

Syntheses and spectroscopic characterization of double-armed benzo-15-crown-5 derivatives and their sodium and potassium complexes

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Abstract A series of new benzo-15-crown-5 derivatives (**1–6**) containing formyl and imine groups were prepared. New formyl crown ethers (**1** and **2**) were prepared by reaction of 4',5'-bis(bromomethyl)benzo-15-crown-5 with 2-hydroxy-3-methoxybenzaldehyde (*o*-vanillin) and 2-hydroxy-5-methoxybenzaldehyde in the presence of NaOH. New Schiff bases (**3–6**) were synthesized by the condensation of corresponding aldehydes with 1,3-diaminopropane and 1,4-diaminobutane. Sodium and potassium complexes (**1a–6a** and **1b–6b**) of the crown compounds forming crystalline complexes of 1:1 (Na⁺:ligand) and 1:2 (K⁺:ligand) stoichiometries were also synthesized. The structures of the aldehydes **1** and **2**, imines **3–6** and complexes (**1a–3a** and **1b–3b**) were confirmed on the basis of elemental analyses, IR, ¹H- and ¹³C-NMR, and mass spectroscopy.

Keywords Crown compounds · Schiff bases · Aldehydes · Alkali metal complexes · Macrocycles

Introduction

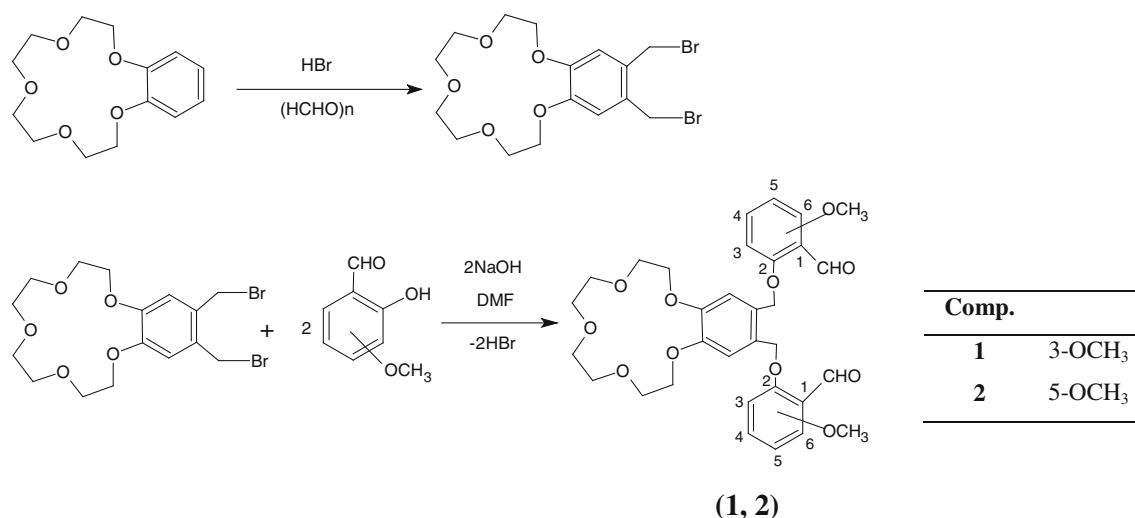
It is well known that crown ethers can be considered as molecular receptors for selective binding of ionic and molecular guests forming host–guest complexes or supramolecular species [1–3]. Crown ether derivatives with different functional groups have received much attention in the last few years both in chemistry and biology [4–7]. For example, crown ether derivatives with ether or anionic

groups on the periphery of the macrocycles have been synthesized, in order to increase metal ion selectivity and complex stability in analytical and separation methods as well as in biological membranes [8–10]. As biologic model compounds, crown ethers can interact with many guests including metal ions, organic cations and neutral polar molecules by weak non-covalent interactions [11]. For several years, various simple or complicated chemical systems have been used as model mimics of natural enzymes [12–14]. The crown ethers are generally considered as the first generation organism of mimetic enzyme in the theory of enzymology due to their recognition function of guests and hosts.

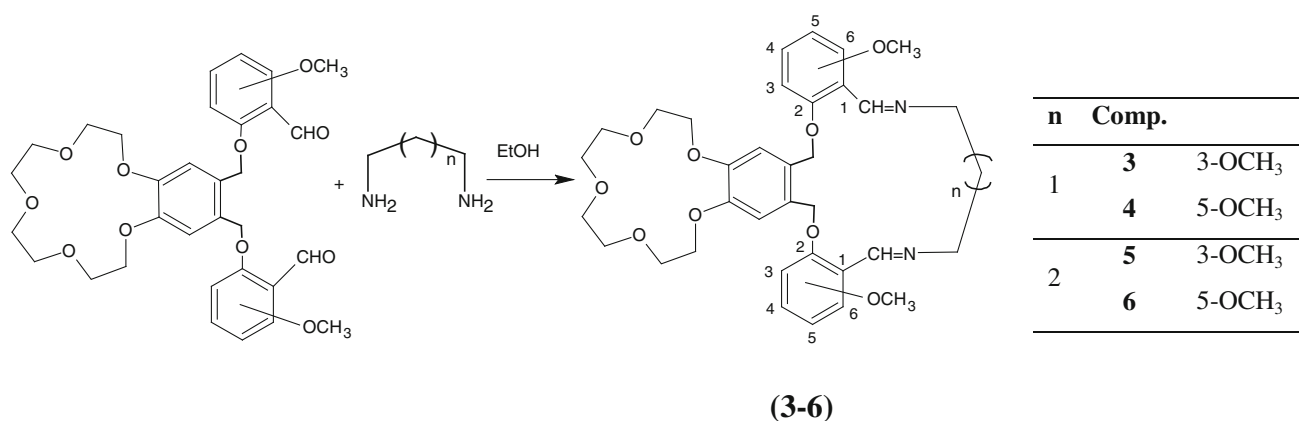
The primary crown ethers, which contain only oxygen binding sites have high affinity toward the alkali metal ions. In other words, crown ethers, which contain a hydrophobic ethylenic residues that surround a hydrophilic cavity of ether oxygen atoms, are able to bind selectively a range of alkali and alkaline earth metal cations [15–18]. The cation-polyether complexes are formed by ion–dipole interaction between the cation and the negatively charged oxygens symmetrically arranged in the polyether ring. If the diameter of the cation is too large to fit inside the available crown cavity, formation of so called “sandwich” complexes with 1:2 and 2:3 metal:crown ether ratios can occur [19, 20].

