobinuclear sodium thiocyanate (**2a**–**4a**) and sodium perchlorate complexes (**2b**–**4b**), heterotrinuclear sodiumnickel(II) complexes (**3c** and **4c**) as well as a mononuclear nickel(II) complex (**3d**) including the salient features of their IR, ^{1}H-, ^{13}C-NMR, UV-VIS and MS spectra are reported.

Synthesis

The starting compounds, benzo-15-crown-5 (B15C5) [17], 4'-formyl -B15C5 [18], 4'-hydroxy-B15C5 [19] and 4'-formyl-5'-hydroxy-B15C5 (**1**) [20] were prepared according to literature methods. The bis(crown ether) Schiff base ligand **2** has been obtained previously [20], unlike the corresponding binuclear sodium complexes **2a** and **2b** of **2** which are new. These complexes (**2a** and **2b**) were prepared to draw a comparison with the binuclear sodium complexes of the ligand homologues **3** and **4** (**3a**, **3b**, **4a** and **4b**) in order to see the effect of the linking aliphatic chain length [-(CH$_2$)$_n$-; n = 2, 3, 4]. The ligands **3** and **4** as well as their complexes are new compounds. Yields, elemental analyses and physical data for all new compounds are given in Table 1.

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[1]) Schiff Bases and their Complexes with Metal Ions. Part III (Part II in ref. [29])

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Compounds	R		
2	-(CH$_2$)$_2$-		
3	-(CH$_2$)$_3$-		
4	-(CH$_2$)$_4$-		

Complexes	R	M	X
2a	-(CH$_2$)$_2$-	–	SCN
2b	-(CH$_2$)$_2$-	–	ClO$_4$
3a	-(CH$_2$)$_3$-	–	SCN
3b	-(CH$_2$)$_3$-	–	ClO$_4$
4a	-(CH$_2$)$_4$-	–	SCN
4b	-(CH$_2$)$_4$-	–	ClO$_4$
3c	-(CH$_2$)$_3$-	Ni	ClO$_4$
4c	-(CH$_2$)$_4$-	Ni	ClO$_4$
3d	-(CH$_2$)$_3$-	Ni	–

Scheme 1 Crown compounds and complexes

Table 1 Analytical and experimental details

Compound	Formula	Colour	Yield (%)	Elemental Analyses (%) Calcd. (Found)			
				C	H	N	S
3	C$_{33}$H$_{46}$N$_2$O$_{12}$ · 1/2H$_2$O	Yellow	40	58.95(58.95)	6.99(6.96)	4.16(4.35)	–
4	C$_{34}$H$_{48}$N$_2$O$_{12}$ · H$_2$O	Yellow	54	58.76(58.84)	7.26(6.87)	4.03(4.13)	–
2a	C$_{32}$H$_{44}$N$_2$O$_{12}$Na$_2$(SCN)$_2$ · 2H$_2$O	Yellow	81	48.22(48.32)	5.71(5.33)	6.62(6.56)	7.56(7.41)
2b	C$_{32}$H$_{44}$N$_2$O$_{12}$Na$_2$(ClO$_4$)$_2$ · H$_2$O	Yellow	83	42.15(42.28)	5.04(5.10)	3.07(3.22)	–
3a	C$_{33}$H$_{46}$N$_2$O$_{12}$Na$_2$(SCN)$_2$ · H$_2$O	Yellow	75	49.87(50.28)	5.74(5.53)	6.65(6.72)	7.61(7.45)
3b	C$_{33}$H$_{46}$N$_2$O$_{12}$Na$_2$(ClO$_4$)$_2$	Yellow	76	43.62(43.20)	5.06(5.14)	3.08(3.25)	–
4a	C$_{34}$H$_{48}$N$_2$O$_{12}$Na$_2$(SCN)$_2$ · H$_2$O	Yellow	58	50.46(50.39)	5.88(5.76)	6.54(6.56)	7.48(7.43)
4b	C$_{34}$H$_{48}$N$_2$O$_{12}$Na$_2$(ClO$_4$)$_2$	Yellow	69	44.29(44.74)	5.21(5.17)	3.04(3.18)	–
3c	C$_{33}$H$_{44}$N$_2$O$_{12}$Na$_2$(ClO$_4$)$_2$ · 4H$_2$O	Green	40	38.22(37.74)	5.01(4.48)	2.70(2.57)	–
4c	C$_{34}$H$_{46}$N$_2$O$_{12}$Na$_2$(ClO$_4$)$_2$ · 2H$_2$O	Green	31	40.26(39.84)	4.97(4.74)	2.76(2.47)	–
3d	C$_{33}$H$_{44}$N$_2$O$_{12}$Ni · H$_2$O	Green	89	53.75(53.70)	6.29(6.07)	3.80(4.16)	–

