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Molecular structure of novel polymer-like complexes of armed-azacrown ethers with alkali-metal cations

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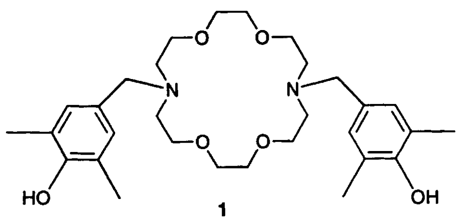
Armed-azacrown ethers *N*,*N'*-bis(4-hydroxy-3,5-dimethylbenzyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane *N*-(4-hydroxy-3,5-dimethylbenzyl)-1,4,7,10-tetraoxa-13-azacyclopentadecane **2** and -1,4,7-trioxa-10-azacyclododecane **3**, and their alkali-metal complexes were prepared. Single crystal structures have been determined for **1**, **1**·KI·$3H_2O$, **1**·KSCN·H_2O, **2**·NaSCN, **2**·KSCN, **2**·RbSCN and **2**·CsSCN, **3**, **3**·LiSCN·H_2O, **3**·LiBr·$3H_2O$ and **3**·RbSCN. The compounds **1**·KI·$3H_2O$ and **1**·KSCN·H_2O are normal 1 : 1 complexes, but **2**·NaSCN, **2**·KSCN, **2**·RbSCN and **2**·CsSCN are novel polymer-like (1 : 1)*n* complexes in which the phenolic OH group in the side arm of the crown ether co-ordinates to the cation incorporated in the crown moiety of another molecule. In the complexes of **3**, when Li^+ is used as guest cation, the normal 1 : 1 complex is obtained, but Rb^+ forms a polymer-like (2 : 2)*n* complex. Fourier-transform IR spectra showed that the O–H stretching band of the phenolic OH group in the polymer-like complexes shifted to lower frequency by *ca.* 210–290 cm^{-1} compared with those of the corresponding host compounds. Also, ^{13}C NMR titration experiments indicated that the stoichiometry of the alkali-metal complexes with **2** and **3** in CD_3CN–CD_3OD (5 : 1) solution is 1 : 1, and thus they do not form polymer-like complexes under these conditions.

Increasing attention has been focused on the lariat and armed crown compounds having one or more additional pendant binding sites.[1,2] These compounds can bind cations selectively, because they form complexes in such a way that the side arm binds to the guest cation incorporated in the crown moiety. On the other hand, recently some research groups have reported polymer-like complexes using armed macrocycles. In those complexes the side arms are used for intermolecular interaction and the units are repeated. For example, Gluzinski *et al.*[3] reported that carboxylic acid-armed diaza-18-crown-6 (1,4,10,13-tetraoxa-7,16-diazacyclooctadecane) forms a polymer-like complex *via* copper ions which are not incorporated in the crown ring. Shu *et al.*[4] and Sibert *et al.*[5] also reported that cyclic polyamine and thia crown ethers having CN groups as pendants can form polymer-like complexes using heavy metal ions (Ni^{2+} and Ag^+, respectively) incorporated in a neighbouring crown cavity.* On the other hand, Olsher *et al.*[6] reported that hydroxy- and hydroxymethyl-substituted dibenzo-14-crown-4 (5,6,7,12,13,14-hexahydrodibenzo[*b*,*i*][1,4,8,11]tetraoxacyclotetradecine) derivatives form polymer-like complexes using counter anions to the incorporated Li^+ ion. However, there is no report on polymer-like complexes using armed-aza crown ether/alkali-metal ion systems.

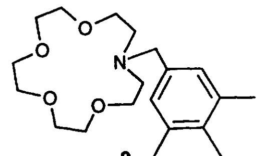
We are interested in structural changes between 1 : 1 and polymer-like complexes. If both can be prepared separately from the same host compound new properties of the crown ethers may be found. In order to develop new polymer-like complexes from armed-azacrown ethers, we designed and synthesized *N*,*N'*-bis(4-hydroxy-3,5-dimethylbenzyl)-armed diaza-18-crown-6 **1** and the *N*-(4-hydroxy-3,5-dimethylbenzyl)-armed monoaza-15-crown-5 (1,4,7,10-tetraoxa-13-azacyclopentadecane) **2** and monoaza-12-crown-4 derivatives (1,4,7-trioxa-10-azacyclododecane) **3** as host compounds. Corey–Pauling–Kolton (CPK) and computer-modelling studies show that the phenolic OH group in the side arms of these compounds cannot bind to a guest cation incorporated in the crown moiety.† The OH group of the side arm can bind only metal cations incorporated in the other host molecules.

Host Complex



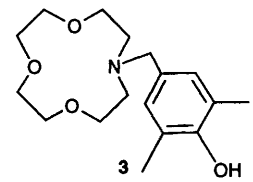
1

1•KI•$3H_2O$
1•KSCN•H_2O



2

2•NaSCN
2•KSCN
2•RbSCN
2•CsSCN



3

3•LiSCN•H_2O
3•LiBr•$3H_2O$
3•RbSCN

Now we describe the preparation of the new armed diaza- and monoaza-crown ethers **1** and **3** and their crystal structures and those of nine complexes **1**·KI·$3H_2O$, **1**·KSCN·H_2O, **2**·NaSCN, **2**·KSCN, **2**·RbSCN, **2**·CsSCN, **3**·LiSCN·H_2O, **3**·LiBr·$3H_2O$ and **3**·RbSCN. Also, we report Fourier-transform IR spectral studies of these complexes and alkali-metal cation binding profiles of **2** and **3** in CD_3CN–CD_3OD (5 : 1) solution by means of a ^{13}C NMR titration technique.

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* The authors used terms such as polymeric cation, polymeric form or polymeric complex.

† CAChe™ (Version 3.7, CAChe Scientific Inc., 1994) was used as the computer-modelling software. Minimization was carried out using the MM2 parameter (conjugate gradient and block-diagonal Newton–Raphson techniques were used).[7]

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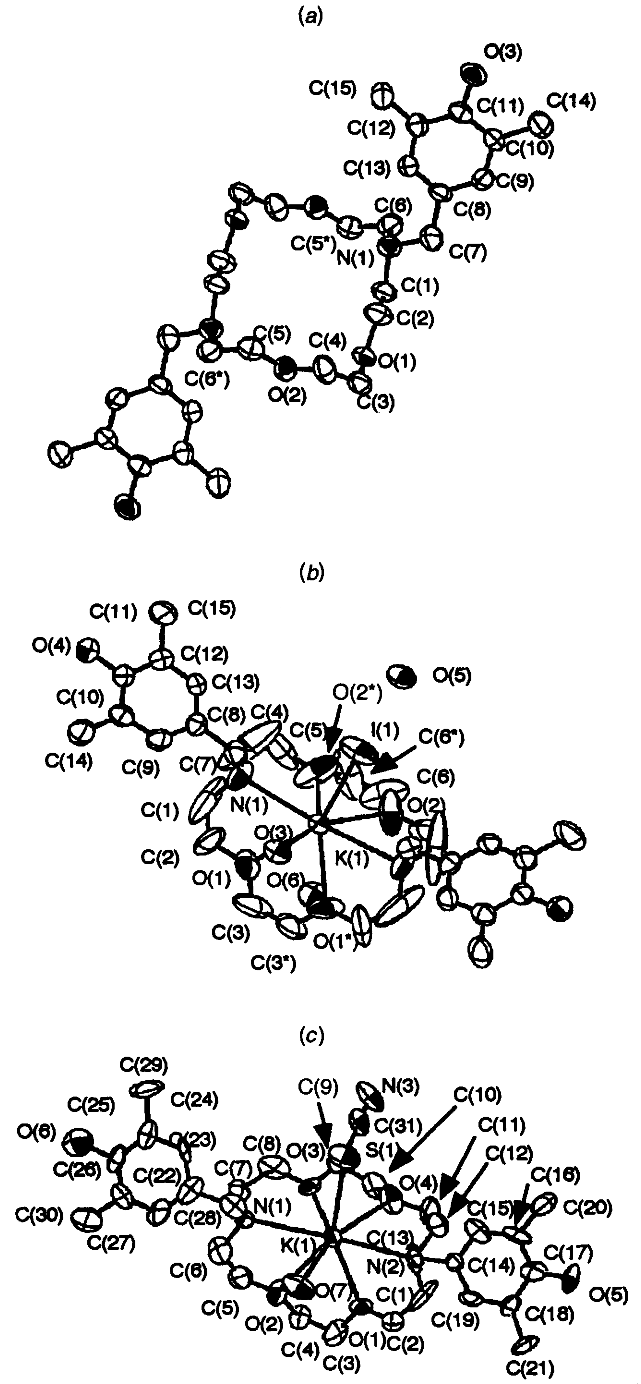

Fig. 1 The ORTEP diagrams (non-hydrogen atoms) of (*a*) compound **1** (oxygen atoms of two water molecules are omitted), (*b*) **1**·KI·3H$_2$O and (*c*) **1**·KSCN·H$_2$O. Thermal ellipsoids are drawn at the 50% probability level

Results and Discussion

Preparation of 4-hydroxy-3,5-dimethylbenzyl-armed diaza- and aza-crown ethers and their alkali-metal complexes

The diaza-18-crown-6 (**1**) and monoaza-12-crown-4 (**3**) derivatives were prepared by the Mannich reaction of the *N*-methoxymethyl azacrown ethers and 2,6-xylenol in dry benzene. The structures of these compounds were confirmed by ^{1}H, ^{13}C NMR, electron impact (EI) mass spectrometry and elemental analyses. We also prepared the monoaza-15-crown-5 derivative **2** according to the procedure described in the literature[8] (only the synthetic method was reported previously).

