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Unexpected Structural Diversity in Alkali Metal Azide-Crown Ether Complexes: Syntheses, X-ray Structures, and Quantum-Chemical Calculations

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Abstract: A series of alkali metal azide-crown ether complexes, $[Li([12]\text{crown-}4)(N_3)]$, $[Na([15]\text{crown-}5)(N_3)]$, $[Na([15]\text{crown-}5)(H_2O)_2]N_3$, $[K([18]\text{crown-}6)(N_3)(H_2O)]$, $[Rb([18]\text{crown-}6)(N_3)(H_2O)]$, $[Cs([18]\text{crown-}6)(N_3)]_2$, and $[Cs([18]\text{crown-}6)(N_3)(H_2O)(MeOH)]$, has been synthesised. In most cases, single crystals were obtained, which allowed X-ray crystal structures to be derived. The structures obtained have been compared with molecular structures computed by density functional theory (DFT) calculations. This has allowed the effects of the crystal lattice on the structures to be investigated. Also, a study of the $M{-}N_{terminal}$ metal–azide bond length and charge densities on the metal (M) and terminal nitrogen centre ($N_{terminal}$) in these complexes has allowed the nature of the metal–azide bond to be probed in each case. The bonding in these complexes is believed to be predominantly ionic or ion-dipole in character, with the differences in geometries reflecting the balance between maximising the coordination number of the metal centre and minimising ligand-ligand repulsions. The structures of the crown ether complexes determined in this work show the subtle interplay of such factors. The significant role of hydrogen bonding is also demonstrated, most clearly in the structures of the K and Rb dimers, but also in the chain structure of the hydrated Cs complex.

Keywords: alkali metals • azides • crown ether complexes • density functional calculations • X-ray structures

Introduction

The discovery and characterisation of $[N_5]^+$ has stimulated considerable interest in polynitrogen species.[1] Related species include arylpentazoles, tetrazole azide, and nitrosyl azide (ONNNN).[2–5] The most readily available polynitrogen species are hydrazoic acid, HN_3, and the derived azide anion $[N_3]^-$, which were first reported over 100 years ago[5] but are now the subject of renewed study both in their own right and as possible synthons for larger polynitrogen species. Examples of newly reported azide compounds[6,7] include $[Ti(N_3)_4]$, $[Ti(N_3)_5]^-$, and $[Te(N_3)_6]^{2-}$.

The alkali metal azides MN_3 (M = Li–Cs) are among the more stable known azides, and two (Na and Cs) are commercially available. During the development of the crown ether complexation chemistry of the alkali metals in the 1960s and 1970s, a few examples of crown ether complexes with alkali metal azides were briefly mentioned in the literature, and it was shown that crown ethers could facilitate the phase transfer of alkali metal azides into organic solvents, making for improved reactivities in various organic syntheses.[8] However, the alkali metal azide-crown ether complexes themselves were not examined in any detail. Only one example was structurally characterised, in a charge density study of $[K([18]\text{crown-}6)(N_3)(H_2O)]$, in which interest was focussed on the K-([18]crown-6) interaction.[9] As part of an investigation into polynitrogen species, we report here the synthesis and X-ray crystal structures of a range of such complexes. DFT calculations have been carried out to compute the minimum-energy structures and infrared spectra of these systems. We have recently shown that the simple azides MN_3 (M = K, Rb or Cs) can be vapourised on heating under vacuum and the molecular MN_3 species can be

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characterised by matrix-isolation techniques.[10] Following on from this, the corresponding crown ether complexes have now been synthesised and attempts to vapourise them are described herein.

Experimental Section

General: Infrared spectra were recorded in the range 4000–200 cm^{-1} from samples as Nujol mulls between CsI plates using a Perkin-Elmer 983 G spectrometer. ^{1}H NMR spectra were recorded from samples in CDCl$_3$ solution using a Bruker AC300 spectrometer. Microanalyses were undertaken by the University of Strathclyde microanalytical service. Sodium azide and cesium azide were obtained from Aldrich and were used as received. Lithium azide monohydrate was prepared by the method of Hofman-Bang[11] by metathesis of lithium sulfate and sodium azide in aqueous ethanol, and was recrystallised twice from hot ethanol. Potassium azide was prepared from nBuNO$_2$ and N$_2$H$_4$·H$_2$O in alcoholic KOH solution[12] and recrystallised by precipitation with ethanol from a saturated aqueous solution. RbN$_3$ was similarly prepared by using RbOH. The crown ethers [12]crown-4, [15]crown-5, and [18]crown-6 were purchased from Aldrich and were used as received.

***CAUTION**: Although no problems were experienced in this work, azide complexes may be unpredictably explosive and HN$_3$, which is liberated in acid solution, is extremely toxic and highly explosive when concentrated.*

[Li([12]crown-4)(N$_3$)]: Lithium azide hydrate (0.09 g, 1.3 mmol) and [12]crown-4 (0.23 g, 1.3 mmol) were dissolved in boiling methanol (25 mL). The solution was concentrated to a volume of about 5 mL, diethyl ether (10 mL) was added, and the solution was refrigerated. Colourless crystals separated after about 2 d, which were filtered off and dried in vacuo. Yield 0.19 g (65 %). Elemental analysis calcd (%) for C$_8$H$_{16}$LiN$_3$O$_4$ (227.2): C 42.7, H 7.3, N 18.7; found: C 42.5, H 7.3, N 18.4; ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta = 3.6$ ppm (s); IR (Nujol): $\tilde{\nu} =$ 2043 (s, br), 1350 (m), 1291 (m), 1236 (w), 1134 (m), 1083 (s), 1011 (m), 906 (m), 858 (w), 735 (s), 623 (m), 480 cm^{-1} (w).

[Na([15]crown-5)(N$_3$)]: Sodium azide (0.12 g, 2.0 mmol) and [15]crown-5 (0.44 g, 2.0 mmol) were dissolved in anhydrous methanol (20 mL) and the solution was heated to reflux. It was then cooled to room temperature and concentrated to a volume of 5 mL on a rotary evaporator. Dry diethyl ether was added dropwise until turbidity appeared (ca. 5 mL) and then the solution was refrigerated overnight. The white solid that separated was filtered off, rinsed with diethyl ether (2 mL), and dried in vacuo. Yield 0.42 g (75 %). Elemental analysis calcd (%) for C$_{10}$H$_{20}$N$_3$NaO$_5$ (285.3): C 42.1, H 7.2, N 15.2; found: C 42.2, H 7.2, N 15.2; ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta = 3.65$ ppm (s); IR (Nujol): $\tilde{\nu} = 3372$ (sh) (combination band?), 2035 (vs, br), 1350 (m), 1293 (m), 1277 (m), 1247 (m), 1115 (vs, br), 1090 (vs, br), 944 (s), 865 (m), 842 (w), 826 (m), 625 (m), 544 (m), 526 cm^{-1} (m).

[Na([15]crown-5)(H$_2$O)$_2$]N$_3$: The preparation was carried out as above, but the solvent was allowed to evaporate from the concentrated methanolic solution in air until a few very small crystals formed, and then the solution was refrigerated for two weeks. The small clear crystals that separated were filtered off and dried in vacuo. Yield 25 %. Elemental analysis calcd (%) for C$_{10}$H$_{24}$N$_3$NaO$_7$ (321.3): C 37.4, H 7.4, N 13.1; found: C 36.3, H 6.9, N 13.3; ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta = 3.6$ (s, 10 H; CH$_2$), 1.8 ppm (s, 2 H; H$_2$O); IR (Nujol): $\tilde{\nu} = 3420$ (m), 2013 (s, br), 1630 (m), 1350 (m), 1293 (m), 1272 (w), 1247 (m), 1115 (vs, br), 1090 (vs, br), 944 (s), 865 (m), 826 (m), 642 (m), 544 cm^{-1} (m).