In this paper, we describe the syntheses and characterization of a series of novel double-armed and bi-macrocyclic ethers and complexes, containing benzo-15-crown-5 moieties. We report (i) the syntheses of double-armed crown ether having two formyl residues (**1** and **2**) (Scheme 1); (ii) the syntheses and characterization of Schiff bases containing with two macrorings (**3–6**) (Scheme 2); (iii) complexation of sodium cation within the crown ether cavity (**1a–6a**) (Scheme 3); (iv) sandwich complexes with potassium (**1b–6b**) (Scheme 3) and (v) analytical, physical and spectral (IR, ¹H-, ¹³C-NMR and MS) data.

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Scheme 1 Syntheses of dialdehydes (**1** and **2**)



Scheme 2 Syntheses of Schiff bases (**3-6**)

Experimental

Materials and methods

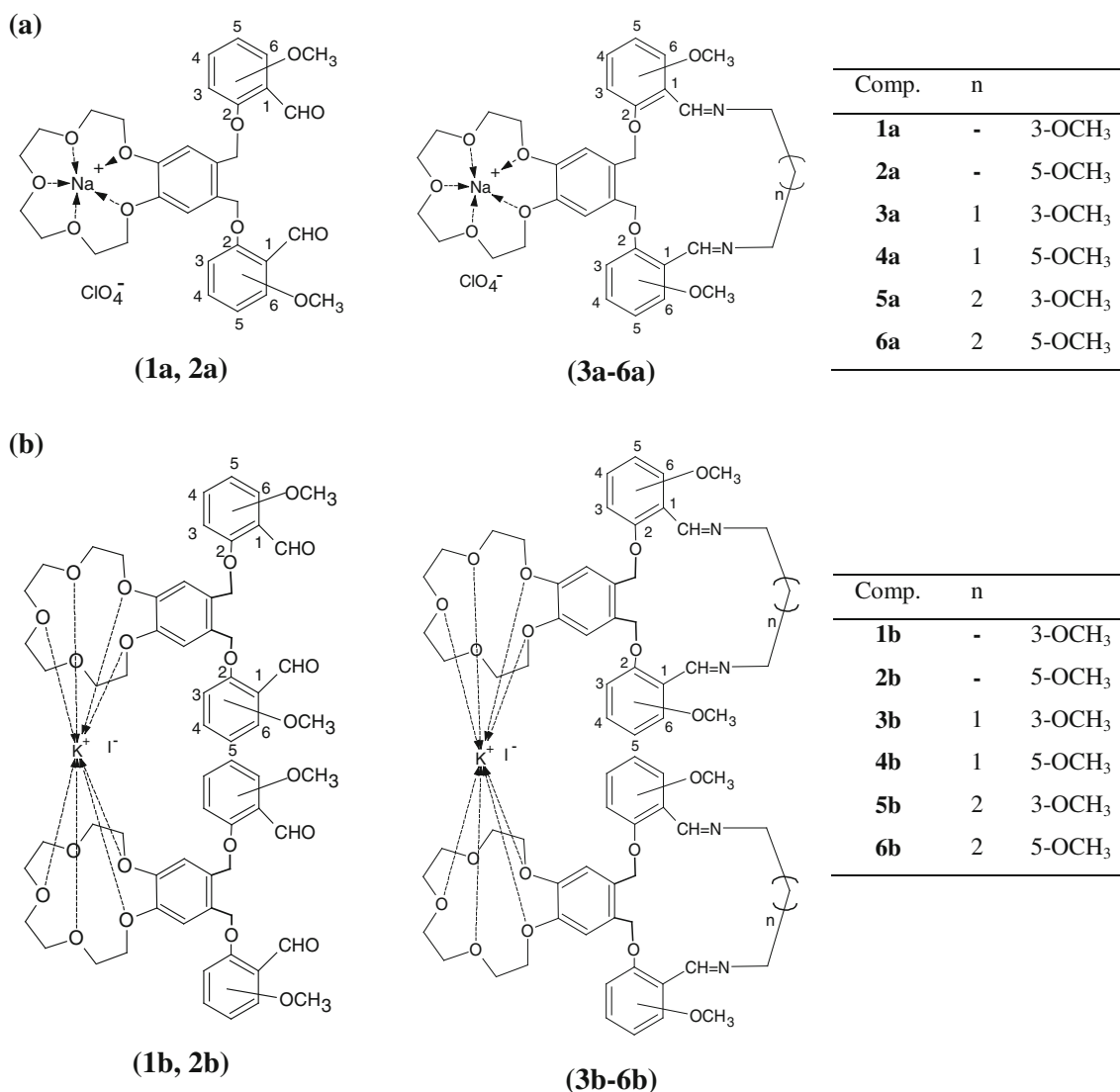
1-Chloro-2-[2-[2-(2-chloroethoxy)ethoxy]ethoxy]ethane [21], benzo-15-crown-5 [22] and 4',5'-bis(bromomethyl)benzo-15-crown-5 [23] were prepared according to the literature. 2-Hydroxy-3-methoxybenzaldehyde (*o*-vanillin) and 2-hydroxy-5-methoxybenzaldehyde were purchased from Aldrich and used without further purification. Solvents were dried and distilled before use according to the standard procedures.

Melting points were measured on a Thomas-Hoover apparatus using a capillary tube. ¹H- and ¹³C-NMR spectra were recorded on a Varian Mercury, High Performance Digital FT-NMR (400 MHz) spectrometer (SiMe₄ as an internal standard). Chemical shifts for proton and carbon resonances were reported in ppm (δ). IR spectra were

obtained from PEL-DATA spectrum 100 series spectrometer KBr pellets. Elemental analyses (C, H, N) were conducted using the Elemental Analyser LECO CHNS-932; the results were found to be in good agreement ($\pm 0.2\%$) with the calculated values. Mass spectrometric analyses were performed on the Waters 2695 Alliance ZQ LC/MS spectrometer.