Alkali-metal complexes were prepared as follows: the host compound in acetonitrile was treated with MSCN, MI or MBr (M = Li, Na, K, Rb or Cs) in methanol. The nine compounds obtained were confirmed by elemental analysis as 1 : 1 complexes of the host and guest. We also tried to prepare the CsSCN complex of **1**,* LiSCN complex of **2**, NaSCN, KSCN and CsSCN complexes of **3**. However, crystals for X-ray analysis could not be obtained.

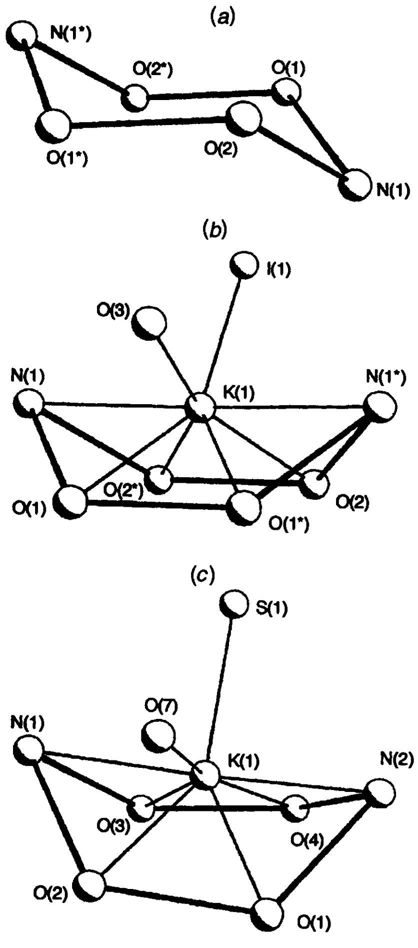

Fig. 2 Skeletal drawings of (*a*) compound **1**, (*b*) **1**·KI·3H$_2$O and (*c*) **1**·KSCN·H$_2$O

Single-crystal structure determinations

The crystal structures were determined for the host compounds, except **2** which is an oil, and all of the complexes. The ORTEP[9] diagrams, skeletal drawings and PLUTO[10] packing diagrams are shown in Figs. 1–10 and selected bond lengths, dihedral angles and mean deviations from planes are summarized in Tables 1, 2 and 3, respectively. There are big ellipsoids for some carbons of the crown rings, for example C(1)–C(5) in **1**·KI·3H$_2$O, C(1), C(2), C(9) and C(10) in **2**·NaSCN, C(7)–C(10) in **2**·KSCN and all ring carbons in **3**·LiBr·3H$_2$O. These disorders may be due to the flexible ring.

1, 1·KI·3H$_2$ and 1·KSCN·H$_2$O. The ORTEP views of compounds **1**, **1**·KI·3H$_2$O, **1**·KSCN·H$_2$O are illustrated in Fig. 1 and skeletal drawings are shown in Fig. 2. The skeletal drawings reveal that the donor atoms of host **1** adopt a chair conformation with a crystallographic centre of symmetry

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* The RbSCN complex of compound **1** was obtained and measured by X-ray analysis. Although the structure was confirmed as the normal 1 : 1 complex similar to **1**·KI·3H$_2$O and **1**·KSCN·H$_2$O, we do not report it because several non-hydrogen atoms could not be refined anisotropically.

bisecting the C(3*)–C(3) and C(6*)–C(6) bonds. On the other hand, the macroring donor atoms in **1**·KI·3H$_2$O and **1**·KSCN·H$_2$O are arranged in a boat conformation. Although **1**·KI·3H$_2$O has a mirror plane containing I(1), O(3), O(5), O(6) and K(1) (Fig. 1), **1**·KSCN·H$_2$O has no mirror plane owing to a slight distortion of the boat conformation. The K$^+$ ions in both complexes are eight-co-ordinated by the two ring N, four ring O, I or S (SCN) as a counter anion and the O atom of a water molecule. The phenolic OH groups in the side arms do not co-ordinate to the K$^+$ ions [Fig. 1(*b*) and 1(*c*)]. The K(1)–O (ring) bond lengths are in the range 2.881(6)–2.713(6) Å for **1**·KI·3H$_2$O and 2.91(1)–2.74(1) Å for **1**·KSCN·H$_2$O. The K(1)–N (ring) bond lengths are 2.959(7) Å for **1**·KI·3H$_2$O and in the range 3.01(1)–2.89(1) Å for **1**·KSCN·H$_2$O. These K(1)–O (ring) and K(1)–N(1) distances are comparable to those observed in the double-armed diaza-18-crown-6 complexes of K$^+$ reported by Gokel and co-workers.[11] The four ether oxygens of the crown ring of **1**·KSCN·H$_2$O are coplanar within 0.1299 Å. The K$^+$ ion lies 1.4070 Å for **1**·KI·3H$_2$O and 1.4009 Å for **1**·KSCN·H$_2$O from the best plane of the ring oxygens and nearly on the line between the two nitrogen atoms. The packing diagrams of **1**·KI·3H$_2$O and **1**·KSCN·H$_2$O (Fig. 3) suggest that the crown ring and aromatic ring moieties are stacked, and the phenolic OH groups in the side arms do not co-ordinate to any K$^+$ ions.

2·NaSCN, 2·KSCN, 2·RbSCN and 2·CsSCN. The ORTEP view of compound **2**·NaSCN is illustrated in Fig. 4(*a*) and a skeletal drawing is shown in Fig. 5(*a*); a PLUTO packing diagram is shown in Fig. 6(*a*). The Na$^+$ ion of the complex is co-ordinated by the four ring O atoms, the ring N atom and the O atom of the phenolic OH group in the side arm of the nearest-neighbour molecule [Figs. 5(*a*) and 6(*a*)]. The SCN$^-$ ion as a counter anion is not co-ordinated because the Na$^+$ ion is completely incorporated in the crown cavity. Therefore, the Na$^+$ ion is six-co-ordinated and **2**·NaSCN appears to be a (1:1)*n* polymer, *i.e.* the host:guest ratio is 1:1 and the unit is repeated. The Na(1)–O (ring) and Na(1)–O(5A) (the nearest molecule phenolic OH) bond lengths are in the range 2.51(1)–2.39(1) and 2.349(8) Å, respectively (Table 1). The Na(1)–N(1) bond length is 2.576(9) Å. Rodrigue *et al.*[12] reported that the Na(1)–O (phenol) distance in a 1:1:1 dicyclohexano-18-crown-6–PhONa–PhOH complex is 2.3637 Å.* The Na(1)–O(5A) distance in **2**·NaSCN is comparable with that of the above complex. Also, the Na(1)–O (ring) and Na(1)–N(1) are comparable with those of the sodium complex of a lariat monoaza-15-crown-5 compound.[11] The four ether oxygens of the crown ring are coplanar within 0.1036 Å (Table 3). As shown in Table 2, the dihedral angles N(1)–C(11)–C(12)–C(13) and Na(1)–N(1)–C(11)–C(12) are 79(1) and −171.3(9)°, respectively. The Na$^+$ ion lies 1.091 Å from the best plane of the ring oxygen atoms. The mean deviation from the plane is larger (0.3904 Å) when the plane includes the N(1) atom. This result indicates that the skeleton of the donor atoms in the crown ring is bent at N(1). The angle between the aromatic ring of one molecule and that of the next is 33.53°.