[K([18]crown-6)(N$_3$)(H$_2$O)]: This complex was similarly prepared from KN$_3$ (0.16 g, 2.0 mmol) and [18]crown-6 (0.52 g, 2.0 mmol) in methanol/diethyl ether. The white solid that separated after storage in a refrigerator overnight was dried in vacuo. Yield 0.46 g (68 %). Further refrigeration of the filtrate gave colourless crystals (ca. 0.02 g). Elemental analysis calcd (%) for C$_{12}$H$_{26}$KN$_3$O$_7$ (363.5): C 39.6, H 7.1, N 11.5; found: C 38.8, H 7.6, N 10.8; ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta = 3.80$ (s, 12 H; CH$_2$), 2.6 ppm (s, 1 H; H$_2$O); IR (Nujol): $\tilde{\nu} = 3420$ (br), 2011 (vs, br), 1619 (m), 1350 (m), 1295 (w), 1240 (m), 1110 (sh), 1101 (vs, br), 1090 (sh), 962 (s), 836 (m), 634 (w), 540 (m), 528 cm^{-1} (m).

[Rb([18]crown-6)(N$_3$)(H$_2$O)]: This complex was prepared following a method analogous to that used for the potassium salt; it was obtained as a white powder in 56 % yield. Elemental analysis calcd (%) for C$_{12}$H$_{26}$N$_3$O$_7$Rb (409.8): C 35.1, H 6.9, N 10.2; found: C 35.25, H 6.6, N 10.2; ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta = 3.75$ (s, 12 H; CH$_2$), 2.6 ppm (s, 1 H; H$_2$O); IR (Nujol): $\tilde{\nu} = 3424$ (br), 2023 (vs, br), 1662 (m), 1352 (m), 1295 (w), 1249 (m), 1115 (sh), 1101 (vs, br), 1090 (sh), 957 (s), 835 (m), 634 (w), 629 (w), 540 cm^{-1} (m).

[Cs([18]crown-6)(N$_3$)]$_2$: CsN$_3$ (0.35 g, 2.0 mmol) was dissolved in anhydrous methanol (10 mL) and a solution of [18]crown-6 (0.50 g, 2.0 mmol) in methanol (5 mL) was added. The mixture was heated to boiling, then cooled and concentrated under reduced pressure to a volume of about 5 mL. Diethyl ether (10 mL) was slowly added to the stirred solution, resulting in the deposition of a white precipitate; this was filtered off and dried in vacuo. Yield 0.55 g (65 %). Elemental analysis calcd (%) for C$_{12}$H$_{24}$CsN$_3$O$_6$ (439.2): C 32.8, H 5.5, N 9.6; found: C 32.9, H 5.6, N 8.9; ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta = 3.55$ ppm (s, CH$_2$); IR (Nujol): $\tilde{\nu} = 3283$ (sh) (combination band?), 1997 (vs), 1352 (m), 1286 (m), 1250 (m), 1120 (sh), 1101 (vs, br), 955 (s), 835 (m), 631 (w), 527 cm^{-1} (m).

[Cs([18]crown-6)(N$_3$)(H$_2$O)(MeOH)]: This complex was prepared following a similar method to that used for the anhydrous complex, but was isolated by allowing the solvent from the concentrated methanolic solution to slowly evaporate in air. White crystals were obtained. Yield 46 %. Elemental analysis calcd (%) for C$_{13}$H$_{30}$CsN$_3$O$_8$ (489.3): C 31.9, H 6.2, N 8.6; found: C 31.0, H 5.8, N 8.3; ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta = 3.55$ (s, 24 H; CH$_2$), 3.4 (s, 3 H; CH$_3$), 2.3 ppm (s, 2 H; H$_2$O); IR (Nujol): $\tilde{\nu} =$ 3420 (vs, br), 2011 (vs), 1636 (m), 1350 (s), 1282 (m), 1251 (m), 1105 (s), 1021 (m), 957 (s), 834 (m), 639 (w), 523 cm^{-1} (w).

X-ray crystallography: Crystals of [Li([12]crown-4)(N$_3$)] were obtained when the above-mentioned reaction mixture was kept in a freezer. On warming to room temperature the crystals dissolved but, by working quickly, it was possible to mount crystals for X-ray examination. The sodium compound was obtained as very small crystals from a reaction mixture stored in a freezer for several weeks. Crystals of the Rb and Cs compounds were obtained by vapour-phase diffusion of diethyl ether into concentrated solutions of the compounds in methanol. The two Cs compounds were obtained from different tubes containing methanolic solutions enclosed in the same sealed container.

Brief details of the crystal data and refinement are given in Table 1. Data collections were carried out using a Bruker-Nonius Kappa CCD diffractometer with graphite-monochromated Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) and with crystals held at 120 K in a gas stream. Structure solution and refinement was routine[13–15] except, as described below, with H atoms of the crown introduced in calculated positions. The eight H atoms of the water molecules were identified in the electron-density map of the Na compound and were introduced into the model but not refined. In this case, there was some disorder in the crown ring, which was modelled at C5−C6 with two conformations requiring the use of DFIX instructions on the C−C and C−O distances. For the Rb compound, the H atoms of the water (O7) were refined. For [Cs([18]crown-6)(N$_3$)(H$_2$O)0.75-(MeOH)], the H atoms on the water O (O13, O14) were not refined. The MeOH groups were found to be disordered and one showed much larger isotropic atomic displacement parameter (adp) values, which were compensated for by reducing the occupation factor for the C26 and O16 atoms to 0.5. The four largest peaks in the difference Fourier map were close ($<$1.2 Å) to C and O of the methanol solvates.

CCDC-272473 (Li), CCDC-272474 (Na), CCDC-272475 (Rb), CCDC-272476 (Cs anhydrous), and CCDC-272477 (Cs monohydrate methanol solvate) contain supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational details: All calculations were performed at the density functional theory (DFT) level, using the BP86 functional[16] along with the resolution of the identity approximation (RI-DFT[17]). The basis sets selected were as follows: the triple valence plus polarisation basis set 6–311 G (d,p) was used for H, C, N, O atoms in all calculations, and for Li

Table 1. Crystal data and structure refinement details.[a]

Compound	[Li([12]crown-4)(N_3)]	[Rb([18]crown-6)(N_3)(H_2O)]	[Cs([18]crown-6)(N_3)]$_2$	[Cs([18]crown-6)(N_3)(H_2O)·0.75(MeOH)]	[Na([15]crown-5)(H_2O)$_2$]N_3
formula	$C_8H_{16}LiN_3O_4$	$C_{12}H_{26}N_3O_7Rb$	$C_{24}H_{48}Cs_2N_6O_{12}$	$C_{25.5}H_{58}Cs_2N_6O_{15.5}$	$C_{20}H_{48}N_6Na_2O_{14}$
M_r	225.18	409.83	878.50	962.60	642.62
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	$C2/c$ (no. 15)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)
a [Å]	11.260(4)	9.948(1)	11.927(2)	8.340(1)	9.936(2)
b [Å]	8.883(3)	9.673(2)	8.286(2)	20.338(3)	12.469(2)
c [Å]	11.368(4)	18.805(2)	17.250(3)	24.618(2)	13.047(3)
α [°]	90.0	90.0	90.0	90.0	89.19(2)
β [°]	90.01(1)	92.42(1)	93.674(8)	90.838(8)	80.50(2)
γ [°]	90.0	90.0	90.0	90.0	89.60(2)
U [Å^3]	1137.1(7)	1808.0(5)	1701.3(4)	4175.4(8)	1594.0(6)
Z	4	4	2	4	2
μ [mm^{-1}]	0.103	2.775	2.207	1.812	0.134
F(000)	480	848	880	1948	688
total no. of obsns. (R_{int})	5340 (0.058)	15199 (0.061)	25214 (0.060)	47691 (0.044)	19585 (0.039)
unique obsns.	1310	4122	3897	9487	7207
min., max. transmission	0.683, 1.000	0.864, 1.000	0.788, 1.000	0.781, 1.000	0.845, 1.000
no. of parameters, restraints	100, 0	215, 0	200, 0	435, 2	379, 9
goodness-of-fit on F^2	1.036	1.060	1.059	1.069	1.044
resid. electron density [e Å^{-3}]	−0.23 to +0.34	−0.56 to +0.48	−0.82 to +0.88	−1.37 to +2.31	−0.72 to +0.90
$R1$, $wR2$ ($I > 2\sigma(I)$)[b]	0.045, 0.104	0.033, 0.063	0.030, 0.054	0.036, 0.093	0.064, 0.162
$R1$, w$R2$ (all data)	0.080, 0.121	0.064, 0.071	0.047, 0.059	0.049, 0.101	0.108, 0.188