2,2'-[2,3,5,6,8,9,11,12-Octahydro-1,4,7,10,13-benzopentaoxacyclopentadecine-15,16-diyl bis(methyleneoxy)]bis(3-methoxybenzaldehyde) (**1**)

2-Hydroxy-3-methoxybenzaldehyde (0.50 g, 3.29 mmol) was dissolved in DMF (50 cm³). NaOH (0.13 g, 3.29 mmol) was added in small portions and the resulting reaction mixture was refluxed for 1 h. Subsequently, 4',5'-bis(bromomethyl)benzo-15-crown-5 (0.75 g, 1.65 mmol) in DMF (20 cm³) was added dropwise to the reaction mixture. The



Scheme 3 Proposed structures of **a** sodium complexes (**1a–6a**), **b** potassium complexes (**1b–6b**)

resulting solution was refluxed for 10 h until the complete consumption of the starting material was observed by TLC (silicagel, eluent: CHCl₃). Then water was added until the solution turned cloudy. The beige precipitate formed was isolated and recrystallized from ethanol. Properties of compound (**1**) are given in Table 1.

2,2'-[2,3,5,6,8,9,11,12-Octahydro-1,4,7,10,13-benzopentaoxacyclopentadecine-15,16-diyl bis(methyleneoxy)]bis(5-methoxybenzaldehyde) (**2**)

Compound **2** was prepared analogously to compound **1** as above by using a solution of 2-hydroxy-5-methoxybenzaldehyde (0.50 g, 3.29 mmol). After recrystallization from EtOH, beige needle crystals were obtained. Data for compound (**2**) are given in Table 1.

General methods for preparing Schiff bases (**3–6**)

The corresponding amines (1,3-diaminopropane or 1,4-diaminobutane) (2.0 mmol) were dissolved in EtOH (20 mL). Crown aldehydes (1.0 mmol) were dissolved in EtOH and added dropwise to the amine solution. The resulting solution was stirred under reflux for 3 h and the reaction mixture was allowed to stand for 2 h at room temperature. The crude product was recrystallized from EtOH, Table 1.

General methods for preparing sodium complexes (**1a–6a**)

The respective crown ethers (**1–6**) (1.00 mmol) and NaClO₄ (1.00 mmol) were dissolved in dry EtOH (20 mL) and refluxed for 2 h. The crude complexes were filtered

Table 1 Analytical data and experimental details of compounds (**1–6**, **1a–6a** and **1b–6b**)

| Comp. | Formula | Colour | Yield (%) | m.p. (°C) | Elemental analyses (%) Calc. (found) | | |
|-----------|--|--------|-----------|-----------|--------------------------------------|-------------|-------------|
| | | | | | C | H | N |
| 1 | C ₃₂ H ₃₆ O ₁₁ | Beige | 47 | 130 | 64.42 (64.45) | 6.08 (6.09) | – |
| 2 | C ₃₂ H ₃₆ O ₁₁ | Beige | 32 | 115 | 64.42 (64.67) | 6.08 (6.41) | – |
| 3 | C ₃₅ H ₄₂ N ₂ O ₉ + 2H ₂ O | Beige | 60 | 164–166 | 62.67 (62.38) | 6.91 (6.57) | 4.18 (4.36) |
| 4 | C ₃₅ H ₄₂ N ₂ O ₉ | White | 79 | 138–140 | 66.23 (66.63) | 6.67 (6.61) | 4.41 (4.79) |
| 5 | C ₃₆ H ₄₄ N ₂ O ₉ + 2H ₂ O | Beige | 66 | 157–159 | 63.14 (63.43) | 7.07 (6.89) | 4.09 (4.25) |
| 6 | C ₃₆ H ₄₄ N ₂ O ₉ + H ₂ O | Beige | 51 | 142–144 | 64.85 (64.67) | 6.95 (6.86) | 4.20 (4.27) |
| 1a | C ₃₂ H ₃₆ O ₁₁ NaClO ₄ | Yellow | 78 | 67–70 | 53.45 (53.41) | 5.05 (4.95) | – |
| 2a | C ₃₂ H ₃₆ O ₁₁ NaClO ₄ | Beige | 58 | 193–195 | 53.45 (53.65) | 5.05 (5.16) | – |
| 3a | C ₃₅ H ₄₂ N ₂ O ₉ NaClO ₄ + H ₂ O | Beige | 78 | 257 | 54.23 (53.93) | 5.72 (5.56) | 3.61 (3.86) |
| 4a | C ₃₅ H ₄₂ N ₂ O ₉ NaClO ₄ | Beige | 72 | 115–118 | 55.52 (55.37) | 5.59 (5.41) | 3.70 (3.91) |
| 5a | C ₃₆ H ₄₄ N ₂ O ₉ NaClO ₄ + 2H ₂ O | White | 49 | 232 | 53.57 (53.50) | 5.99 (6.16) | 3.47 (3.42) |
| 6a | C ₃₆ H ₄₄ N ₂ O ₉ NaClO ₄ | Yellow | 66 | 217 | 56.07 (55.63) | 5.75 (5.71) | 3.63 (3.98) |
| 1b | C ₆₄ H ₇₂ O ₂₂ KI | Yellow | 28 | 163–165 | 56.55 (56.13) | 5.34 (5.22) | – |
| 2b | C ₆₄ H ₇₂ O ₂₂ KI | Beige | 26 | 86–88 | 56.55 (56.37) | 5.34 (5.71) | – |
| 3b | C ₇₀ H ₈₄ N ₄ O ₁₈ KI | Yellow | 46 | 195–197 | 58.57 (58.45) | 5.90 (6.01) | 3.90 (3.72) |
| 4b | C ₇₀ H ₈₄ N ₄ O ₁₈ KI | Beige | 44 | 168–170 | 58.57 (58.16) | 5.90 (5.77) | 3.90 (3.89) |
| 5b | C ₇₂ H ₈₈ N ₄ O ₁₈ KI + H ₂ O | Yellow | 74 | 198 | 58.37 (58.60) | 6.12 (5.83) | 3.78 (3.76) |
| 6b | C ₇₂ H ₈₈ N ₄ O ₁₈ KI + 2H ₂ O | Beige | 64 | 118–120 | 57.67 (57.92) | 6.18 (6.71) | 3.74 (3.39) |

and washed with diethyl ether. For characteristic see Table 1.

General methods for preparing potassium complexes (**1b–6b**)

The respective crown ethers (**1–6**) (2.00 mmol) and KI (1.00 mmol) were dissolved in dry EtOH (50 mL) and refluxed for 2 h. Crude complexes were filtered and washed with diethyl ether, Table 1.