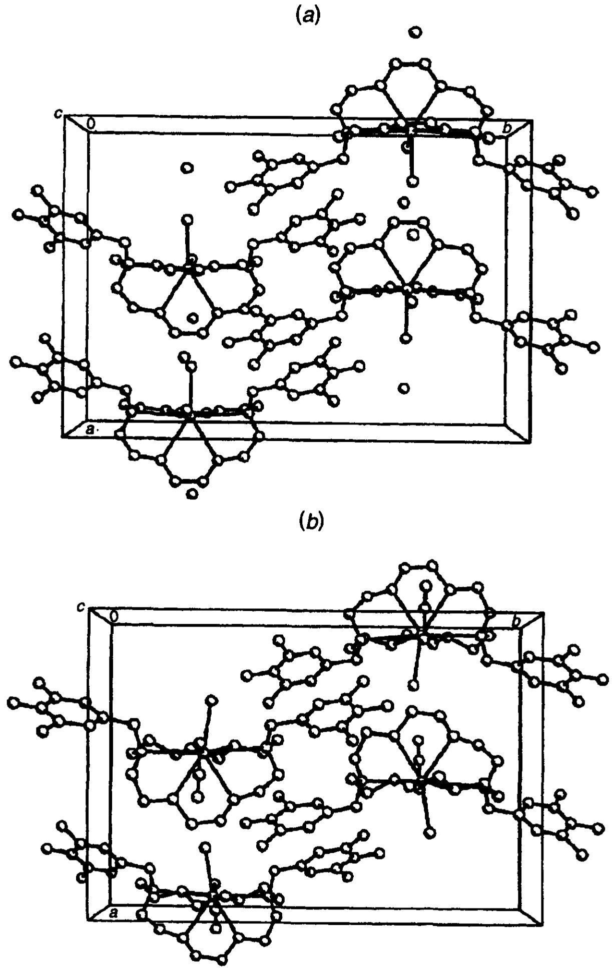

Fig. 3 The PLUTO diagrams of (*a*) compound **1**·KI·3H$_2$O and (*b*) **1**·KSCN·H$_2$O showing the unit-cell packing (hydrogen atoms omitted)

The ORTEP view of compound **2**·KSCN is illustrated in Fig. 4(*b*) and a skeletal drawing is shown in Fig. 5(*b*). The K$^+$ ion is seven-co-ordinated by the four ring O, the ring N, the O atom of the phenolic OH group in the side arm of the nearest-neighbour molecule and the N atom of SCN$^-$ as a counter ion. The compound is a polymer-like (1:1)*n* complex similar to **2**·NaSCN [Fig. 6(*b*)]. The K(1)–O (ring), K(1)–O(5A), K(1)–N(1) and K(1)–N(2) (SCN) bond lengths are in the range 2.78(1)–2.73(1), 2.707(8), 2.874(9) and 3.01(1) Å, respectively (Table 1). The distances K(1)–O (ring) and K(1)–N(1) are also comparable with those of the potassium complex of a lariat monoaza-15-crown-5 compound.[11] As shown in Table 2, the dihedral angles N(1)–C(11)–C(12)–C(13) and K(1)–N(1)–C(11)–C(12) are 101(1) and 52(1)°, respectively. The four ether oxygens of the crown ring are coplanar within 0.1215 Å (Table 3). The K$^+$ ion lies 1.631 Å from the best plane of the ring oxygens. The mean deviation from the plane including the N(1) atom is the smallest (0.3142 Å) among the alkali-metal complexes of **2**. The result indicates that K$^+$ best fits the cavity of the armed monoaza-15-crown-5 ether. The angle between the aromatic ring of one molecule and that of the next is 30.79°.

As shown in the ORTEP views [Fig. 4(*c*) and 4(*d*)], skeletal drawings [Fig. 5(*c*) and 5(*d*)] and packing diagrams [Fig. 6(*c*) and 6(*d*)], compounds **2**·RbSCN and **2**·CsSCN are isomorphous. The Rb$^+$ and Cs$^+$ ions are seven-co-ordinated by the four ring O, the ring N, the O atom of the phenolic OH group in the side arm of the nearest-neighbour molecule and the N atom of SCN$^-$. The compounds are polymer-like (1:1)*n* complexes similar to those of Na$^+$ and K$^+$. The M(1)(M = Rb or Cs)–O (ring) and M(1)–O(5A) bond lengths are in the range 2.884(9)–2.984 and 2.963(8) Å for **2**·RbSCN, and in the range of 3.020(5)–3.182(5) and 3.104(4) Å for **2**·CsSCN. The M(1)–N(1) bond lengths are 2.99(1) and 3.131(6) Å, respectively. The M(1)–O (ring) bond distances are comparable with those of 2:1 complexes between 15-crown-5 and Rb$^+$ or Cs$^+$.[13] The dihedral angles N(1)–C(11)–C(12)–C(13) and M(1)–N(1)–C(11)–C(12) of **2**·MSCN (M = Rb and Cs) are about 80 and −180°, respectively. The four ether oxygens of the crown

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* Dicyclohexano-18-crown-6 = icosahydrodibenzo[*b*,*k*][1,4,7,10,13,16]hexaoxacyclooctadecine. The authors commented that 'it is not possible to distinguish the phenol from the phenoxide oxygen from O–H distances', and they used the term phenoxide oxygen to refer to the oxygen that is 'co-ordinated to the sodium ion'.

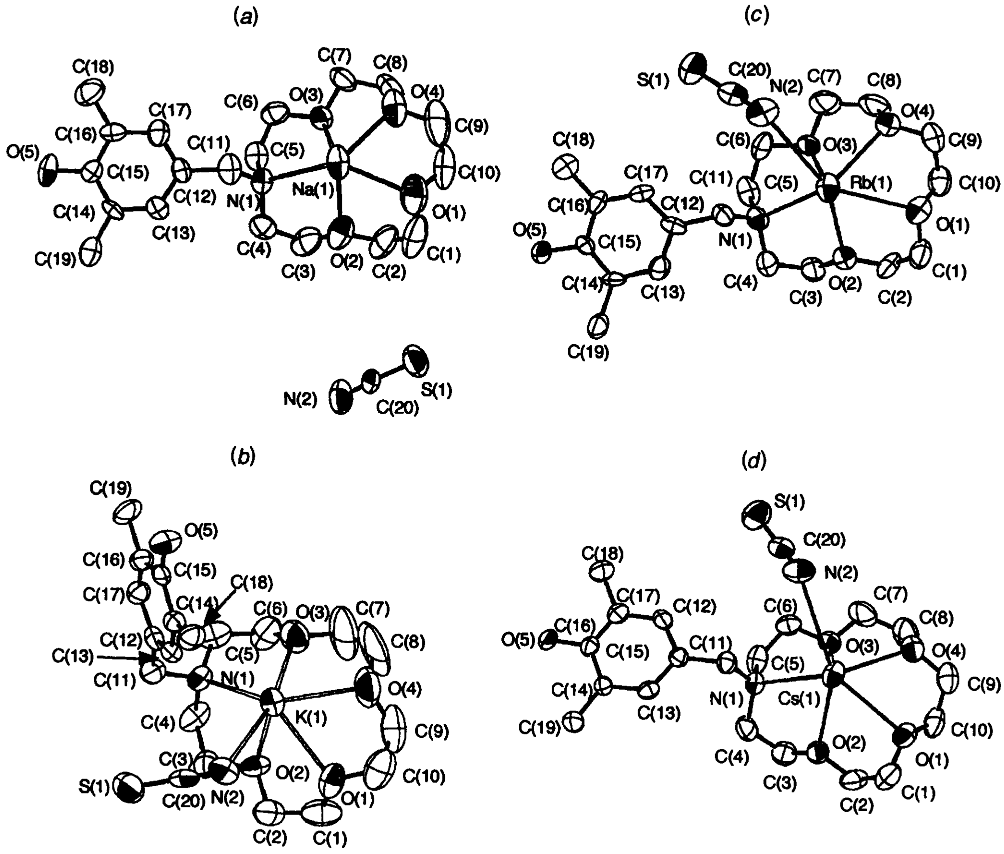


Fig. 4 The ORTEP diagrams (hydrogen atoms omitted) of single repeating units of (*a*) compound **2**·NaSCN, (*b*) **2**·KSCN, (*c*) **2**·RbSCN and (*d*) **2**·CsSCN. Details as in Fig. 1

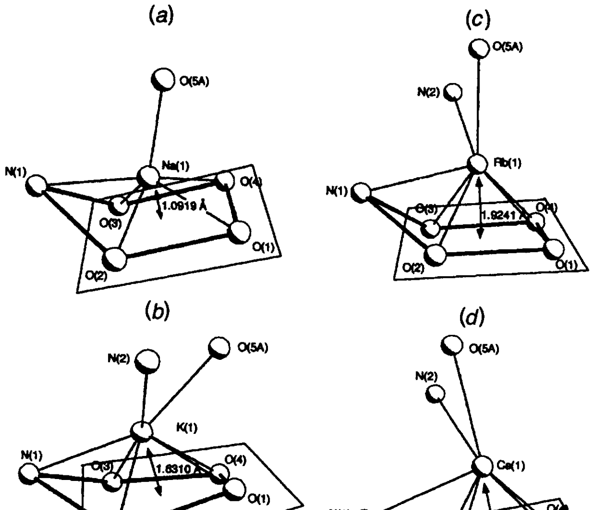


Fig. 5 Skeletal drawings of (*a*) compound **2**·NaSCN, (*b*) **2**·KSCN, (*c*) **2**·RbSCN and (*d*) **2**·CsSCN

ring of **2**·RbSCN and **2**·CsSCN are coplanar within 0.0599 and 0.0437 Å, respectively. The Rb^+ and Cs^+ ions lie 1.924 and 2.169 Å from the best plane of the ring oxygens. The angles between the aromatic ring of one molecule and that of the next are 81.4° for **2**·RbSCN and 81.33° for **2**·CsSCN.