[a] Common items: temperature = 120 K; $\lambda(\mathrm{Mo}_{K\alpha}) = 0.71073$ Å; $\theta(\max) = 27.5°$. [b] $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma wF_o^4]^{1/2}$.

and Na atoms in their crown ether complexes. The Stuttgart '97 effective core potentials (ECPs)[18] were used for K, Rb, and Cs[19] atoms; these are relativistic small core quality ECPs that describe 10, 28, and 46 core electrons for potassium, rubidium, and cesium, respectively, and use a basis set contraction scheme (7s6p)/[5s4p] for the valence electrons. The auxiliary basis set for the RI-DFT calculations was generated during the run time. The molecular structure of each complex was optimised by checking the Hessian matrix. Vibrational frequencies and zero-point energies were estimated by using the harmonic approximation. All calculations were performed by using the Gaussian 03 package.[20]

Results and Discussion

The aim of this work was to obtain examples of neutral complexes of the type [M(crown)N_3] with the azide coordinated to the alkali metal. Hence, we used the crown ether of optimum ring size for each metal[21] and, to simplify the electronic structure calculations, the simplest crown ligands, that is to say [12]crown-4 (Li), [15]crown-5 (Na) and [18]crown-6 (K, Rb, Cs). A few other combinations with mismatched cavity sizes were examined, including LiN_3-([15]crown-5) and RbN_3-([15]crown-5), but these failed to give crystalline products. The general synthesis method was to react the crown ether with the appropriate MN_3 in anhydrous methanol and then crystallise the product by addition of anhydrous diethyl ether. The complexes formed were identified by a combination of analysis, IR and ^{1}H NMR spectroscopy. They were found to be extremely soluble in alcohols, moderately so in acetone and chlorinated hydrocarbons, and, like all alkali metal coordination complexes, undergo rapid ligand exchange in solution, as evidenced by the singlet ^{1}H NMR resonance for the crown methylene protons being slightly shifted to higher frequency compared to that of the free crown. The linear symmetrical azide ion has three vibrations: the antisymmetric stretch ν_3 at about 2100 cm^{-1}, the symmetric stretch ν_1 at around 1300 cm^{-1}, and the bend ν_2 at around 630–660 cm^{-1}, with only ν_3 and ν_2 being IR-active,[5,22] although in some cases combination bands appear in the spectra, allowing ν_1 to be estimated. The IR spectra of the crown ether complexes showed very strong features at around 2000–2100 cm^{-1} and weak features in the region 650–620 cm^{-1}; generally, the band derived from ν_1 (N_3) was not observed; it either remained of very low intensity or was obscured by the intense crown ether vibrations in this region. The pattern of azide vibrational frequencies showed differences from those of the parent MN_3[1], suggesting significant interactions of the azide in most of the crown ether complexes, but since the coordination modes were unclear from the IR spectra, crystal structures of the complexes were obtained, which revealed an unexpected diversity of M–N_3 linkages. It is convenient to discuss the complexes in turn.

[Li([12]crown-4)(N_3)]: This was the only species isolated from the LiN_3/[12]crown-4 system. The structure consists of discrete molecules with crystallographic two-fold symmetry (see Figure 1a and Table 2). The atoms Li1, N1, N2, and N3 are necessarily colinear and the geometry around the five-

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[1] Literature values for the azide vibrations in alkali metal salts are surprisingly variable.[5,21] Our $\tilde{\nu}$ values recorded from samples in Nujol mulls are: $LiN_3{\cdot}H_2O$ 2065 (s), 630 (w); NaN_3 2142 (vbr), 639 (m); KN_3 2048 (vbr), 648 (m); RbN_3 2007 (vbr), 641 (m); CsN_3 2011 (vs), 636 cm^{-1} (m).

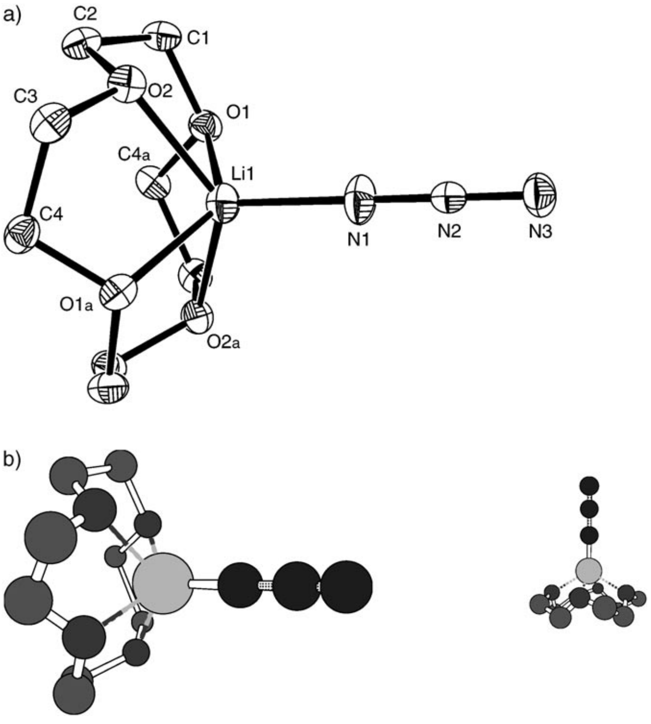

Figure 1. a) The crystal structure of [Li([12]crown-4)(N_3)] showing the atom-labelling scheme. The molecule has twofold symmetry along the Li–N1 bond. Hydrogen atoms have been omitted for clarity and the ellipsoids are drawn at the 50% probability level. Symmetry operation: *a* = 1–*x*, *y*, 3/2–*z*. b) Calculated (DFT-BP86) structure of [Li([12]crown-4)(N_3)].

coordinate Li1 is to a good approximation a square pyramid with Li1 0.858(4) Å out of the plane of the four O atoms of the crown. There are few structurally characterised lithium azide complexes and in the one example[23] with a μ_4-bonded N_3, the shortest N–Li distance (1.96(1) Å) is similar to that in the present compound (1.913(4) Å). Groth[24,25] has reported two thiocyanate lithium complexes with crown ether ligands containing four O atoms. In both cases, square-pyramidal lithium is found with axial N-bonded thiocyanate and in the [12]crown-4 complex[25] the Li–N (1.96(1) Å) distance and Li–O (2.05(1)–2.14(1) Å) distances are comparable to the values reported here. The Li–N distance is considerably shorter than the sum of the van der Waals radii (ca. 3.5 Å) and the description of the complex as containing coordinated azide is unequivocal.