Results and discussion

Syntheses

The synthetic procedure for the preparation of the crown ether aldehydes (**1** and **2**) proceeds in two steps. Firstly, 2-hydroxy-3-methoxybenzaldehyde and 2-hydroxy-5-methoxybenzaldehyde were reacted with NaOH in DMF to give the corresponding sodium alkoxide. Secondly, the obtained sodium salts were converted into the corresponding new crown ether aldehydes (**1** and **2**) by reacting with 4',5'-bis(bromomethyl)benzo-15-crown-5. Compounds (**1** and **2**) were successfully synthesized with yields in the range of 47–32 %, respectively.

Direct reaction of one equivalent of **1** or **2** with one equivalent of the appropriate amine (1,3-diaminopropane

or 1,4-diaminobutane) in ethanol gives the corresponding double-macroyclic Schiff bases (**3–6**).

The sodium complexes (**1a–6a**) were prepared (Na⁺:ligand (1:1) “filling complex”) by treating a solution of one mole of compounds (**1–6**) with one mole NaClO₄. But potassium complexes were prepared [K⁺:ligand (1:2) “sandwich complex”] by treating a solution of two moles of compounds (**1–6**) with one mole KI. The elemental analyses confirm the potassium complexes are of 1:2 (K⁺:ligand) stoichiometry. Free ligands (**1–6**) are soluble in EtOH, CHCl₃, THF, acetone, DMSO, CH₃CN, *n*-hexane and *n*-heptane, whereas sodium and potassium complexes (**5a**, **6a**, **3b–6b**) are insoluble in CHCl₃ and EtOH. The structures of the ligands, sodium and potassium complexes were verified by the elemental analysis, FT-IR, ¹H-, ¹³C-NMR and mass spectra. Analytical data and experimental details for compounds (**1–6**, **1a–6a** and **1b–6b**) are given in Table 1. Various attempts to obtain single crystals of the ligands and complexes have so far been unsuccessful.

IR spectra

Selected IR data of the crown ethers and alkali metal complexes are shown in Table 2. In the infrared spectra of crown ether aldehydes (**1**, **2**, **1a**, **2a**, **1b** and **2b**) strong bands in the 1,666–1,699 cm⁻¹ region can be assigned to the ν(C=O) stretching, which disappear for imine compounds (**3–6**, **3a–6a** and **3b–6b**) indicating the condensation of the

Table 2 Selected IR bands

| Comp. | $\nu_{\text{C=O}}$ | $\nu_{\text{C=N}}$ | $\nu_{\text{C=C}}$ | $\nu_{\text{C-H(aliph)}}$ | $\nu_{\text{C-O-C(arom.)}}$ | $\nu_{\text{C-O-C(aliph.)}}$ |
|-----------|--------------------|--------------------|--------------------|---------------------------|-----------------------------|------------------------------|
| 1 | 1693(s) | – | 1584, 1481 (m) | 2936, 2861 (m) | 1362, 1248 (s) | 1123, 1063 (s) |
| 2 | 1683;1671(m) | – | 1609, 1497 (m) | 2928, 2875 (m) | 1389, 1274 (s) | 1120, 1046 (s) |
| 3 | – | 1637 (m) | 1579, 1457 (m) | 2918, 2867 (m) | 1363, 1276 (s) | 1123, 1084 (s) |
| 4 | – | 1635 (m) | 1606, 1490 (s) | 2925, 2889 (m) | 1378, 1200 (m) | 1133, 1035 (s) |
| 5 | – | 1644 (m) | 1583, 1478 (m) | 2922, 2881 (m) | 1367, 1272 (s) | 1118, 1077 (s) |
| 6 | – | 1636 (m) | 1608, 1492 (m) | 2918 (m) | 1374, 1201 (m) | 1118, 1038 (s) |
| 1a | 1699;1677(m) | – | 1584, 1479 (m) | 2920, 2880 (m) | 1372, 1251 (s) | 1098, 1067 (s) ^a |
| 2a | 1681(s) | – | 1616, 1495 (s) | 2922, 2861 (m) | 1387, 1280 (s) | 1103, 1048 (s) ^a |
| 3a | – | 1634 (m) | 1580, 1478 (m) | 2916, 2836 (s) | 1363, 1270 (s) | 1105, 1065 (s) ^a |
| 4a | – | 1639 (m) | 1613, 1496 (m) | 2923, 2882 (w) | 1372, 1204 (m) | 1104, 1034 (s) ^a |
| 5a | – | 1638 (m) | 1584,1477 (m) | 2988, 2901 (m) | 1366, 1273 (m) | 1103, 1076 (s) ^a |
| 6a | – | 1639 (m) | 1611, 1495 (m) | 2938, 2889 (m) | 1376, 1203 (m) | 1095, 1033 (s) ^a |
| 1b | 1678(s) | – | 1585,1480 (s) | 2934, 2877 (m) | 1373, 1249 (s) | 1114, 1061 (s) |
| 2b | 1683;1666(s) | – | 1611, 1493 (s) | 2916, 2864 (m) | 1385, 1281 (s) | 1120, 1037 (s) |
| 3b | – | 1641 (m) | 1581, 1458 (s) | 2923, 2876 (m) | 1380, 1272 (m) | 1118, 1077 (s) |
| 4b | – | 1638 (m) | 1611, 1495 (m) | 2921, 2873 (m) | 1371, 1207 (m) | 1113, 1034 (s) |
| 5b | – | 1645 (m) | 1583, 1479 (m) | 2875, 2832 (m) | 1360, 1273 (s) | 1114, 1081 (s) |
| 6b | – | 1635 (m) | 1609, 1492 (m) | 2923, 2869 (m) | 1376, 1202 (m) | 1117, 1034 (s) |

W weak, m medium, s strong

^a $\nu_{\text{ClO}_4^-}$ peaks overlapping with $\nu_{\text{C-O-C(aliph.)}}$

aldehyde groups. The characteristic imine ($\nu_{\text{C=N}}$) stretching bands attributable to the azomethine group (HC=N) were observed at 1,634–1,639 cm^{-1} for ligands (**3–6**) and complexes (**3a–6a** and **3b–6b**). The intense bands at 1,616–1,457 cm^{-1} correspond to the stretching vibrations of the benzene rings ($\nu_{\text{C=C}}$) of the compounds. The asymmetric and symmetric $\nu_{\text{C-O-C}}$ stretching vibration bands are observed at 1389, 1281 and at 1123; 1084 cm^{-1} both for ligands and complexes. The 3- OCH_3 substituted compounds (**1**, **3**, **5**, **1a**, **3a**, **5a**, **1b**, **3b** and **5b**) show C=C and C-O-C(_{arom.}) stretching vibration bands at 1,580–1,585 and 1,360–1,380 cm^{-1} while the corresponding C=C and C-O-C(_{arom.}) bands of the 5- OCH_3 substituted compounds (**2**, **4**, **6**, **2a**, **4a**, **6a**, **2b**, **4b** and **6b**) are shifted to higher frequencies (1,606–1,616 and 1,371–1,389 cm^{-1}). The frequencies for the ligands (**1–6**) and complexes (**1a–6a** and **1b–6b**) were almost of the same frequency.