Spectroscopy

IR spectra

Selected IR data for the bis(crown ether)s and their complexes are listed in Table 2. The uncomplexed ligands (**2**–**4**) show characteristic imine (C = N) absorptions at 1 639 – 1 643 cm^{-1}, while the imine bands present in the IR spectra of the corresponding binuclear sodium complexes (**2a**, **2b**–**4a**, **4b**) are little shifted to lower frequency. However, in the IR spectra of the Ni(II) complexes (**3c**, **4c** and **3d**), the imine stretching bands are observed at 1 624 – 1 628 cm^{-1} indicating a shift of ca. 15 cm^{-1} to lower frequency. The alkyl ether and aryl ether stretching bands are observed at 1 144 – 1 048 and 1 244 – 1 225 cm^{-1}, respectively.

NMR spectra

The ^{1}H NMR data of representative compounds are given in Table 3. Considering the N–CH$_2$ and N–CH$_2$–CH$_2$- proton chemical shifts for the ligands (**2**, **3** and **4**), we note a shielding of 0.17 to 0.11 and 0.41 ppm on passing from -(CH$_2$)$_2$- to -(CH$_2$)$_4$- for the alkylene groups of the corresponding bis (crown ether)s, respectively. In the ^{1}H NMR spectra of the ligands **2** and **3** and the complexes **2a**, **3a** and **4b**, the OH protons appear as singlets between 13.30 and 12.99 ppm, respectively. The

Table 2 Selected IR bands

Compound	$\nu_{C-H(aliph.)}$	$\nu_{C=N}$	$\nu_{C=C}$	$\nu_{C-O-C(arom.)}$	$\nu_{C-O-C(aliph.)}$	$\nu_{ClO_4^-}$	ν_{SCN^-}
2	2927; 2873	1639	1500	1231	1132; 1053	–	–
3	2928; 2869	1639	1502	1233	1130; 1057	–	–
4	2935; 2877	1643	1533	1227	1120; 1055	–	–
2a	2921; 2873	1635	1508	1225	1125; 1048	–	2067
2b	2917; 2873	1631	1500	1227	1127; 1088	1088	–
3a	2919; 2875	1641	1529	1227	1128; 1080	–	2063
3b	2928; 2878	1641	1508	1227	1096	1096	–
4a	2923; 2873	1641	1524	1225	1130; 1000	–	2059
4b	2917; 2876	1637	1514	1227	1098	1098	–
3c	2923; 2880	1624	1547	1244	1144; 1090	1090	–
4c	2929; 2876	1628	1537	1229	1100	1100	–
3d	2921; 2876	1624	1525	1242	1130; 1075	1075	–

Table 3 ^{1}H NMR spectral data. Chemical shifts (δ) are reported in ppm (s: singlet, m: multiplet, t: triplet and w: weight).