The experimental bond lengths determined from the crystal structure and the bond lengths computed at the DFT level using a BP86 functional are compared in Table 2, and the computed minimum-energy structure is shown in Figure 1b. As can be seen from Table 2, the agreement between the experimental and calculated geometrical parameters is good. The Li1–N1 distance is underestimated by about 5%, while the Li1–O1 and Li1–O2 distances are overestimated by about 6%. The experimental results indicate that the two N–N bonds are virtually equivalent, whereas in the calculated geometry the N1–N2 bond is slightly longer than the N2–N3 bond, by about 2%. Also, the calculated C–H bond lengths are longer than the experimental bond lengths. The computed and experimental IR spectra obtained show good agreement, with the most intense absorption computed at 2154 cm^{-1} (N_3 antisymmetric stretch) and observed at 2043 cm^{-1}.

Table 2. Comparison of the more important experimental and computed (BP86-DFT) bond lengths [Å] and angles [°] for the complex [Li([12]-crown-4)(N_3)].[a]

	Experimental	Calculated
Li1–N1	1.913(4)	1.819
Li1–O1	2.114(2)	2.234
Li1–O2	2.123(2)	2.256
N1–N2	1.179(3)	1.204
N2–N3	1.172(3)	1.173
O1–C1	1.437(2)	1.432
O2–C3	1.440(2)	1.432
O2–C2	1.440(2)	1.436
C1–C2	1.506(2)	1.527
C3–C4	1.505(2)	1.527
C1–H1A	0.97(2)	1.108
C1–H1B	0.98(2)	1.109
N1-Li1-O1a	113.8(1)	121.3
N1-Li1-O1	113.8(1)	118.8
N1-Li1-O2a	114.0(1)	118.2
N1-Li1-O2	114.0(1)	121.5
O1a-Li1-O1	132.5(2)	119.8
O1a-Li1-O2a	80.9(1)	75.5
O1-Li1-O2a	80.2(1)	75.4
O1a-Li1-O2	80.2(1)	75.4
O1-Li1-O2	80.9(1)	75.7
O2a-Li1-O2	132.0(2)	120.3
N2-N1-Li1	180.0	179.6
N3-N2-N1	180.0	179.9
C1-O1-C4a	114.0(1)	115.3
C1-O1-Li1	107.7(1)	108.9
C4a-O1-Li1	108.2(1)	112.5
C3-O2-C2	113.4(1)	115.4
C3-O2-Li1	109.1(1)	112.5
C2-O2-Li1	108.5(1)	109.0
O1-C1-C2	111.0(1)	106.2

[a] Symmetry operation: a = 1–*x*, *y*, $^3/_2$–*z*.

[Na([15]crown-5)(N_3)] and [Na([15]crown-5)(H_2O)$_2$](N_3): A similar synthetic route to that used for the lithium compound above, but using NaN_3 and [15]crown-5, reproducibly gave [Na([15]crown-5)(N_3)] as a white powder, but repeated attempts to obtain this complex in a crystalline form for an X-ray study failed. Spectroscopically, the complex seems analogous to [Li([12]crown-4)(N_3)], with IR-active azide vibrations at 2035 (vs, br) and 625 cm^{-1} (w) and no evidence of the presence of water in the IR spectrum. A structure with coordinated azide and a six-coordinate Na centre with five oxygen atoms and one nitrogen atom coordinated to the metal centre seems likely, and is supported by the DFT calculations. However, if the solvent of the reaction mixture was allowed to evaporate in air, a crystalline species was produced, the IR spectrum of which showed the presence of water and featured azide vibrations at 2013 (vs, br) and 642 cm^{-1} (m). This structure does not contain a coordinated azide anion, the sodium coordination being made up of the five O atoms of the crown and either two (Na1) or one

(Na2) bonded water molecules giving seven- and six-coordinate Na atoms, respectively (Figure 2 and Table 3). All of the hydrogen atoms of the water ligands were located in the structure, and there is extensive hydrogen-bonding mainly of the type O−H···N (O···N 2.840–2.943 Å). Similar hydrogen-bonded networks have been studied in some detail in sodium [18]crown-6 complexes with a variety of anions.[26]

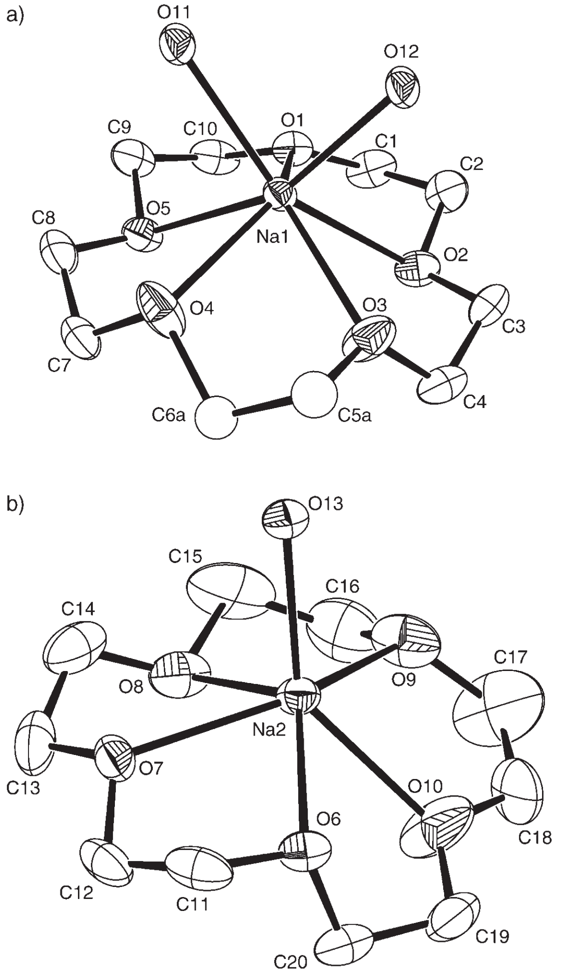

Figure 2. The crystal structure of [Na([15]crown-5)$(H_2O)_2$]N_3 showing the environment around the two distinct sodium atoms Na1 (a) and Na2 (b) in the unit cell. There is some disorder in the crown residues, which is most pronounced at atoms C5/C6. Only C5a and C6a are shown in the diagram, with C5b/C6b omitted. Hydrogen atoms have been omitted for clarity and the ellipsoids are drawn at the 50 % probability level.

Table 3. Selected bond lengths [Å] and angles [°] for [Na([15]crown-5)$(H_2O)_2$]N_3.

Na1−O1	2.475(2)	Na2−O6	2.440(2)
Na1−O2	2.603(2)	Na2−O7	2.402(2)
Na1−O3	2.516(2)	Na2−O8	2.374(2)
Na1−O4	2.460(2)	Na2−O9	2.453(2)
Na1−O5	2.468(2)	Na2−O10	2.378(3)
Na1−O11	2.514(2)	Na2−O13	2.293(2)
Na1−O12	2.318(2)		
N1−N2	1.171(3)	N2−N3	1.175(3)
N4−N5	1.179(3)	N5−N6	1.199(3)
O1-Na1-O2	64.18(7)	O6-Na2-O7	69.49(8)
O2-Na1-O3	65.36(7)	O7-Na2-O8	69.46(8)
O3-Na1-O4	67.03(8)	O8-Na2-O9	69.91(9)
O4-Na1-O5	67.00(7)	O9-Na2-O10	66.89(9)
O5-Na1-O1	65.94(7)	O10-Na2-O6	68.04(8)
N1-N2-N3	179.0(3)	N4-N5-N6	179.8(3)

DFT calculations were only performed on the [Na([15]crown-5)(N_3)] complex. The computed BP86/RIDFT structure is similar to that of the [Li([12]crown-4)(N_3)] complex in Figure 1. No comparison with experimental values is possible because no crystals of [Na([15]crown-5)(N_3)] were obtained. In the infrared spectrum computed at the BP86/RIDFT level, the most intense absorptions occur at 2119 cm^{-1} (N_3 antisymmetric stretch) and 1327 cm^{-1} (N_3 stretching) (experimental values 2035 and 1350 cm^{-1}). The vibrational mode between Na and N_3 is computed at 277 cm^{-1}, and azide bending vibrations, computed at 608 and 610 cm^{-1}, are calculated to have very low intensity. Comparison of the experimental spectrum with the BP86/RIDFT computed spectrum shows good agreement.