¹H- and ¹³C-NMR spectroscopy in CDCl_3 , DMSO, and $\text{CDCl}_3 + \text{DMSO}$

The ¹H-NMR spectral data are summarized in Table 3. In the ¹H-NMR spectra, the integral ratio of the aliphatic and aromatic protons for all compounds (**1–6**, **1a–6a** and **1b–6b**) indicates the molecules to be symmetric.

The ¹H-NMR spectra of the aldehydes (**1** and **2**), imines (**3–6**) and complexes (**1a–6a** and **1b–6b**) show singlets

corresponding to $-\text{OCH}_3$ protons. The singlets at 10.21, 10.23, 10.24, 10.21, 10.14 and 10.38 ppm for aldehyde protons ($-\text{CHO}$) (for **1**, **2**, **1a**, **2a**, **1b** and **2b**) disappear after the condensation with diamines. The azomethine protons were observed as singlets at 8.69, 8.46, 8.38 and 8.55 (for **3–6**), at 8.62, 8.45, 8.29 and 8.41 (for **3a–6a**) and at 8.32, 8.38 and 8.44 (for **3b–6b**). The benzylic protons ($-\text{OCH}_2-$) were seen as singlets at 4.87–5.26 ppm. ¹H-NMR spectra of all compounds show the aromatic protons as multiplets between 6.87 and 7.59 ppm, whereas the crown ether protons ($\text{OCH}_2-\text{CH}_2\text{O}$) appear as multiplets between 3.52 and 4.26 ppm. Considering the $-\text{C}-\text{CH}_2-$ proton chemical shifts for the Schiff bases (**3** and **5**) and (**4** and **6**), we note a shielding of 0.64 and 0.52 ppm on passing from $-(\text{CH}_2)_2-$ to $-(\text{CH}_2)_3-$ for the alkylene groups of the corresponding Schiff bases, respectively.

For sodium complexes (**3a** and **5a**) and (**4a** and **6a**) these shielding were found to be equal 0.61 and 0.78 ppm, respectively. The ¹H-NMR spectra of the sodium and potassium complexes are approximately the same as spectra of the corresponding ligands, but the ¹H-NMR spectra provide compelling evidence for the ligand and their sodium or potassium complexes, because different shape of multiplet peaks was seen for $\text{OCH}_2-\text{CH}_2\text{O}$ region (between 3.5 and 4.5 ppm) of the ligand and each sodium and potassium complexes [24] (Figs. 1, 2). Although three multiplet peaks were seen for the ligands (**1**, **3**), four peaks

Table 3 $^1\text{H-NMR}$ spectral data

| Comp. | –CHO | –C–CH ₂ – | –N–CH ₂ – | –CH ₂ –O–CH ₂ – | –OCH ₃ | –O–CH ₂ – | Ar–H | –HC=N– |
|-----------------|---------------|----------------------|----------------------|---------------------------------------|-------------------|----------------------|-------------------|--------------|
| a1 | 10.21 (s, 1H) | – | – | 3.75–4.14 (m, 8H) | 3.87 (s, 3H) | 5.23 (s, 2H) | 6.96–7.39 (m, 4H) | – |
| a2 | 10.23 (s, 1H) | – | – | 3.61–4.10 (m, 8H) | 3.74 (s, 3H) | 5.26 (s, 2H) | 7.14–7.28 (m, 4H) | – |
| a3 | – | 2.32 (m, 2H) | 3.61 (t, 2H) | 3.79–4.24 (m, 8H) | 3.96 (s, 3H) | 5.13 (s, 2H) | 7.05–7.61 (m, 4H) | 8.69 (s, 1H) |
| a, d, e4 | – | 2.21 (s, 2H) | 3.56 (t, 2H) | 3.73–4.09 (m, 11H) | 3.74 (s, 3H) | 5.11 (s, 2H) | 6.91–7.42 (m, 4H) | 8.46 (s, 1H) |
| a5 | – | 1.68 (s, 2H) | 3.53 (t, 2H) | 3.78–4.17 (m, 8H) | 3.92 (s, 3H) | 5.16 (s, 2H) | 7.00–7.51 (m, 4H) | 8.38 (s, 1H) |
| a,d,e6 | – | 1.69 (m, 2H) | 3.79 (s, 2H) | 3.81–4.23 (m, 11H) | 3.81 (s, 3H) | 4.98 (s, 2H) | 6.97–7.49 (m, 4H) | 8.55 (s, 1H) |
| a1a | 10.24 (s, 1H) | – | – | 3.77–4.26 (m, 8H) | 3.88 (s, 3H) | 5.24 (s, 2H) | 7.06–7.41 (m, 4H) | – |
| a2a | 10.21 (s, 1H) | – | – | 3.65–4.14 (m, 8H) | 3.75 (s, 3H) | 5.21 (s, 2H) | 7.12–7.20 (m, 4H) | – |
| a3a | – | 2.20 (m, 2H) | 3.59 (m, 2H) | 3.79–4.28 (m, 8H) | 3.97 (s, 3H) | 5.14 (s, 2H) | 7.02–7.59 (m, 4H) | 8.62 (s, 1H) |
| a4a | – | 2.23 (m, 2H) | 3.56 (t, 2H) | 3.73–4.18 (m, 8H) | 3.82 (s, 3H) | 5.12 (s, 2H) | 6.95–7.44 (m, 4H) | 8.45 (s, 1H) |
| a5a | – | 1.59 (m, 2H) | 3.43 (s, 2H) | 3.52–4.13 (m, 8H) | 3.81 (s, 3H) | 5.07 (s, 2H) | 6.97–7.61 (m, 4H) | 8.29 (s, 1H) |
| b6a | – | 1.45 (s, 2H) | 3.49 (t, 2H) | 3.60–4.07 (m, 16H) | 3.66 (s, 3H) | 4.99 (s, 2H) | 6.96–7.29 (m, 4H) | 8.41 (s, 1H) |
| a1b | 10.14 (s, 2H) | – | – | 3.69–4.01 (m, 16H) | 3.87 (s, 6H) | 5.23 (s, 4H) | 6.87–7.34 (m, 8H) | – |
| a2b | 10.38 (s, 2H) | – | – | 3.75–4.09 (m, 16H) | 3.81 (s, 6H) | 5.18 (s, 4H) | 6.99–7.33 (m, 8H) | – |
| a3b | – | 2.23 (s, 4H) | 3.38 (t, 4H) | 3.64–4.13 (m, 16H) | 3.90 (s, 6H) | 4.87 (s, 4H) | 6.70–7.51 (m, 8H) | 8.32 (s, 2H) |
| b5b | – | 2.09 (m, 4H) | 3.43 (t, 4H) | 3.59–4.15 (m, 16H) | 3.73 (s, 6H) | 5.18 (s, 4H) | 7.02–7.37 (m, 8H) | 8.38 (s, 2H) |
| b6b | – | 1.51 (m, 4H) | 3.51 (t, 4H) | 3.63–4.10 (m, 16H) | 3.69 (s, 6H) | 5.02 (s, 4H) | 6.99–7.32 (m, 8H) | 8.44 (s, 2H) |