Compound	N–C$\underline{H}_2$	N–CH$_2$–C$\underline{H}_2$-	OC$\underline{H}_2$–C$\underline{H}_2$-O	Ar–$\underline{H}_6$	Ar$\underline{H}_3$	$\underline{H}$–C=N	OH
2 [a]	3.86(s, 2H)	–	3.74–4.15(m,16H)	6.42(s,1H)	6.72(s,1H)	8.15(s,1H)	13.30(w,1H)
3 [a]	3.69(t,2H)	2.10(t, 2H)	3.85–4.24(m,16H)	6.43(s,1H)	6.73(s,1H)	8.15(s,1H)	13.50(w,1H)
4 [a]	3.58(t,2H)	1.69(t, 2H)	3.81–4.15(m,16H)	6.40(s,1H)	6.71(s,1H)	8.09(s,1H)	[d]
2a [b]	3.77(m,2H)	–	3.64–4.08(m,16H)	6.37(s,1H)	6.81(s,1H)	8.21(s,1H)	13.34(s,1H)
3a [b]	4.37(m,2H)	2.77(t,2H)	4.42–4.88(m,16H)	7.12(s,1H)	7.58(s,1H)	8.94(s,1H)	14.38(s,1H)
4b [b]	2.95(m,2H)	1.11(m,2H)	3.04–3.48(m,16H)	5.75(s,1H)	6.20(s,1H)	7.58(s,1H)	12.99(s,1H)
4c [b]	[c]	[c]	3.36–4.36(m,16H)	6.52(s,1H)	7.15(s,1H)	9.97(s,1H)	–
3d [b]	[c]	[c]	3.20–3.60(m,16H)	5.85(s,1H)	6.15(s,1H)	7.80(s,1H)	–

[a] In CDCl$_3$, [b] in CDCl$_3$+D$_6$-DMSO, [c] overlapping with DMSO peaks, [d] not observed clearly.

OH peaks of the free ligands are much broader than for the complexes. The azomethine protons are observed as singlets between 8.15 and 8.09 ppm for the ligands **2** – **4** and 7.58 – 9.97 for the complexes **2a**, **3a**, **4b**, **4c** and **3d**.

The ^{13}C NMR data for the new bis(crown ether) ligands **3** and **4** and their sodium complexes **2a**, **3b** and **4b** are summarized in Table 4. Since the nickel complexes are only very low soluble in CDCl$_3$ and DMSO, the spectra of these compounds could not be recorded. In the ^{13}C decoupled NMR spectra of the ligands and complexes, as expected, eight crown ether carbons (C$_{1'}$ – C$_{8'}$) are observed between 67.10 and 73.96 ppm [21, 22]. In addition to that, the spectra show the characteristic signals for the N–C$\underline{H}_2$, N–CH$_2$–C$\underline{H}_2$-, $\underline{C}$ = N and aromatic ring carbons.

MS spectra

In the FAB mass spectrum of the bis(crown ether) **3**, the molecular ion peak is observed at *m/z* 663.5 (highest peak in multiplet, 14%), while in the electron impact (EI) mass spectrum of **3**, the molecular ion peak (M$^+$) could not be determined but only the important

fragments at *m/z* 430.4, 357.3, 312.3 and 281.2 corresponding to the loss of {2[(CH$_2$CH$_2$O)$_2$CH$_2$CH$_2$]}, {2[(CH$_2$CH$_2$O)$_2$CH$_2$CH$_2$] + CH$_2$CH$_2$OH + CH$_2$O}, {2(CH$_2$CH$_2$O)$_4$-2H} and {2[O(CH$_2$CH$_2$O)$_4$]-3H}, respectively. This fragmentation pattern proceeding by the loss of etheric chains is in accordance with the literature [23]. In the FAB mass spectrum of the trinuclear complex **3c**, the dominant peaks at *m/z* 863.1 (14%) and 741.1 (100%) corresponding to the loss of (ClO$_4^-$ + 4H$_2$O) and (Na$^+$ + 2ClO$_4^-$ + 4H$_2$O), respectively, are fragments significant of the ligand molecule.