[K([18]crown-6)(N_3)(H_2O)] and [Rb([18]crown-6)(N_3)(H_2O)]: These two complexes have similar IR spectra and were the only species isolated from the respective syntheses. The crystal structure of [K([18]crown-6)(N_3)(H_2O)] has been determined previously[9] so only the structure of [Rb([18]crown-6)(N_3)(H_2O)] was determined in this work. The structure of the [K([18]crown-6)(N_3)(H_2O)] complex taken from reference [9] is shown in Figure 3a, where it is compared with the computed DFT structures obtained in this work for the monomer (Figure 3b) and the dimer (Figure 3c). Comparison of the computed structures shown in Figure 3b and Figure 3c shows that on going from the monomer to the dimer a flattening of the N_3 unit occurs, which is consistent with the structure found experimentally. The computed dimer structure and the experimental structure are very similar, with the experimental structure being of higher symmetry; the K−$N_{terminal}$ bonds are equal for the K–N_3 groups in the experimental structure but not in the computed structure. These K−$N_{terminal}$ bond lengths are computed as 2.784 and 2.905 Å (the experimental value from ref. [9] is 2.896 Å (×2)). Experimentally, the K−O_{ring} distances are in the range 2.78–2.97 Å, and this is also the case in the computed dimer structure. The K−O_{water} distances are computed as 3.403 and 3.773 Å, and are thus longer than the experimental value of 2.880 Å (×2). This, as well as the higher symmetry of the experimental structure, is probably the result of packing in the lattice.

The N_3 asymmetric stretching modes for [K([18]crown-6)(N_3)(H_2O)$]_2$ are calculated at 2081 and 2095 cm^{-1}, with the 2081 cm^{-1} absorption calculated to have ten times the intensity of the 2095 cm^{-1} absorption (experimental value 2011 cm^{-1}).

The structure of the [Rb([18]crown-6)(N_3)(H_2O)] complex is also dimeric. It consists of a rubidium atom coordinated by the six O atoms of the crown, N1 of the azide, and O7 of a water molecule. There is an hydrogen bond between O7 and N1 (see Figure 4a) and the Rb atom is out of the plane defined by the six O atoms of the crown by 0.96 Å. In addi-

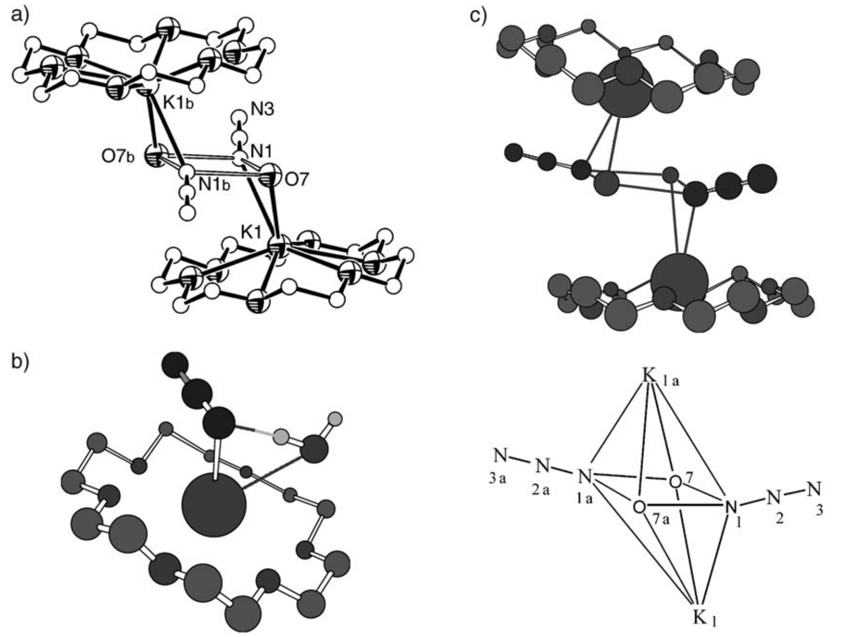

Figure 3. a) The crystal structure obtained for [K([18]crown-6)(N_3)(H_2O)] from reference [9]; coordinates and atom-labelling scheme taken from the CSD (Refcode: LIBKAI). b) Computed (DFT-BP86) structure obtained in this work for [K([18]crown-6)(N_3)(H_2O)]. c) Computed (DFT-BP86) structure obtained in this work for [K([18]crown-6)(N_3)(H_2O)]$_2$. (The H atoms have been omitted from the computed structures). Comparison of the computed (c) and experimental (a) structures shows them to be very similar.

tion, there are interactions between two of these residues to form a centrosymmetric dimeric unit with additional hydrogen-bonding between O7 and N1 (see Figure 4b and Table 4). The N1a–Rb1 and O7a–Rb1 distances are about 0.5 Å longer than the corresponding N1–Rb1 and O7–Rb1 distances and this would give a ten-coordinate Rb atom were these atoms to be counted as within the coordination sphere. Both of the H atoms of O7 are involved in hydrogen-bonding, and the O7–N1 and O7–N1a distances are equal (2.89 Å). The shorter Rb–N distance (Rb1–N1, 3.020(2) Å) is comparable to those found in an Rb/Cr azide derivative[27] (3.010(8)–3.136(5) Å). The complex [Rb([18]crown-6)(NCS)]$_2$ has also been reported,[28,29] which has six Rb–O distances (2.929–3.146 Å), similar to those in the present compound, and rather symmetrical bridging thiocyanate Rb–N distances (3.314, 3.226 Å), which do not show the disparity in bond lengths observed here. The structure of [Rb([18]crown-6)(N_3)(H_2O)] is very similar to the known structure of [K([18]crown-6)(N_3)(H_2O)],[9] but the "dimer unit" is more distorted in the potassium complex (Figure 3a). The central hydrogen-bonded unit is very similar in each, suggesting that the "dominant" factor is the O–H···N interactions and that these assemble the dimers, with the very long M···N/O distances being a consequence of this rather than the O–H···N interactions significantly contributing to M···N/O binding.

For [Rb([18]crown-6)(N_3)(H_2O)]$_2$, the computed structure is very similar to that computed for [K([18]crown-6)(N_3)(H_2O)]$_2$ (see Figure 4c) and is of lower symmetry than the experimental structure. The Rb–$N_{terminal}$ bond lengths for the Rb–N_3 groups are computed as 3.030 and 3.161 Å compared with the experimental value of 3.020 Å (×2). Experimentally, the Rb–O_{ring} distances are in the range 2.87–3.12 Å, and this is also the case in the computed [Rb([18]crown-6)(N_3)(H_2O)]$_2$ structure. The Rb–O_{water} distances are computed as 3.175 and 3.364 Å, compared to the experimental value of 3.210 Å (×2). The N_3 asymmetric stretching modes for [Rb([18]crown-6)(N_3)(H_2O)]$_2$ are calculated as 2077 and 2091 cm^{-1}, with the 2077 cm^{-1} absorption being calculated to have ten times the intensity of the 2091 cm^{-1} absorption (the experimental value is 2023 cm^{-1}).