In the polymer-like complexes of compound **2** the dihedral angles M(1)–N(1)–C(11)–C(12) and N(1)–C(11)–C(12)–C(13) of **2**·MSCN (M = Na, Rb or Cs) are about −180 and 80° (Table 2), while those of **2**·KSCN are 52 and 101°, respectively. The mean deviations of the planes (Table 3) and skeletal drawing [Fig. 5(*b*)] show that the conformation of the crown ring in **2**·KSCN differs from those of the other polymer-like complexes. Therefore, the difference in these dihedral angles may be due to the conformational changes in the crown ring.

3, 3·LiSCN·H_2O, 3·LiBr·$3H_2O$ and 3·RbSCN. The ORTEP view of compound **3** is illustrated in Fig. 7(*a*) and a skeletal drawing is shown in Fig. 8(*a*). The skeletal drawing reveals that the four donor atoms are coplanar within 0.0702 Å. The ORTEP views of **3**·LiSCN·H_2O and **3**·LiBr·$3H_2O$ are illustrated in Fig. 7(*b*) and 7(*c*), and skeletal drawings are shown in Fig. 8(*b*) and 8(*c*); PLUTO packing diagrams are also shown in Fig. 9(*a*) and 9(*b*). The Li^+ ions of both complexes are five-co-ordinated by the three ring O atoms, the ring N(1) and the O atom of a water molecule. The complexes are not polymer-like as shown in Fig. 9(*a*) and 9(*b*). The Li(1)–O (ring), Li(1)–N(1) and Li(1)–O(5) bond lengths are in the range 2.21(2)–1.97(2), 2.17(1) and 1.87(2) Å for **3**·LiSCN·H_2O, and 2.05(1)–2.08(2), 2.16(2) and 1.93(2) Å for **3**·LiBr·$3H_2O$ (Table 1). The Li(1)–O (ring) bond distances are comparable with that of a lithium complex of a carboxylic acid armed-dibenzo-14-crown-4 compound.[14] The dihedral angles N(1)–C(9)–C(10)–C(11) and Li(1)–N(1)–C(9)–C(10) are 78(1) and −179.1(7)° for **3**·LiSCN·H_2O and 100(1) and −171.9(8)° for **3**·LiBr·$3H_2O$ (Table 2). The three oxygen and nitrogen atoms of the crown ring of **3**·LiBr·$3H_2O$ are coplanar within 0.0072 Å. However, the plane in **3**·LiSCN·H_2O is bent 38.79° between the planes O(3)–O(1)–O(2) and O(2)–N(1)–O(3) [Fig. 8(*b*)]. The Li^+ ion lies 1.214 Å from the plane O(1)–O(2)–O(3) for **3**·LiSCN·H_2O, and 0.882 Å from the best plane of the three ring oxygen and nitrogen atoms for **3**·LiBr·$3H_2O$.

We used LiSCN·H_2O to prepare the lithium complex of compound **3**. As described above, the oxygen atom of the water molecule co-ordinates to the Li^+ ion, and the complex is not a polymer. We thought that co-ordination of the oxygen atom of

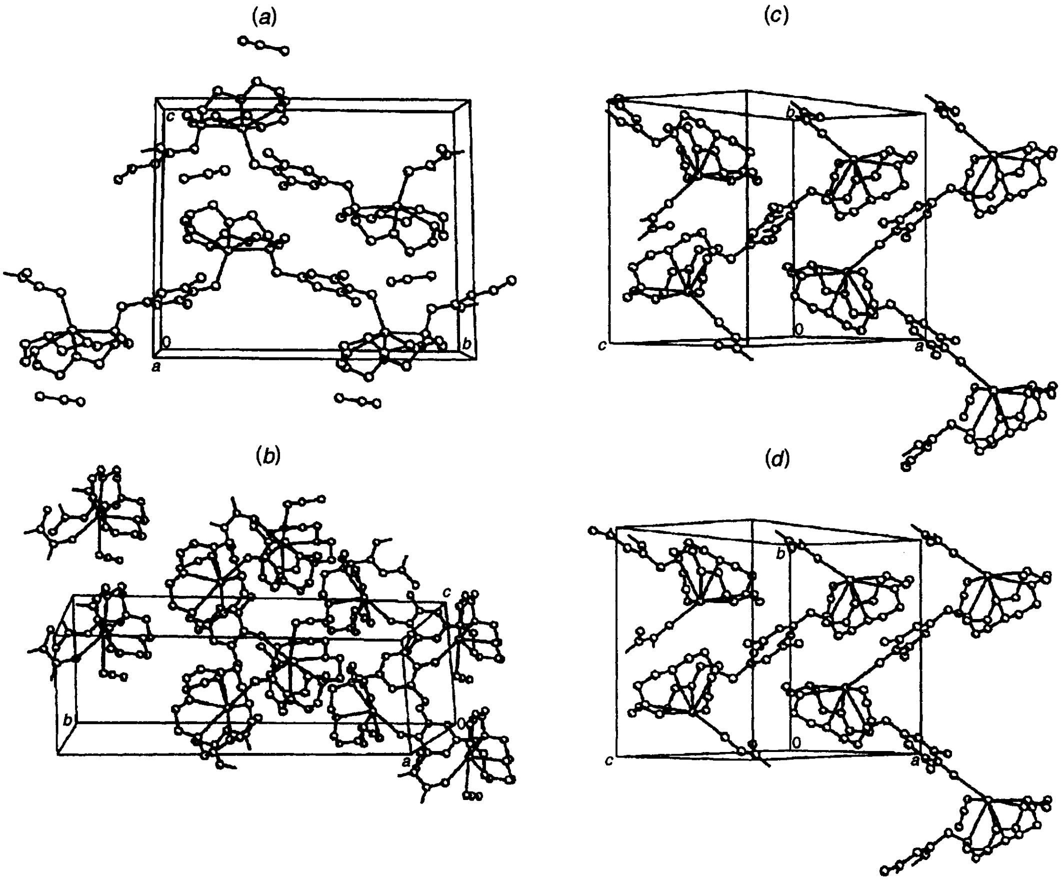


Fig. 6 The PLUTO diagrams of (*a*) compound 2•NaSCN, (*b*) 2•KSCN, (*c*) 2•RbSCN and (*d*) 2•CsSCN with the unit-cell packing (hydrogen atoms omitted)

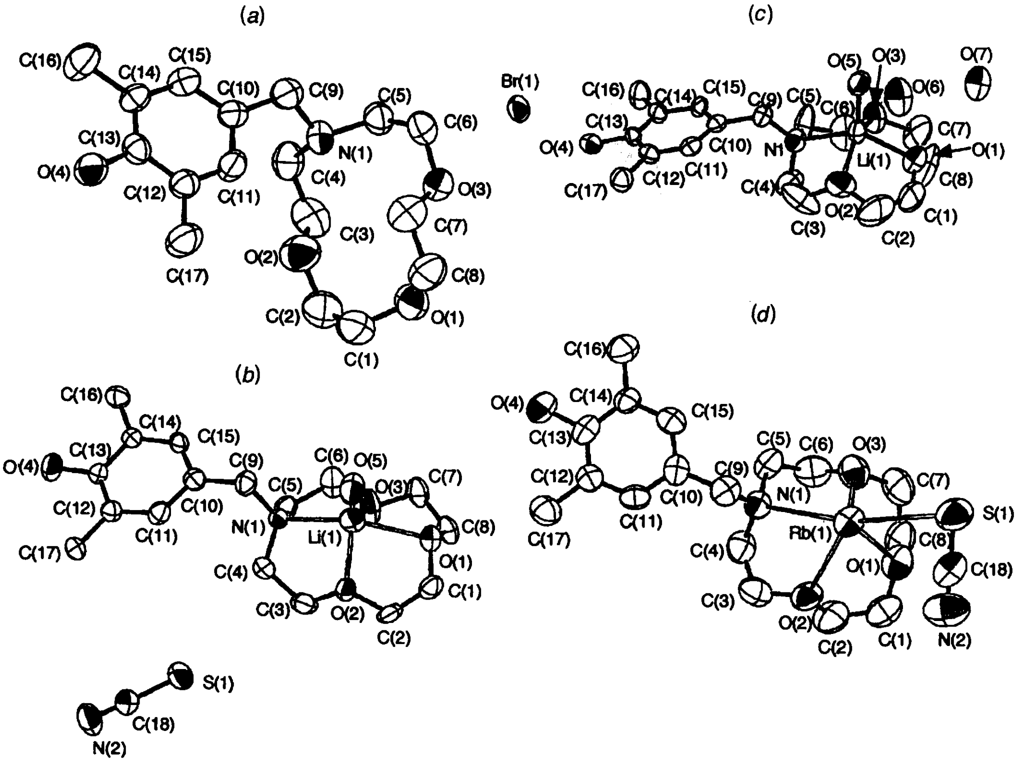


Fig. 7 The ORTEP digrams (hydrogen atoms omitted) of (*a*) compound 3, (*b*) 3•LiSCN•H_2O, (*c*) 3•LiBr•$3H_2O$ and (*d*) 3•RbSCN. Details as in Fig. 1

the water molecule to the Li^+ must interfere with formation of a polymer-like complex. We tried to use LiBr, which does not have a water of hydration, to form a lithium complex. However, as shown in Fig. 9(*b*), the 3•LiBr•$3H_2O$ complex includes three