Chemical shifts (δ) are reported in ppm

S singlet, *M* multiplet, *T* triplet

^a CDCl₃

^b DMSO

^c CDCl₃ + DMSO

^d –OCH₃ peaks overlapping with –CH₂–O–CH₂– peaks

^e Stable isomer peaks

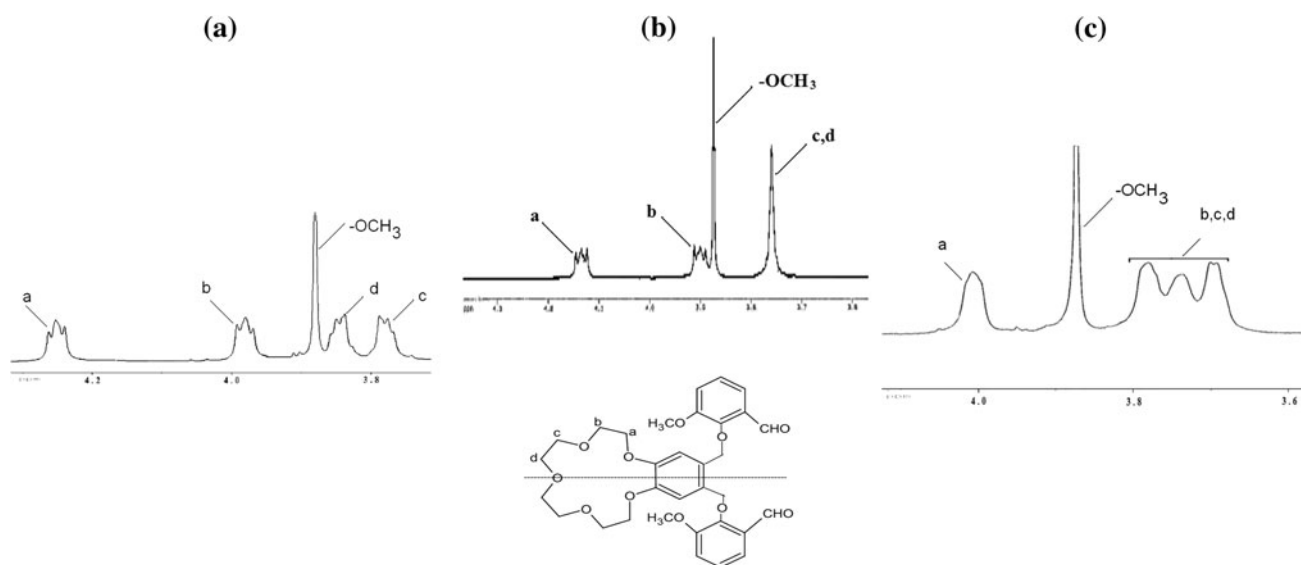


Fig. 1 $^1\text{H-NMR}$ spectra of the crown ether OCH₂–CH₂O protons for **a** sodium complex (**1a**), **b** free ligand (**1**), **c** potassium complex (**1b**) in CDCl₃

were seen for the sodium and potassium complexes (**1a**, **3a** and **1b**, **3b**) for crown ether proton peaks region.

In our study, the presence of two isomers was detected by the $^1\text{H-NMR}$ spectroscopy for 5–OCH₃ substituted

crown ether Schiff bases (**4** and **6**). The presence of two sets of signals for each HC=N, –OCH₂– and Ar–H groups indicates the existence of different possible geometrical isomers. The mono-imine Schiff bases can have two