[Cs([18]crown-6)(N_3)]$_2$ and [Cs([18]crown-6)(N_3)(H_2O)·0.75(MeOH)]: In the case of cesium, it was apparent that two different compounds formed under quite similar reaction conditions. It was established that an anhydrous compound of stoichiometry [Cs([18]crown-6)(N_3)] was precipitated from an anhydrous methanolic solution on addition of anhydrous diethyl ether, and that a complex of composition [Cs([18]crown-6)(N_3)(H_2O)(MeOH)] was obtained by allowing the solvent to evaporate from the methanolic solution of the complex in air until crystallisation occurred. The two compounds are distinguished by quite different azide vibrations in their IR spectra (see the Experimental Section), although again the structural unit present cannot be deduced from the spectra. The crystal structure of the anhydrous complex shows it to be a symmetrical dimer, [Cs([18]crown-6)(N_3)]$_2$, with bridging azide ligands (see Figure 5a and Table 5). Each cesium is eight-coordinate, this coordination sphere being formed by the six O atoms of the crown and two N atoms of different azides. The centrosymmetric dimer has symmetrical bridging azide bonds (Cs1–N1 3.238(3), Cs1–N1a 3.226(3) Å), in sharp contrast to the rubidium compound above, and the Cs atom lies 1.43 Å out of the plane of the six crown O atoms. Comparable compounds are rare: a Cs–N distance (3.198(3) Å) in a μ-bridging azide compares well,[30] and a dimer with bridging N-bonded NCS ligands and dibenzo crown moieties[31] has Cs–N distances (3.19(1), 3.25(1) Å) and Cs–O distances (3.07–3.34 Å) similar to those in the present compound. The crystal structure of the hydrated compound shows the stoichiometry of the crystal examined to be [Cs([18]crown-6)(N_3)(H_2O)·0.75(MeOH)]. This compound has a chain structure with μ_2-azide ligands linking the Cs atoms (note also that the azide

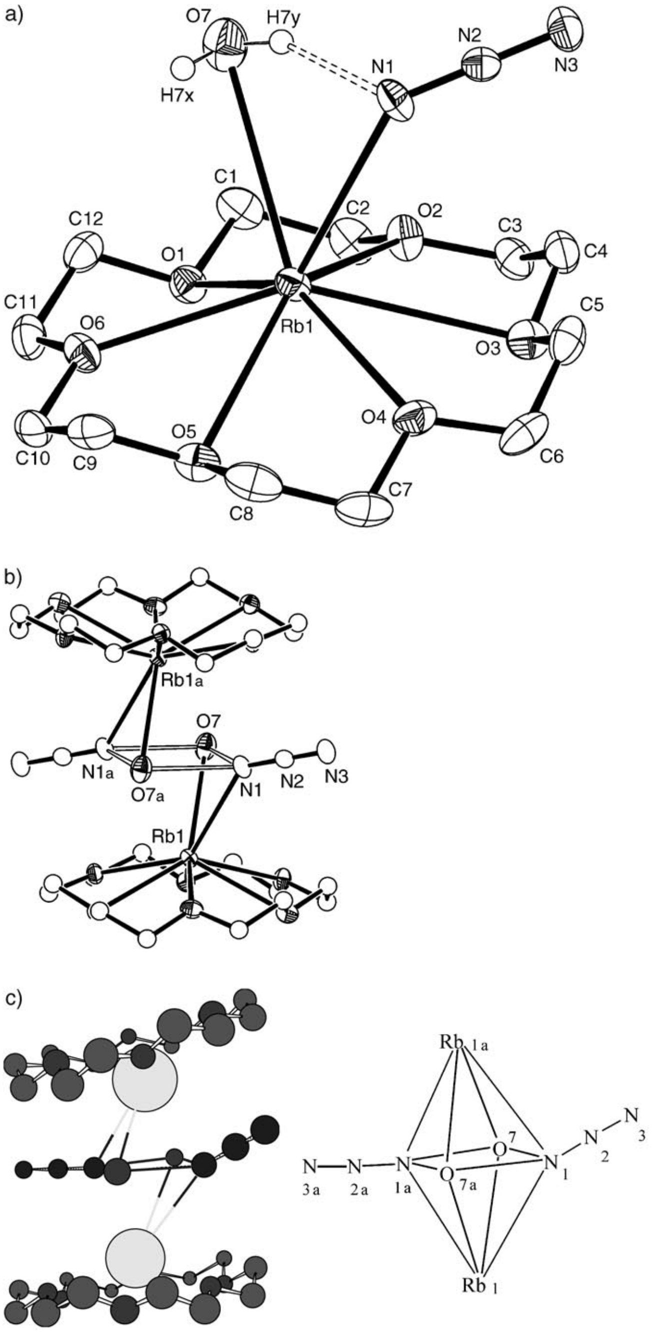

Figure 4. The crystal structure of $[Rb([18]crown\text{-}6)(N_3)(H_2O)]$. a) Representation showing the ellipsoids and the atom-labelling scheme. The O7···N1 H-bond is shown dotted. b) The dimer molecule showing the bonds linking the two Rb1 residues (open bonds). All but two H atoms have been omitted for clarity and the ellipsoids are drawn at the 50% probability level. Symmetry operation: $a = -x, 1-y, -z$. c) Computed (DFT-BP86) structure of $[Rb([18]crown\text{-}6)(N_3)(H_2O)]_2$. (The H atoms have been omitted from the computed structure). Comparison of the computed (c) and experimental structures (b) shows them to be very similar.

Table 4. Selected bond lengths [Å] and angles [°] for $[Rb([18]crown\text{-}6)(N_3)(H_2O)]_2$.[a]

Rb1−O1	3.023(2)	Rb1−O4	2.920(2)
Rb1−O2	2.911(2)	Rb1−O5	2.962(2)
Rb1−O3	3.119(2)	Rb1−O6	2.869(2)
Rb1−N1	3.020(2)	Rb1−O7	3.210(2)
Rb1−N1a	3.558(2)	Rb1−O7a	3.670(2)
N1−N2	1.190(3)	N2−N3	1.166(3)
O7···N1	2.888(3)	O7···N1a	2.891(3)
O−C	1.421(3)–1.436(3)	C−C	1.485(4)–1.501(4)
O1-Rb1-O2	57.30(5)	O4-Rb1-O5	58.04(5)
O2-Rb1-O3	56.37(5)	O5-Rb1-O6	56.77(5)
O3-Rb1-O4	56.37(5)	O6-Rb1-O1	56.30(4)
N1-Rb1-O7	55.14(6)	N1-N2-N3	179.1(3)
N1···O7···N1a	83.13(8)	O7···N1···O7a	96.87(8)
N2-N1···O7	127.1(2)	N2-N1-Rb1	134.7(2)
Rb1-O-C	101.3(2)–122.6(1)	C-O-C	110.8(2)–113.5(2)

[a] Symmetry operation: $a = -x, 1-y, -z$.