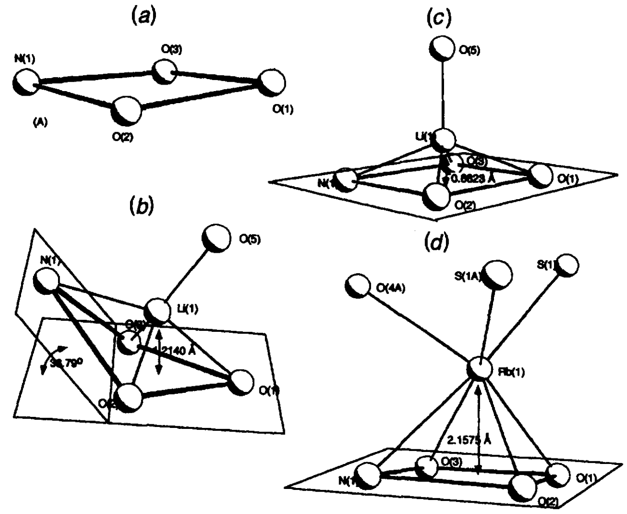


Fig. 8 Skeletal drawings of (*a*) compound **3**, (*b*) **3**·LiSCN·H_2O, (*c*) **3**·LiBr·$3H_2O$ and (*d*) **3**·RbSCN

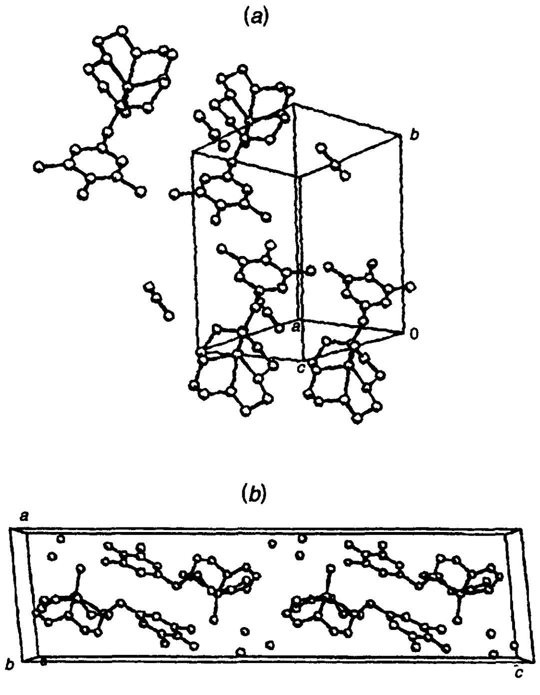


Fig. 9 The PLUTO diagrams of (*a*) compound **3**·LiSCN·H_2O and (*b*) **3**·LiBr·$3H_2O$ with the unit-cell packing (hydrogen atoms omitted)

waters and is hydrated. It is well known that Li^+ ion is strongly hydrated by water.[15] The crystal water in **3**·LiBr·$3H_2O$ arises from air and solvents.

To see if a polymer forms from complexes of compound **3**, we prepared its RbSCN complex. The ORTEP view of **3**·RbSCN is illustrated in Fig. 7(*d*), and the skeletal drawing is shown in Fig. 8(*d*). The PLUTO packing diagram is shown in Fig. 10. The Rb^+ ion is seven-co-ordinated by the three ring O atoms, the ring N [Fig. 7(*d*)], the O atom of the phenolic OH group in the side arm of the nearest-neighbour molecule and two S atoms of SCN^- ions [Fig. 8(*d*)]. The SCN^- ions bridge between two incorporated Rb^+ ions [Rb(1)–S(1) 3.464(3), Rb(1)–S(1A) 3.769(4) Å], thus resulting in the formation of a complicated dimeric (2:2)*n* polymer [Figs. 8(*d*) and 10(*a*)]. The Rb–O (ring) and Rb–O(4A) (the nearest molecule phenolic OH) bond lengths are in the range 2.957(6)–2.875(6) and 3.053(6) Å, respectively (Table 1). The Rb–N(1) bond length is 3.113(6) Å. The Rb–O (ring) bond distances are comparable with that of the 2:2 complex between 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) and Rb^+.[16] As shown in Table 2, the dihedral angles N(1)–C(9)–C(10)–C(11) and Li(1)–N(1)–C(9)–C(10) are 95.7(9) and 169.9(6)°, respectively. The three ether oxygens and nitrogen atoms of the crown ring are coplanar within 0.0138 Å (Table 3). The Rb^+ ion lies 2.157 Å from the best plane of the ring oxygen and nitrogen atoms. The angle between the aromatic ring of one molecule and that of the next which forms a polymer is 37.82°.

Although many crystal structures of complexes of crown ether–alkali-metal ion systems have been reported, there is no report on 1:1 stoichiometric complexes between 15- and 12-membered crown ether and Rb^+ or Cs^+. The present complexes are the first such instances.

Fourier-transform IR spectral study of the complexes

In order to obtain information concerning the phenolic OH group of each complex, we measured their Fourier-transform IR spectra and compared them with similar spectra of the host compounds. Table 4 shows the spectral data along with those for 2,6-xylenol. There are two O–H stretching bands arising from phenolic OH and water at 3367 and 3210 cm^{-1} in the spectrum of diaza-crown ether **1**. For **1**·KI·$3H_2O$ and **1**·KSCN·H_2O the O–H stretching bands appear at 3436 and 3350 cm^{-1}. The O–H stretching band of **3**·LiSCN·H_2O appears at 3376 cm^{-1}. There are two O–H stretching bands arising from phenolic OH and water at 3486 and 3338 cm^{-1} for **3**·LiBr·$3H_2O$. On the other hand, there are significant differences in the O–H stretching bands between polymer-like complexes and the normal complexes. For the polymer-like complexes the O–H stretching band of the phenolic OH was shifted to lower frequency by about 210–290 cm^{-1} and broadened when compared with that of compounds **2** and **3**. This indicates that the O–H bonds were weakened by co-ordination of the oxygen atom in the phenolic OH group to the metal cation (Fig. 11). Therefore, IR spectroscopy is effective to discriminate whether the complex is polymer-like or not.

In addition the FTIR spectra gave useful information about the co-ordination of the SCN^- ions. The C–N stretching bands of **1**·KSCN·H_2O, **2**·KSCN, **2**·RbSCN, **2**·CsSCN and **3**·RbSCN appeared at about 2044–2049 cm^{-1} and those of **2**·NaSCN and **3**·LiSCN·H_2O shifted to higher frequency (2062 and 2092 cm^{-1}, respectively). The difference in the C–N absorption band indicates that the co-ordination mode of SCN^- in **1**·KSCN·H_2O, **2**·KSCN, **2**·RbSCN, **2**·CsSCN and **3**·RbSCN differs from that in **2**·NaSCN and **3**·LiSCN·H_2O. The X-ray analyses show that the SCN^- ions in the **2**·NaSCN and **3**·LiSCN·H_2O are not co-ordinated, while those in **1**·KSCN·H_2O, **2**·KSCN, **2**·RbSCN, **2**·CsSCN and **3**·RbSCN do. In addition the FTIR spectra can discriminate whether the complex is co-ordinated by sulfur or nitrogen of SCN^-. For **1**·KSCN·H_2O and **3**·RbSCN which are co-ordinated by sulfur, the C–N absorption bands appeared at 2048 and 2049 cm^{-1}. On the other hand the bands of **2**·KSCN, **2**·RbSCN and **2**·CsSCN, which are co-ordinated by nitrogen, appeared at 2044 cm^{-1}.