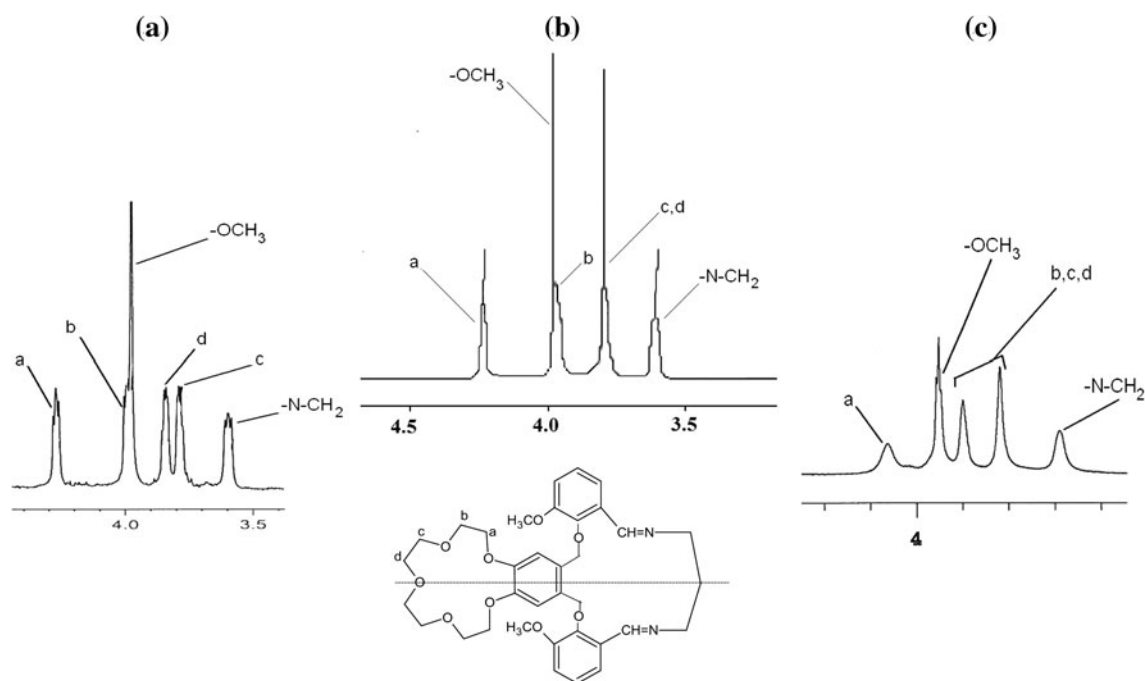
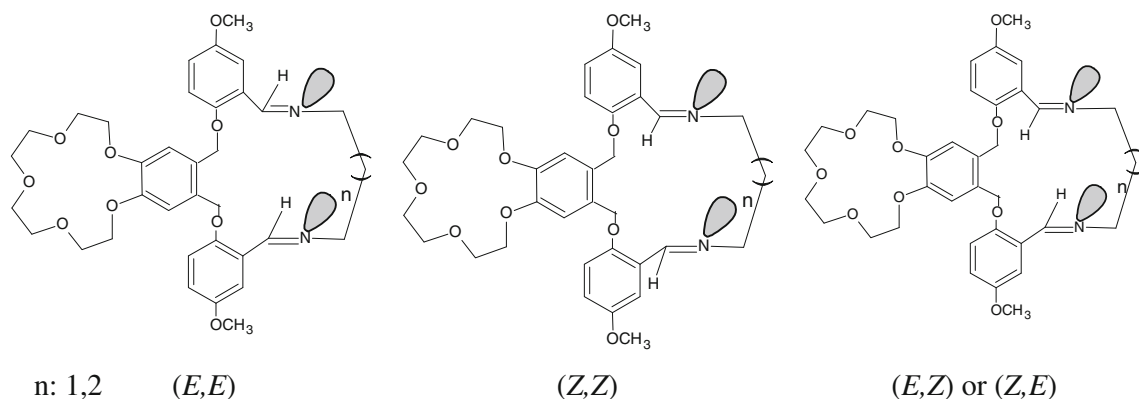


Fig. 2 $^1\text{H-NMR}$ spectra of the crown ether protons ($\text{OCH}_2\text{-CH}_2\text{O}$), **a** sodium complex (**3a**), **b** free ligand (**3**), **c** potassium complex (**3b**) in CDCl_3



Scheme 4 Possible isomers for compounds (**4** and **6**); n 1, 2

possible configurations: *E* and *Z*. Hence two imine bonds of the Schiff bases can have three possible configurations, (*E*, *E*), (*Z*, *Z*) and (*E*, *Z*)/(*Z*, *E*) [25, 26] (Scheme 4).

The $^1\text{H-NMR}$ spectra of compounds **4** and **6** give two singlets attributed to the HC=N protons, two singlets due to the $-\text{OCH}_2-$ protons and two different multiplets due to Ar-H protons. Two different sets of signals present in the $^1\text{H-NMR}$ spectra of the 5- OCH_3 substituted crown Schiff bases **4** and **6** show the presence of both *E* and *Z* isomers. These two peaks suggested the presence of a mixture of

isomers (probably *EE* and *ZZ*). Peak integrations indicated the ratio of the %*E* and %*Z* isomer.

The $^1\text{H-NMR}$ spectra of compounds **4** and **6** were registered at different time intervals and we have seen the different peak intensities of (*E*) and (*Z*) isomer (Fig. 3) (in this figure, each isomer peak was marked with X and Y). One minute after dissolution, the $^1\text{H-NMR}$ spectra showed that the X isomer ratio was higher than the Y one (Fig. 3a). Thirty minutes after dissolution, X and Y isomer ratio were approximately same (Fig. 3b), but after next 30 min Y isomer ratio increased