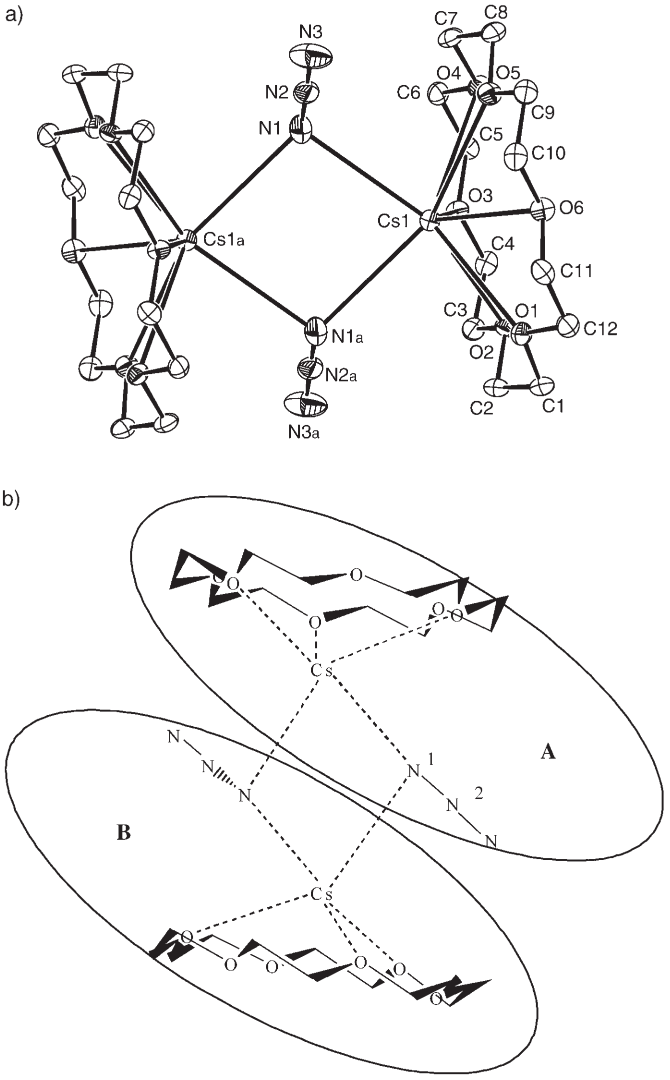

Figure 5. a) The crystal structure of $[Cs([18]crown\text{-}6)(N_3)]_2$ showing the atom-labelling scheme. The molecule has a centre of symmetry. H atoms have been omitted for clarity and the ellipsoids are drawn at the 50% probability level. Symmetry operation: $a = 2-x, 1-y, -z$. b) Computed (DFT-BP86) structure of $[Cs([18]crown\text{-}6)(N_3)]_2$.

bridges here are Cs-N-N-N-Cs compared with Cs-N(N_2)-Cs in the anhydrous dimer). There are three crystallographically distinct azide groups in this complex (Figure 6), two of which are centrosymmetric (at N4 and N6). The environ-

Table 5. Selected bond lengths [Å] and angles [°] for $[Cs([18]crown\text{-}6)(N_3)]_2$. (Computed values at the BP86 DFT level are given in parentheses).[a]

Cs1–O1	3.106(2) (3.239)	Cs1–O4	3.260(2) (3.350)
Cs1–O2	3.156(2) (3.367)	Cs1–O5	3.063(2) (3.270)
Cs1–O3	3.033(2) (3.150)	Cs1–O6	3.282(2) (3.408)
Cs1–N1	3.238(3) (3.197)	Cs1–N1a	3.226(3) (3.318)
N1–N2	1.183(4) (1.201)	N2–N3	1.179(4) (1.189)
O–C	1.421(3)–1.434(3) (1.424–1.436)		
C–C	1.496(4)–1.514(4) (1.515–1.518)		
O1-Cs1-O2	53.76(5) (52.82)	O4-Cs1-O5	53.16(5) (50.64)
O2-Cs1-O3	54.08(5) (52.45)	O5-Cs1-O6	52.06(5) (52.23)
O3-Cs1-O4	54.38(5) (50.64)	O6-Cs1-O1	52.69(5) (52.88)
Cs1-N1-Cs1a	98.41(8) (80.0)	N1-N2-N3	178.8(3) (178.98)
N2-N1-Cs1a	127.9(2) (82.3)	N2-N1-Cs1	116.1(2) (118.3)
Cs1-O-C	98.3(1)–124.5(2) (97.6–123.8)		
C-O-C	110.6(2)–112.4(2) (111.5–113.0)		

[a] Symmetry operation: a = $2-x, 1-y, -z$.

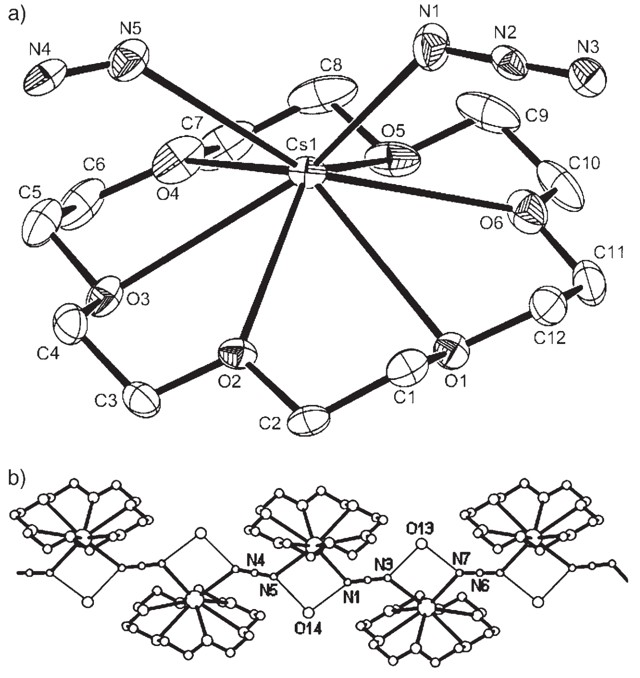

Figure 6. The crystal structure of $[Cs([18]crown\text{-}6)(N_3)(H_2O)\cdot 0.75\,(MeOH)]$. a) The environment around Cs1 showing the atom-labelling scheme. The geometry at Cs2 is very similar. The ellipsoids are drawn at the 50% probability level. b) The chain structure along *c*. The O–H···N hydrogen bonds between azide N and water molecules (O13, O14) are shown as thin lines. There is additional hydrogen-bonding between water and methanol molecules (not shown). There are centres of symmetry at N6 and N4, and H atoms have been omitted for clarity.

ment around Cs1 (Figure 6a and Table 6) shows eightfold coordination based on coordination to the six O atoms of the crown and two N atoms of different azide groups. Cs2 is very similarly disposed. There are two water molecules (O13, O14) in the asymmetric unit, which are hydrogen-bonded between N1 and N5 and between N3 and N7 (Figure 6b). In addition, there is hydrogen-bonding between the water and the disordered solvate methanol. The Cs atoms are positioned 1.34 Å (Cs1) and 1.29 Å (Cs2) out of the plane of the crown. Comparable compounds for Cs crowns and azides have been mentioned in relation to the previous Cs compound.

Comparison of the DFT computed structure of the anhydrous complex with the experimental crystallographic structure shows reasonable agreement. However, the crystal structure has C_i symmetry, whereas the BP86-DFT computed structure has C_1 symmetry. In the experimental structure, each Cs is bonded to one nitrogen atom of each azide group forming a parallelogram (see Figure 5a), and there are two different Cs–N bond lengths of 3.238 and 3.226 Å. In the computed structure, because the symmetry is lower, all four Cs–N bond lengths are unequal and have values of 3.197, 3.318, 3.331, and 3.149 Å. This difference in symmetry may well be due to the effect of the rest of the lattice on the structure of the dimeric unit. In the IR spectrum, the N_3 asymmetric stretching mode is observed at 2011 cm^{-1}, compared to the computed values of 2064 and 2072 cm^{-1}.