Binding profiles in solution

Further information concerning the alkali-metal cation binding behaviour of the armed crown ethers **2** and **3** in solution was obtained *via* ^{13}C NMR spectroscopy in CD_3CN–CD_3OD (5:1) at 298 K. Fig. 12 shows the CsSCN- and LiSCN-induced changes in the ^{13}C NMR spectra of **2** and **3** (typical examples). Remarkable shift changes occurred when 1.0 equivalent of alkali-metal cation was added. The results indicate that **2** and **3** form 1:1 complexes under these conditions even if the cation is larger than the cavity size. Table 5 summarizes the ^{13}C NMR shift changes on addition of alkali-metal ions (1 equivalent) to **2** and **3**. Although remarkable upfield shift changes for carbons b–d were observed the resonances of carbons a which are linked to the OH group were shifted only by +0.4 to +0.8 ppm. Also, the magnitude of the shift changes for **2** and **3** are in the order

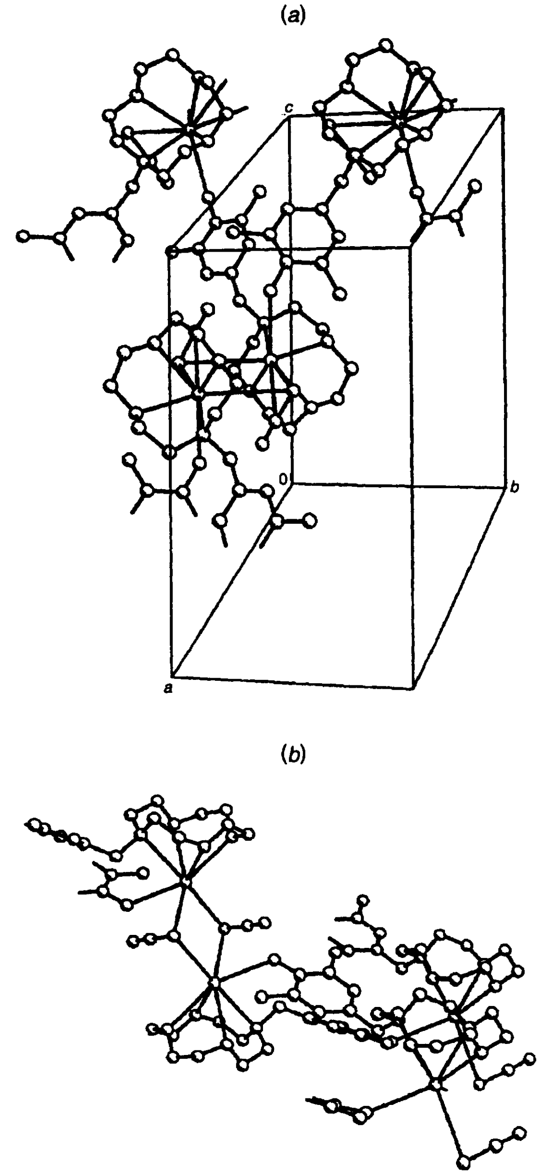
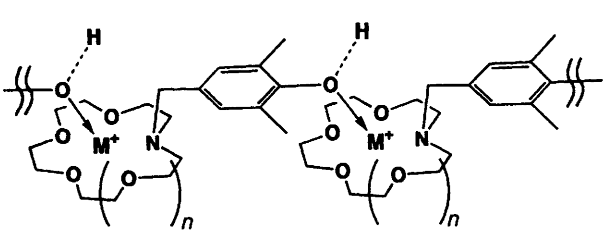


Fig. 10 The PLUTO diagram of the compound 3·RbSCN with the unit-cell packing (*a*) and partial enlargement diagram (*b*) (hydrogen atoms omitted)



2 $n = 1$
3 $n = 0$

Fig. 11 Weakening of the phenolic O–H bond upon co-ordination of the oxygen atom to a metal cation

$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$. These results suggest that **2** and **3** form normal 1 : 1 complexes and the phenolic OH group is not co-ordinated in solution.

Conclusion

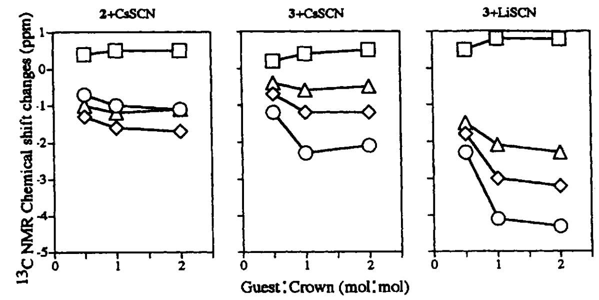


Fig. 12 The CsSCN- and LiSCN-induced changes in the ^{13}C NMR chemical shifts of compounds **2** and **3**. Carbons (denoted as in Table 5): a (□), b (◇), c (○) and d (△)

We have demonstrated that the designed 4-hydroxy-3,5-dimethylbenzyl-substituted monoaza-crown ethers form polymer-like (1 : 1)*n* and (2 : 2)*n* complexes with alkali-metal cations. The phenolic OH group, which cannot co-ordinate intramolecularly, caps the metal cation of a neighbouring complex. This process plays an important role in the formation of the polymer-like complex. From ^{13}C NMR titrations, compounds **2** and **3** were shown to form only 1 : 1 complexes in solution. Also, it is noteworthy that both normal 1 : 1 and polymer-like complexes can be obtained separately as crystals by changing cations in the monoaza-12-crown-4 derivative **3**. The structural changes in the complexes suggested that the armed-azacrown ether–alkali-metal ion complex systems may provide guidelines for the design of novel ionic polymers.

Experimental

Materials and apparatus

Monoaza-15-crown-5,[17] monoaza-12-crown-4[18] and *N*-(4-hydroxy-3,5-dimethylbenzyl)-armed monoaza-15-crown-5 (**2**) were synthesized according to the reported method.[19] Diaza-18-crown-6 was obtained from Merck. Melting points were obtained with a Mel-Temp capillary apparatus and not corrected. Mass spectra were taken on a Hitachi M80 spectrometer, ^1H and ^{13}C NMR spectra on Brucker AC 250 spectrometers with $SiMe_4$ as the internal standard. Correlation and C–H correlated two-dimensional NMR spectroscopies were used for the assignment of ^1H and ^{13}C NMR spectra. The IR spectra were recorded on a JASCO FT/IR-230 spectrometer. Elemental analyses were measured using a Perkin-Elmer 2400 analyser.

Preparations

***N*,*N*′-Bis(4-hydroxy-3,5-dimethylbenzyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane 1.** A mixture of *N*,*N*′-di(methoxymethyl)-1,4,10,13-tetraoxa-7,16-diozacyclooctadecane[19] (10.5 g, 30 mmol) and 2,6-xylenol (3.7 g, 30 mmol) in dry benzene (20 cm^3) under a nitrogen atmosphere was refluxed for 20 h. It was then concentrated under reduced pressure, the residual oil separated and purified by column chromatography on alumina [CH_2Cl_2–MeOH (20 : 1) as eluent]. The main band was collected and concentrated. The residual solid was recrystallized from acetonitrile to gave pure compound **1** as pale yellow plates, 8.4 g (53%), m.p. 113.0–114.0 °C: IR (KBr disc) 3464, 3200 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.04–6.90 (m, 4 H), 4.37–4.36 (m, 20 H), 2.99 (t, 8 H, $J = 5.4$ Hz) and 2.33–2.11 (m, 12 H). Mass spectrum (20 eV, *ca.* 3.2×10^{-18} J): *m*/*z* 531 ($M^+ + 1$, 5%) (Found: C, 63.85; H, 8.70; N, 5.05. Calc. for $C_{30}H_{46}N_2O_6 + 2H_2O$: C, 63.6; H, 8.90; N, 4.95%).

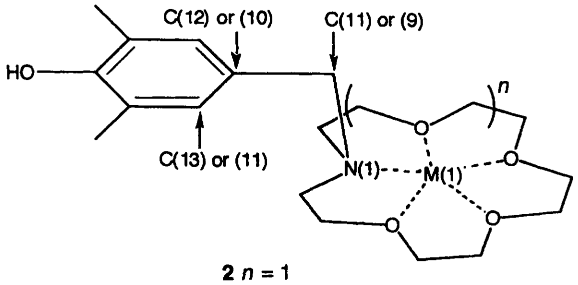
***N*-(4-Hydroxy-3,5-dimethylbenzyl)-1,4,7-trioxa-10-azacyclododecane 3.** A mixture of monoaza-12-crown-4 (2.3 g, 13 mmol) and paraformaldehyde (0.39 g, 3.13 mmol) in methanol (10 cm^3) was stirred at room temperature under a nitrogen atmosphere for 20 h. After the reaction was completed the solvent was removed under reduced pressure. It was confirmed that the residual oil was pure by TLC, and its identity as *N*-(methoxymethyl)-1,4,7-trioxa-10-azacyclododecane by means

Table 1 Selected bond lengths (Å)