UV-VIS spectra

The UV-VIS spectra of the ligands **2**, **3** and **4** and dinuclear sodium perchlorate complexes **2b**, **3b** and **4b** were studied in polar, acidic and basic media (Table 5). The trinuclear complexes proved not sufficiently soluble in these solvents to allow recording of their UV-VIS spectra. With reference to the spectra of the ligands and the complexes, the existence of phenol–imine/keto–amine tautomerism, O–H···N $\rightleftharpoons$ O···H–N, typical of 2-hydroxy Schiff base derivatives [24–29], depending on the formation of intramolecular hydro-

Table 4 Selected ^{13}C NMR spectral data (δ, ppm)
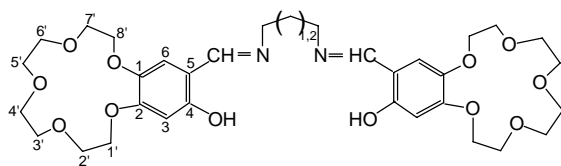
Numbering of the crown ether carbons

Comp.	C_1	C_2	C_3	C_4	C_5	C_6	$\underline{C}H=N$	$C_{1'-8'}$	$N–\underline{C}H_2–$	$N–CH_2–\underline{C}H_2–$
3 [a]	142.20	111.00	100.15	161.16	154.45	118.03	164.48	68.58, 69.55, 70.22, 70.63, 71.14, 71.28, 71.37, 71.48	56.00	31.14
4 [b]	140.85	109.37	103.18	157.73	147.50	116.87	162.96	68.27, 69.20, 69.95, 70.27, 70.73, 70.78, 70.88, 71.06	53.68	28.21
2a [c]	143.63	114.39	106.72	164.90	158.22	121.37	169.19	71.27, 71.96, 72.55, 72.61, 72.76, 72.84, 73.26, 73.73	59.53	–
3b [b]	143.79	115.10	107.92	165.00	159.24	121.49	168.97	71.80, 72.70, 73.34, 73.37, 73.58, 73.70, 73.87, 73.96	56.82	36.05

[a] In $CDCl_3$,   [b] in $CDCl_3 + CD_3OD$,   [c] in CD_3OD.

Table 5 UV-VIS spectral data for the ligands and complexes

Comp.	Solvent	λ, nm (log ε)	% Keto isomer		
			Solvent medium	Acidic medium	Basic medium
2	DMSO	330(4.35), 404(3.72)	19.35	0.0	–
	EtOH	302(4.22), 408(3.91)	32.87	0.0	13.31
	$CHCl_3$	330(4.56), 412(3.87)	17.02	0.0	–
3	DMSO	330(4.42), 404(3.82)	20.10	0.0	–
	EtOH	302(4.58), 406(4.32)	35.54	0.0	20.15
	$CHCl_3$	324(4.02), 406(3.56)	25.53	0.0	–
4	DMSO	328(4.44), 410(3.94)	23.72	0.0	–
	EtOH	301(3.65), 405(3.50)	41.69	0.0	26.40
	$CHCl_3$	326(4.38), 410(3.97)	28.09	0.0	–
2b	DMSO	332(4.26), 406(3.63)	18.83	0.0	–
	EtOH	330(4.19), 404(3.90)	33.64	0.0	12.11
	$CHCl_3$	328(3.95), 410(3.37)	21.07	0.0	–
3b	DMSO	330(4.35), 4404(3.77)	20.85	0.0	–
	EtOH	302(4.43), 400(4.15)	34.57	0.0	22.53
	$CHCl_3$	326(4.04), 404(3.79)	35.94	0.0	–
4b [a]	DMSO	328(4.20), 402(3.75)	26.22	0.0	–
	EtOH	302(4.44), 406(4.27)	40.39	0.0	27.52

[a] Not sufficiently soluble in $CHCl_3$.