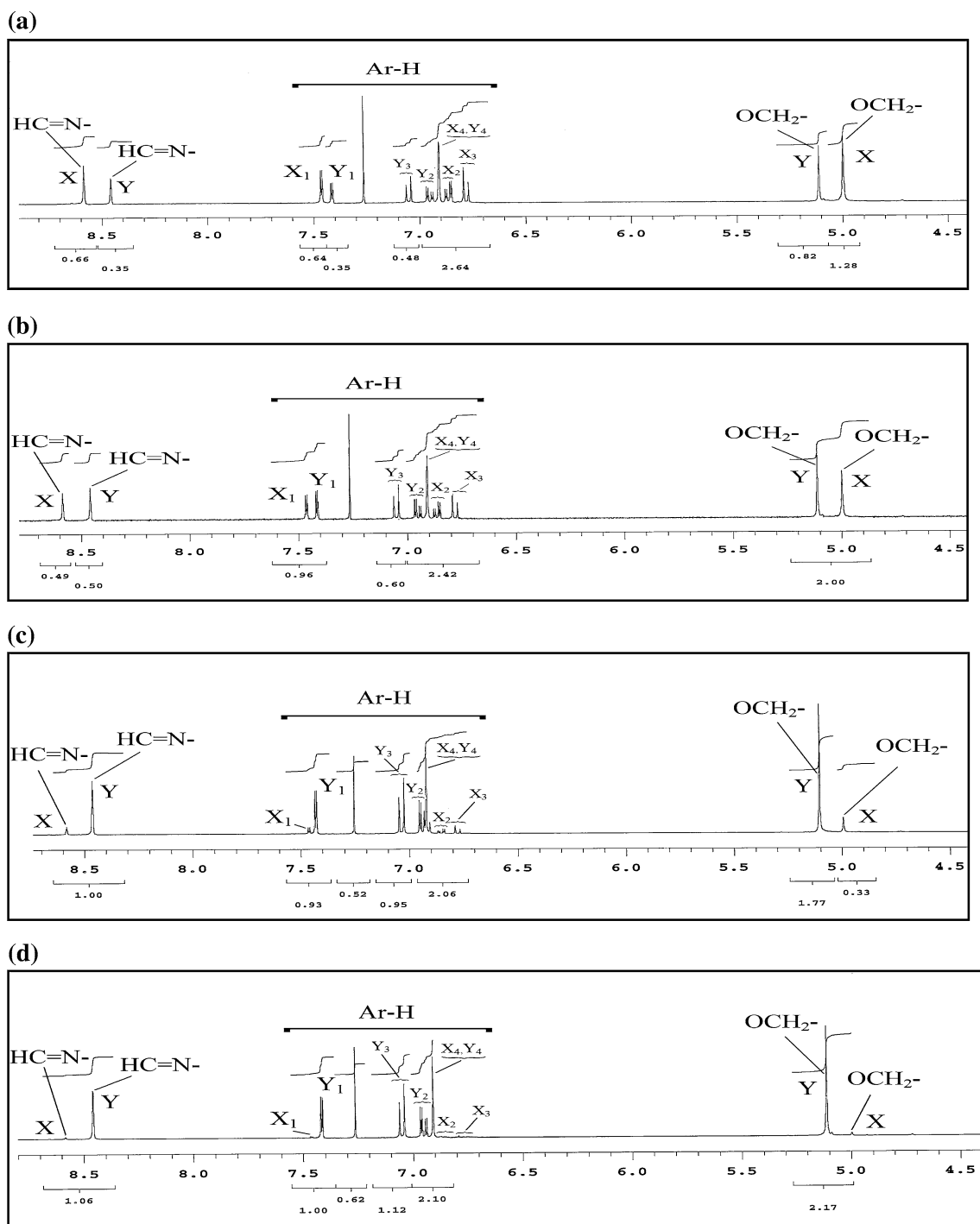


Fig. 3 $^1\text{H-NMR}$ spectra of compound (4) (registered at different time intervals); **a** after 1 min; **b** after 30 min; **c** after 2 h; **d** after 18 h. X and Y: *E* or *Z* isomer peaks (X is related the one isomer while Y is related the another isomer)

(Fig. 3b, c). 18 h after dissolution, the X isomer practically disappears and Y isomer ratio was $\sim 100\%$ (Fig. 3d).

The $^{13}\text{C-NMR}$ spectral data are summarized in Table 4. The aldehyde carbons ($-\text{CHO}$) of compounds **1** and **2** were observed at 191.0 and 189.13 ppm, respectively. The

azomethine carbons were detected at 157.28, 157.37 and 158.88 ppm for compounds **3–5**, respectively. In the $^{13}\text{C-NMR}$ spectra, four crown ether carbon ($\text{OCH}_2\text{-CH}_2\text{O}$) peaks, aliphatic and aromatic carbons indicate that the molecules **1–5** are symmetric.

Table 4 Selected ^{13}C -NMR spectral data (δ , ppm; in CDCl_3)

| Comp. | $-\text{CH}_2-$ | $-\text{OCH}_3$ | $-\text{NCH}_2-$ | $-\text{CH}_2-\text{O}-\text{CH}_2-$ | $-\text{OCH}_2-$ | Ar-C | $-\text{HC}=\text{N}-$ | $-\text{CHO}$ |
|-----------|-----------------|-----------------|------------------|--------------------------------------|------------------|--|------------------------|---------------|
| 1 | – | 56.38 | – | 69.85, 70.88 71.47, 73.77 | 69.54 | 116.82, 118.68, 119.96, 125.16, 129.28 131.1, 150.16, 151.95, 154.01 | – | 191.00 |
| 2 | – | 55.83 | – | 69.26, 69.50 70.52, 71.14 | 69.13 | 110.78, 115.05, 115.31, 123.43, 125.54 127.43, 149.24, 154.07, 155.5 | – | 189.13 |
| 3 | 28.13 | 55.57 | 56.62 | 68.70, 69.08 70.02, 70.60 | 73.50 | 113.91, 116.50, 118.48, 123.91, 128.80 129.97, 147.96, 148.75, 152.09 | 157.28 | – |
| 4 | 29.05 | 56.05 | 57.47 | 69.31, 69.67 70.65, 71.21 | 71.24 | 110.42, 116.36, 117.42, 119.04, 127.80 128.62, 148.94, 152.41, 154.84 | 158.88 | – |
| 5 | 26.56 | 55.90 | 60.05 | 69.16, 69.50 70.44, 71.01 | 72.95 | 114.06, 114.26, 118.73, 124.50, 128.22 130.25, 147.97, 148.53, 152.74 | 157.37 | – |
| 2a | – | 55.83 | – | 68.78, 68.82 69.50, 70.07 | 68.54 | 110.97, 115.53, 115.89, 123.08, 125.36 128.26, 148.30, 153.81, 155.43 | – | 188.83 |

Mass spectra

The fragmentation patterns of the compounds were in good agreement with the suggested structures. For compound (**1**) molecular peak was not observed, but important fragments were detected at m/z 326.2 (20 %), 325.1 (100 %), 295.2 (28.1 %), 237.1 (6.25 %), 207.1 (12.5 %) and 163.1 (21.9 %). The major fragments for compounds (**2**, **3** and **5**) at m/z 614.2 (81.25 %), 671.3 (100 %) and 685.2 (97 %) corresponding to the $[\text{M} + \text{H}_2\text{O}]^+$, $[\text{M} + \text{H} + 2\text{H}_2\text{O}]^+$, and $[\text{M} + \text{H} + 2\text{H}_2\text{O}]^+$, respectively.

In the API-ES mass spectra of complexes (**3a** and **3b**) the dominant peak at m/z 329.9 (100 %) corresponds to the $[\text{C}_{16}\text{H}_{24}\text{O}_7 + \text{H}]^+$. For sodium complex (**3a**) the peak at m/z 657.9 (34 %) corresponds to the ligand plus sodium $[\text{M} + \text{Na}]^+$. For sodium and potassium complexes (**3a** and **3b**) important fragments at m/z 635.9 correspond to the $[\text{M} + \text{H}]^+$ (ligand molecular ion peak). All of the mass spectra show that this fragmentation pattern proceeds by the loss of ether chains in accordance with literature [27–30]. The molecular ion peaks and fragments of the ligands and complexes support the proposed structures.

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