Table 6. Selected bond lengths [Å] and angles [°] for $[Cs([18]crown\text{-}6)(N_3)(H_2O)\cdot 0.75\,(MeOH)]$.[a]

Cs1–O1	3.220(3)	Cs1–O4	3.030(3)
Cs1–O2	3.018(3)	Cs1–O5	3.189(3)
Cs1–O3	3.213(3)	Cs1–O6	3.084(3)
Cs1–N1	3.116(4)	Cs1–N5	3.220(4)
N1–N2	1.180(5)	N2–N3	1.174(5)
N4–N5	1.180(4)	Cs1···O14a	4.399(4)
Cs2–O7	3.051(3)	Cs2–O10	3.184(3)
Cs2–O8	3.170(3)	Cs2–O11	3.018(3)
Cs2–O9	3.027(3)	Cs2–O12	3.193(3)
Cs2–N3	3.143(3)	Cs2–N7	3.151(4)
N7–N6	1.177(4)	Cs2···O13	3.566(5)
O14···N1b	2.836(5)	O14···N5b	2.869(5)
O13···N3	2.820(6)	O13···N7	2.846(6)
O1-Cs1-O2	54.92(7)	O4-Cs1-O5	55.04(9)
O2-Cs1-O3	54.06(7)	O5-Cs1-O6	53.91(9)
O3-Cs1-O4	53.87(8)	O6-Cs1-O1	53.17(8)
Cs1-N1-N2	130.9(3)	N1-N2-N3	179.1(4)
Cs1-N5-N4	138.1(2)	N1-Cs1-N5	79.35(9)
O7-Cs2-O8	54.61(8)	O10-Cs2-O11	53.98(7)
O8-Cs2-O9	54.96(7)	O11-Cs2-O12	55.36(7)
O9-Cs2-O10	54.33(7)	O12-Cs2-O7	54.40(7)
Cs2-N3-N2	140.4(3)	Cs2-N7-N6	136.2(3)
N3-Cs2-N7	77.58(10)		

[a] Symmetry operations: a = $3/2-x, y-1/2, 1/2-z$; b = $3/2-x, y+1/2, 1/2-z$.

Thermal decomposition of the azide complexes: The work described above has demonstrated conclusively that alkali metal azide-crown ether complexes are stable at room temperature, with well defined crystal structures. It is of some interest to explore whether the corresponding *molecular* species also exist in the gas phase, and whether they may be produced by sublimation of the heated solids. Many high-temperature salt molecules that can be produced in this way are now known, and these have been routinely detected and characterised by mass spectrometry and matrix-isolation IR spectroscopy; in general, the cesium salts have been found to be the most stable in the vapour phase.

Several experiments were therefore carried out on anhydrous [Cs([18]crown-6)(N_3)], in which the material was heated in high vacuum, the products were condensed with an excess of nitrogen under matrix-isolation conditions, and the low-temperature deposits were probed by IR spectroscopy. If *molecular* crown-azide complexes could be produced in this way, they should be readily detectable by the simultaneous presence of intense characteristic azide *and* ligand absorptions.

The results of these experiments, however, did not support the existence of vapour-phase complexes. At a relatively low temperature (ca. 500 K), the anhydrous cesium crown azide began to decompose, and the only vapour-phase species detected was the free ligand. Further heating to around 700 K resulted in essentially complete release of the crown, together with a residue of solid CsN_3. Still further heating to about 800 K resulted in the formation of a metallic film of elemental cesium, together with molecular CsN_3, as would be anticipated from previous work on the parent azide.[10] The other alkali metal azide-crown ether complexes were also found to decompose to the free ligand and alkali azide.

Table 7. Comparison of M–N bond lengths and computed metal-nitrogen charge densities.

Compound	Nearest M–N(terminal) distance [Å]	Mulliken Charges		Comments
		M	N(terminal)	
Li ([12]crown-4)-N_3	1.913 (expt) 1.819 (calcd)	0.413	−0.497	this work
LiN_3	1.699 (calcd)	0.316	−1.084	B3LYP, linear
Na ([15]crown-5)-N_3	2.263 (calcd)	0.507	−0.508	this work
NaN_3	2.067 (calcd)	0.860	−1.394	B3LYP, linear
[K([18]crown-6)-N_3·H_2O]$_2$	2.896 (expt) K_1–N_1: 2.784 K_{1a}–N_{1a}: 2.905 (calcd)	 K_1: 0.622 K_{1a}: 0.606	 N_1: −0.590 N_{1a}: −0.588	ref. [9]
KN_3	2.443 (calcd)	0.987	−0.845	B3LYP, linear
[Rb([18]crown-6)-N_3·H_2O]$_2$	3.020 (expt) Rb_1–N_1: 3.030 Rb_{1a}–N_{1a}: 3.161 (calcd)	 Rb_1: 0.628 Rb_{1a}: 0.634	 N_1: −0.600 N_{1a}: −0.585	this work
RbN_3	2.930 (calcd)	0.975	−0.712	B3LYP, triangular
[Cs([18]crown-6)-N_3]$_2$	3.226, 3.238 (expt) 3.197 (calcd)	0.744; 0.750	−0.519; −0.530	this work
CsN_3	3.053 (calcd)	0.962	−0.673	B3LYP, triangular

Concluding Remarks

In this work, a series of alkali metal azide-crown ether complexes has been synthesised and their crystal structures determined. Their properties have been investigated by infrared spectroscopy and DFT calculations.

The bonding in complexes of the alkali metals is believed to be predominantly ionic or ion-dipole in character, with the irregular geometries reflecting a balance between maximising the coordination number of the metal centre and minimising ligand–ligand repulsions.[32] The structures of the crown ether complexes determined in this work show the subtle interplay of such factors. The significant role of hydrogen bonding is also demonstrated, most clearly in the structures of the K and Rb dimers, but also in the chain structure of the hydrated Cs complex. Packing within the lattice may also play a role in determining the observed structures. The ionic radii of alkali metal ions are markedly dependent upon the metal coordination number,[33] and this factor also complicates comparisons between the different complexes. A major factor on going from Li to Cs is the decrease in the charge/radius ratio as the metal ion radius increases. Comparisons within each complex are more informative. For [Li([12]crown-4)(N_3)], the Li–N distance is about 0.2 Å (~100σ) shorter than the average Li–O distance, reflecting the strong interaction of the small lithium ion with the azide anion. In contrast, for the heavier alkali metals (K, Rb, Cs), the M–O and M–N distances are very similar, showing that the significant decrease in charge/radius ratio reduces this difference.

Table 7 shows the calculated M–$N_{terminal}$ distances (isolated molecules) for MN_3 and [Li([12]crown-4)(N_3)], [Na([15]-crown-5)(N_3)], [K([18]crown-6)(N_3)]$_2$, [Rb([18]crown-6)(N_3)]$_2$, and [Cs([18]crown-6)(N_3)]$_2$, as well as the computed Mulliken charges for the M and N centres in the M–$N_{terminal}$ bond in each case. The effect of O→M electron transfer in reducing the Mulliken charges in the crown ether complexes compared to the parent MN_3 is clearly evident. Comparison of the calculated bond lengths for isolated molecules with the X-ray crystallographic bond lengths of the solid complexes clearly neglects differences in phase and the effects of hydrogen bonding and lattice packing in the solids. Nevertheless, as can be seen from Table 7, for Li, Na and K, the M–$N_{terminal}$ bond lengths are considerably shorter in the MN_3 complexes than in the M([*n*]crown-*m*)N_3 complexes, whereas in the case of Rb and Cs, the M–$N_{terminal}$ bond lengths are similar for both the MN_3 and M([*n*]crown-*m*) complexes, with the MN_3 values still being lower. The reduced differences in M–$N_{terminal}$ distances between MN_3 and [M(crown)N_3] as Group 1 is descended is probably again attributable to the decreased charge/radius ratio, which makes Rb and Cs less sensitive to their surrounding ligands than Li or K.

Although the reaction enthalpies for nitrogen release from all of the crown ether complexes considered in this work have not been calculated, the reaction enthalpy has been calculated in one case, that is, Na([15]crown-5)$N_3 \rightarrow$ Na([15]crown-5) + $^3/_2$ N_2. This process was found to be endothermic with $\Delta E = 16.2\,\mathrm{kJ\,mol^{-1}}$ and $\Delta H = +20.5\,\mathrm{kJ\,mol^{-1}}$.

Acknowledgements

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