gen bonding, is observed. In the solid state, the keto–amine form has been found for naphthaldimine, while in salicylaldimine ligands the phenol–imine form is present [30, 31]. In solution, the tautomerism depends on solvent polarity [26, 27]. For instance, in polar solvents, a new band at > 400 nm arises that is not observed in non-polar solvents. This absorption band belongs to the keto–amine tautomer of the ligands. As it is shown in Table 5, the ligands (**2**, **3** and **4**) and the complexes (**2b**, **3b** and **4b**) show absorptions in the range > 400 nm indicative of the keto–amine tautomer in DMSO, EtOH and $CHCl_3$. However, this band (> 400 nm) is absent in acidic (CF_3COOH, pH = 3) solutions of DMSO, EtOH and $CHCl_3$, but can be observed in

basic (Et$_3$N, pH = 10) solution of EtOH. In pure solvents, acidic and basic media, the phenol–imine (O–H···N) tautomer is dominant. In EtOH, the ratio of the keto–amine tautomer is higher than in DMSO and CHCl$_3$, which is possibly a consequence of the hydrogen bonding character of EtOH. The calculated ratios of the keto–amine tautomer are listed in Table 5, indicating that the tautomerism is enhanced as the alkyl chain [-(CH$_2$)$_n$-; n = 2, 3 and 4] increases (*cf.* **2**–**4** and **2b**–**4b**).

Experimental

^{1}H and ^{13}C NMR spectra were measured on a Bruker DPX FT-NMR (400 MHz) spectrometer (SiMe$_4$, as internal standard). IR spectra were recorded on a Mattson 1000 FTIR spectrometer in KBr discs and were reported in cm^{-1} units. UV-VIS spectra were obtained using a UNICAM UV2-100 series spectrometer. Microanalyses were carried out by the microanalytical service of TÜBITAK-SAGE Ankara (Turkey), Electron impact (El) (70 eV, ca. 1.12 10^{-17}j) and fast atomic bombardment (FAB) spectra were obtained on a VG-ZAPSPEC spectrometer.

Tetrahydrofuran (THF), diethyl ether and dichloromethane were dried by refluxing over sodium and phosphorus pentoxide, respectively. Tetraethylene glycol dichloride [32], benzo-15-crown-5 [17]. 4'-formylbenzo-15-crown-5 [18, 33], 4'-hydroxybenzo-15-crown-5 [19], 4'-formyl-5'-hydroxybenzo-15-crown-5 (**1**) [20] and bis(crown ether) **2** [20] were prepared according to the published methods.

Bis(crown ether)s **3** *and* **4**

To a solution of 4'-formyl-5'-hydroxybenzo-15-crown-5 (**1**) (1.00 g, 3.20 mmol) in dry THF (50 ml) was added dropwise (0.5 h) a solution of the respective 1, ω-diaminoalkane (1.60 mmol) in THF (50 ml) with stirring. The mixture was refluxed for 1h and then allowed to come to ambient temperature. Bright yellow needls were formed (**3**: *m.p.* 150 °C, **4**: *m.p.* 216 °C). Experimental and analytical data are summarized in Table 1.

Dinuclear Sodium Complexes **2a**–**4a** *and* **2b**–**4b**

The respective bis(crown ether) (1.38 mmol) and NaSCN (0.22 g, 2.76 mmol) or NaClO$_4$ (0.33 g, 2.76 mmol) were dissolved in dry THF (100 ml) and heated to reflux for 1 h. The precipitated complex was filtered and washed with diethyl ether. Specific details for each compound are given in Table 1.

Trinuclear Sodium-Nickel(II) Complexes **3c** *and* **4c**

To a solution of **3b** or **4b** (0.55 mmol) in dry acetonitrile (50 ml) at room temperature was added a solution of

Ni(CH$_3$COO)$_2$ · 6H$_2$O (0.14 g, 0.55 mmol) in methanol (20 ml) with stirring. The mixture was refluxed for 5 h and the solvents distilled off. The residue was allowed to come to ambient temperature, triturated with diethyl ether and filtered off. Specific details for each compound are given in Table 1.

Mononuclear Nickel(II) Complex **3d**

Solutions of compound **3** (1.00 g, 1.48 mmol) in dry acetonitrile (50 ml) and Ni(CH$_3$COO)$_2$ · 6H$_2$O (0.37 g, 1.48 mmol) in methanol (20 ml) were combined under stirring at room temperature. The precipitated complex was filtered and washed with diethyl ether. Details are given in Table 1.

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