		1·KI·3H_2O	**1**·KSCN·H_2O	**2**·NaSCN	**2**·KSCN	**2**·RbSCN	**2**·CsSCN	**3**·LiSCN·H_2O	**3**·LiBr·3H_2O	**3**·RbSCN
M^+–O	ring O	2.881(6)	2.817(9)	2.51(1)	2.78(1)	2.896(9)	3.020(5)	2.21(2)	2.06(2)	2.906(6)
		2.713(6)	2.91(1)	2.39(1)	2.750(7)	2.884(9)	3.020(5)	1.97(2)	2.08(2)	2.875(6)
			2.77(1)	2.393(8)	2.73(1)	2.984(8)	3.182(5)	2.02(1)	2.05(1)	2.957(6)
			2.74(1)	2.45(1)	2.74(1)	2.920(9)	3.088(6)			
	Phenolic OH[a]			2.349(8)	2.707(8)	2.963(8)	3.104(4)			3.053(6)
	H_2O	2.704(8)	2.692(8)					1.87(2)	1.93(2)	
M^+–N		2.959(7)	3.01(1)	2.576(9)	2.874(9)	2.99(1)	3.131(6)	2.17(1)	2.16(2)	3.113(6)
			2.89(1)							
M^+–X^-		3.610(3)	3.485(5)	[b]	3.01(1)	3.20(1)	3.481(7)	[b]	[b]	3.464(3)
										3.769(4)
		(X = I)	(X = *S*CN)[c]	(X = SCN)	(X = SC*N*)[c]	(X = SC*N*)[c]	(X = SC*N*)[c]	(X = SCN)	(X = Br)	(X = *S*CN)[c]

[a] Interaction with the nearest molecule. [b] The counter anion is not co-ordinated. [c] Italicized atom co-ordinates.

Table 2 Dihedral angles (°)



2 $n = 1$
3 $n = 0$

Compound	M(1)–N(1)–C(11)–C(12)	N(1)–C(11)–C(12)–C(13)
2·NaSCN	−171.3(9)	79(1)
2·KSCN	52(1)	101(1)
2·RbSCN	−178(1)	79(2)
2·CsSCN	−179.0(5)	81.4(8)
	M(1)–N(1)–C(9)–C(10)	N(1)–C(9)–C(10)–C(11)
3·LiSCN·H_2O	−179.1(7)	78(1)
3·LiBr·$3H_2O$	−171.9(8)	100(1)
3·RbSCN	169.9(6)	95.7(9)

The dihedral angles M(1)–N(1)–C(11)–C(12) for the complexes of compound **2** and M(1)–N(1)–C(9)–C(10) for those of **3** are within 180 ± 10°. Also, N(1)–C(11)–C(12)–C(13) for complexes of **2** and N(1)–C(9)–C(10)–C(11) for those of **3** are within 90 ± 10°.

Table 3 Mean deviations (Å) from planes

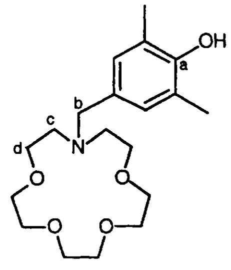
	Plane	
Compound	O(1)–O(2)–O(3)–O(4)	N(1)–O(1)–O(2)–O(3)–O(4)
2·NaSCN	0.1036	0.3904
2·KSCN	0.1215	0.3142
2·RbSCN	0.0599	0.3320
2·CsSCN	0.0437	0.3411
		N(1)–O(1)–O(2)–O(3)
3·LiSCN·H_2O		0.3689
3·LiBr·$3H_2O$		0.0072
3·RbSCN		0.0138

Table 4 Infrared spectral data (cm^{-1}) for alkali-metal complexes of compounds **1**–**3**

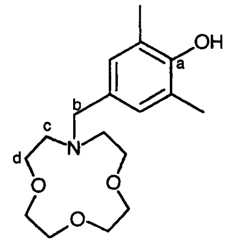
Compound	ν(O–H)	ν(C≡N)
2,6-Xylenol[a]	3377	
1[a]	3367, 3210	
1·KI·$3H_2O$[a]	3436	
1·KSCN·H_2O[a]	3350	2048
2[b]	3330	
2·NaSCN[a]	3043 (br)	2062
2·KSCN[a]	3080 (br)	2044
2·RbSCN[a]	3080 (br)	2044
2·CsSCN[a]	3080 (br)	2044
3[a]	3310	
3·LiSCN·H_2O[a]	3376	2092
3·LiBr·$3H_2O$[a]	3486, 3338	
3·RbSCN[a]	3401, 3100 (sh)	2049

[a] As KBr disc. [b] Neat.

Table 5 The ^{13}C NMR shift changes (positive downfield) on addition of alkali-metal cations (1 equivalent) to the armed aza crown ethers



2



3

		Carbon			
Host	Additive salt	a	b	c	d
2	LiSCN	0.6	−4.4	−2.6	−2.5
	NaSCN	0.6	−3.5	−1.5	−2.4
	KSCN	0.6	−1.7	−1.1	−1.7
	RbSCN	0.5	−1.4	−0.9	−1.3
	CsSCN	0.5	−1.6	−1.0	−1.2
3	LiSCN	0.8	−3.1	−4.1	−2.1
	NaSCN	0.7	−1.4	−3.8	−2.9
	KSCN	0.5	−1.9	−3.5	−2.0
	RbSCN	0.4	−1.4	−2.6	−1.0
	CsSCN	0.4	−1.2	−2.3	−0.6

of mass spectroscopy (20 eV): *m/z* 219 ($M^+ + 1$, 8%). Therefore, we used the residual oil for the next reaction without further purification.

The *N*-(methoxymethyl) derivative (2.7 g, 12 mmol) and 2,6-xylenol (1.5 g, 12 mmol) in dry benzene (5 cm^3) were allowed to react and separated as described above. The residual solid was recrystallized from hexane to give pure compound **3** as white plates, 1.4 g (overall yield from monoaza-12-crown-4, 35%), m.p. 69.5–70.0 °C. IR (KBr disc): 3310 cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.94 (s, 2 H), 3.72–3.67 (m, 8 H), 3.62 (t, 4 H, J = 5.0), 3.52 (s, 2 H), 2.73 (t, 4 H, J = 5.0 Hz) and 2.21 (s, 6 H). Mass spectrum (20 eV): *m/z* 309 ($M^+ + 1$, 100%) (Found: C, 65.8; H, 8.80; N, 4.40. Calc. for $C_{17}H_{27}NO_4$: C, 66.0; H, 8.80; N, 4.55%).

General method for alkali-metal complexes. The host compound (0.01 mmol) in MeCN (1 cm^3) was treated with MSCN, MI or MBr (M = Li, Na, K, Rb or Cs, 0.01 mmol) in MeOH (1 cm^3). After the solvent had vaporized, the crystals were recrystallized using MeCN or MeOH, washed with $CHCl_3$ or MeCN and dried with an Abderhalden's dryer (60 °C, 0.1 Torr, *ca.*, 13.3 Pa). Equant crystals were quantitatively obtained.

1·KI·$3H_2O$ (Found: C, 51.5; H, 6.60; N, 4.15. Calc. for $C_{30}H_{46}N_2O_6$ + KI: C, 51.7; H, 6.65; N, 4.00%): m.p. 169.0–169.5 (decomp.). Half the water molecules in **1**·KI·$3H_2O$ were removed by drying under reduced pressure which destroyed the single crystal. We used a crystal without drying for the X-ray analysis.

1·KSCN·H_2O (Found: C, 57.3; H, 7.25; N, 7.20. Calc. for $C_{30}H_{46}N_2O_6$ + KSCN + H_2O + $0.5CH_3CN$: C, 57.65; H, 7.50; N, 7.35%): m.p. 168.0–168.5 (decomp.). The complex was recrystallized from MeCN. The single crystal used for X-ray analysis and IR spectroscopy was obtained by recrystallization from MeOH. The complex containing MeCN could not be used for X-ray analysis.

2·NaSCN (Found: C, 55.05; H, 7.30; N, 6.60. Calc. for $C_{19}H_{31}NO_5$ + NaSCN: C, 55.3; H, 7.20; N, 6.45%): m.p. 168–168.5 (decomp.).

2·KSCN (Found: C, 53.45; H, 6.70; N, 6.25. Calc. for $C_{19}H_{31}NO_5$ + KSCN: C, 53.3; H, 6.95; N, 6.20%): m.p. 169.0–170.0 (decomp.).

2·RbSCN (Found: C, 48.6; H, 6.10; N, 5.75. Calc. for $C_{19}H_{31}NO_5$ + RbSCN: C, 48.35; H, 6.30; N, 5.65%): m.p. 160.0–161.0 (decomp.).

2·CsSCN (Found: C, 44.25; H, 5.60; N, 5.15. Calc. for $C_{19}H_{31}NO_5$ + CsSCN: C, 44.1; H, 5.75; N, 5.15%): m.p. 149.5–150.5 (decomp.).

3·LiSCN·H_2O (Found: C, 55.15; H, 7.35; N, 7.20. Calc. for $C_{17}H_{27}NO_4$ + LiSCN + H_2O: C, 55.1; H, 7.45; N, 7.15%): m.p. 185.0–185.5 (decomp.).

3·LiBr·$3H_2O$ (Found: C, 47.85; H, 7.45; N, 3.10. Calc. for $C_{17}H_{27}NO_4$ + LiBr + $1.5H_2O$: C, 48.25; H, 7.15; N, 3.30%):

Table 6 Crystal and selected experimental data for compounds **1**–**3** and their alkali-metal complexes*

	1	**1**·KI·3H$_2$O	**1**·KSCN·H$_2$O	**2**·NaSCN	**2**·KSCN	**2**·RbSCN
Formula	$C_{30}H_{50}N_2O_8$	$C_{30}H_{49}KIN_2O_9$	$C_{31}H_{48}KN_3O_7S$	$C_{20}H_{31}N_2NaO_5S$	$C_{20}H_{31}KN_2O_5S$	$C_{20}H_{31}N_2O_5RbS$
M	566.73	747.73	645.89	434.53	450.63	497.00
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic
Space group	*Pbca* (no. 61)	*Pnma* (no. 62)	$P2_12_12_1$ (no. 19)	$P2_1/c$ (no. 14)	$P2_12_12_1$ (no. 19)	$P2_1/n$ (no. 14)
a/Å	19.247(6)	15.173(3)	14.80(2)	8.727(4)	10.250(1)	9.593(1)
b/Å	16.754(2)	21.384(6)	21.04(2)	17.605(7)	25.937(4)	14.950(2)
c/Å	9.628(2)	11.258(3)	11.144(7)	15.110(7)	8.880(3)	16.688(9)
α/°						
β/°				99.27(3)		101.701(9)
γ/°						
U/Å^3	3105(2)	3653(2)	3470(9)	2291(2)	2361(1)	2343.7(5)
Z	4	4	4	4	4	4
D_c/g cm^{-3}	1.212	1.359	1.236	1.260	1.268	1.408
F(000)	1232	1548	1384	928	960	1032
μ(Mo-Kα)/cm^{-1}	0.81	10.26	2.53	1.83	3.36	21.70
Crystal dimensions/mm	0.50 × 0.50 × 0.50	0.60 × 0.50 × 0.13	0.75 × 0.5 × 0.5	0.50 × 0.50 × 0.40	0.37 × 0.25 × 0.13	0.50 × 0.50 × 0.25
No. reflections for unit cell determination (2θ range)/°	25 (22.9–25.0)	25 (24.1–24.9)	25 (23.2–24.9)	25 (20.2–24.6)	25 (20.2–24.5)	25 (22.2–24.4)
Scan width/°	1.31 + 0.30 tan θ	0.79 + 0.30 tan θ	1.21 + 0.30 tan θ	1.68 + 0.30 tan θ	0.68 + 0.30 tan θ	1.00 + 0.30 tan θ
h,k,l Ranges	0–20, 0–23, 0–11	0–18, 0–25, 0–13	0–18, 0–25, 0–13	0–10, 0–21, −18 to 18	0–13, 0–34, 0–12	0–11, 0–18, −20 to 20
No. reflections						
measured	3113	3633	3463	4490	3118	4575
unique (R_{int} =)				4201 (0.161)		4304 (0.071)
used[$I > 3.00\sigma(I)$], N_o	1153	1990	1616	956	1000	1221
R	0.060	0.052	0.061	0.056	0.051	0.052
R'	0.064	0.060	0.063	0.058	0.054	0.056
Goodness of fit	2.06	2.09	2.17	1.61	1.44	1.26
No. parameters, N_p	181	202	388	262	262	262
Maximum shift/error in final cycle	0.01	0.01	0.01	0.01	0.01	0.01
Maximum, minimum peaks in final difference map/e Å^{-3}	0.25, −0.24	0.49, −0.57	0.33, −0.27	0.23, −0.28	0.24, −0.27	0.38, −0.40

Table 6 (*continued*)

	2·CsSCN	**3**	**3**·LiSCN·H_2O	**3**·LiBr·3H_2O	**3**·RbSCN
Formula	$C_{20}H_{31}CsN_2O_5S$	$C_{17}H_{27}NO_4$	$C_{18}H_{29}LiN_2O_5S$	$C_{17}H_{33}BrLiNO_7$	$C_{18}H_{27}N_2O_4RbS$
M	544.44	309.40	392.44	450.30	452.95
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
a/Å	9.864(4)	8.42(1)	10.464(3)	8.73(1)	15.806(9)
b/Å	14.913(6)	28.17(8)	11.486(4)	7.86(1)	9.204(6)
c/Å	16.546(8)	7.34(1)	9.486(2)	32.37(3)	15.947(9)
α/°			109.07(2)		
β/°	102.14(4)	90.6(1)	107.59(2)	95.03(9)	114.05(3)
γ/°			75.52(3)		
U/Å^3	2380(2)	1741(5)	1012.6(6)	2214(5)	2218(4)
Z	4	4	2	4	4
D_c/g cm^{-3}	1.520	1.180	1.287	1.351	1.420
F(000)	1104	672	420	944	936
μ(Mo-Kα)/cm^{-1}	16.57	0.78	1.80	18.69	23.90
Crystal dimensions/mm	0.50 × 0.50 × 0.40	0.63 × 0.63 × 0.25	0.25 × 0.15 × 0.25	0.50 × 0.50 × 0.37	0.75 × 0.75 × 0.25
No. reflections for unit cell determination (2θ range)/°	25 (24.7–25.0)	25 (24.5–25.3)	25 (21–24.5)	16 (24.3–25.0)	25 (24.5–25.0)
Scan width/°	1.57 + 0.30 tan θ	1.05 + 0.30 tan θ	1.52 + 0.30 tan θ	0.94 + 0.30 tan θ	1.47 + 0.30 tan θ
h,k,l Ranges	0–12, 0–18, −20 to 20	0–10, 0–34, −9 to 9	0–12, −14 to 14, −11 to 11	0–10, 0–9, −39 to 39	0–19, 0–11, −19 to 19
No. reflections					
measured	4651	3368	3783	4505	4541
unique (R_{int} =)	4382 (0.081)	3151 (0.016)	3568 (0.080)	4209 (0.045)	3983 (0.062)
used[$I > 3.00\sigma(I)$], N_o	2613	1610	1209	1406	1747
R	0.042	0.043	0.061	0.055	0.053
R'	0.048	0.046	0.065	0.057	0.053
Goodness of fit	1.78	1.64	1.63	1.60	1.84
No. parameters, N_p	262	307	244	244	235
Maximum shift/error in final cycle	0.01	0.01	0.01	0.01	0.01
Maximum, minimum peaks in final difference map/e Å^{-3}	0.86, −0.61	0.13, −0.19	0.27, −0.31	0.36, −0.36	0.57, −0.59

* Details in common: ω–2θ scan; scan range 2θ 0–50 or 0–55°; $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$, $w = 4F_o^2/\sigma^2(F_o^2)$, goodness of fit $[\Sigma w(|F_o| - |F_c|)^2/(N_o - N_p)]^{\frac{1}{2}}$.

m.p. 190.0–193.0 (decomp.). Half the water molecules were removed by drying under reduced pressure which destroyed the single crystal. We used a crystal without drying for the X-ray analysis.

3·RbSCN (Found: C, 47.5; H, 5.90; N, 6.55. Calc. for $C_{17}H_{27}NO_4$ + RbSCN: C, 47.75; H, 6.00; N, 6.20%): m.p. 118.0–120.0 (decomp.).

Crystallography

The crystallographic and experimental data are listed in Table 6. Each of the single crystals was mounted in a glass capillary. All measurements were made at 298 K on a Rigaku AFC5S four-circle diffractometer with graphite-monochromated Mo-Kα radiation (λ 0.710 69 Å) and a 12kW rotating-anode generator. Cell contacts and an orientation matrix for data collection were obtained from a least-squares refinement. The data were collected using the ω–2θ scan technique to an above maximum 2θ value of 55.0 (for **1**·KSCN) and 50.0° (all other compounds). All intensities were corrected for Lorentz and polarization effects. The structure was solved by direct methods (MITHRIL).[20] The non-hydrogen atoms were refined anisotropically. The coordinates of all hydrogen atoms were calculated at ideal positions and were refined. Neutral atom scattering factors were taken from Cromer and Waber.[21] Anomalous dispersion effects were included in F_c;[22] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer and Waber.[21] All calculations were carried out on a Digital VAX Station 3100 with the TEXSAN crystallographic software package.[23]

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/180.

Titration experiments

Titration experiments were carried out at 298 K by addition of 0.5, 1.0 and 2.0 equivalents of alkali-metal thiocyanate to the crown ether (0.10 mmol) in CD_3CN–CD_3OD (5:1, 0.65 cm^3).

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