DOI: 10.1002/chem.200701502

Synthesis, Structures and DFT Calculations on Alkaline-Earth Metal Azide-Crown Ether Complexes

Michael D. Brown,[a] Martin F. Davis,[a] John M. Dyke,*[a] Francesco Ferrante,[b] William Levason,*[a] J. Steven Ogden,[a] and Michael Webster[a]

Abstract: The first examples of azide complexes of calcium, strontium or barium with crown ethers have been prepared and fully characterised, notably [Ba([18]crown-6)$(N_3)_2$(MeOH)], [Sr([15]crown-5)$(N_3)_2(H_2O)$], [Ca([15]crown-5)$(N_3)_2(H_2O)$] and [Sr([15]crown-5)$(N_3)(NO_3)$]. Crystal structures reveal the presence of a variety of coordination modes for the azide groups including κ1-, μ-1,3- and linkages via H-bonded water molecules, in addition to azide ions. The [Ba([18]crown-6)$(N_3)_2$(MeOH)]·1/3 MeOH contains dinuclear cations with three μ-1,3-NNN bridges, the first example of this type in main group chemistry. The structures obtained have been compared with molecular structures computed by density functional theory (DFT). This has allowed the effects of the crystal lattice to be investigated. A study of the M−N$_{\text{terminal}}$ metal–azide bond length and charge densities on the metal (M) and terminal nitrogen centre (N$_{\text{terminal}}$) in these complexes has allowed the nature of the metal–azide bond to be investigated in each case. As in our earlier work on alkali metal azide-crown ether complexes, the bonding in the alkaline-earth 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.

Keywords: alkaline earth metals · azides · crown compounds · density functional calculations · stucture elucidation

Introduction

There is considerable current interest in the synthesis, geometric and electronic structures, and reactions of polynitrogen species both from their inherent chemical interest and from their potential in high energy-density materials.[1–4] A major part of this recent work has been renewed interest in azide derivatives, including examples such as the homoleptic azides and azido-anions of Mo, W, Te, Sb, Nb and Ti.[5–7] In a recent paper[8] we reported on the unexpected range of coordination modes found in azide complexes of alkali-metal crown ethers, which included, κ^1 as in [Li([12]crown-4)N_3], two bridging modes—μ-1,1-N_3 as in [{Cs([18]crown-6)(N_3)}$_2$] and μ-1,3-N_3 in [Cs([18]crown-6)$(N_3)(H_2O)$(MeOH)],—whilst in [{M([18]crown-6)$(N_3)(H_2O)$}$_2$] (M = K or Rb) the dimeric units are principally linked by H-bonding between the azide and water ligands. In other systems azide counter-ions are present, for example, [Na([15]crown-5)$(H_2O)_2$]N_3.[8]

Here we report studies of crown ether complexes of the alkaline earth metals. As in the earlier work on the alkali-metal crown-ether azide complexes, we have used the simplest crown-ethers, [12]crown-4, [15]crown-5 and [18]crown-6, to keep the molecular size low and enable the electronic structure calculations to be performed in a reasonable time. Also, we have explored both direct reaction of the crown ether with $M(N_3)_2$ and metathesis routes to introduce the azides. Literature examples of complexes of alkaline-earth metal azides are very few, but include [M{N$(CH_2CH_2OH)_3$}$_2$]$(N_3)_2$, (M = Ca or Sr)[9] in which the metal is eight-coordinate (bonded to two nitrogens and six oxygens in the $N(CH_2CH_2OH)_3$ units) and azide counter-anions, [Ca(dmf)$_2(N_3)_2$] which is polymeric with the calcium O-coordinated to the dmf and to four bridging azides,[10] and [Ca$(N_3)_2(H_2O)_2$]·(bicyclo[4,4,0]-1,4,6,9-tetraazadecane) where the six-coordinate calcium is bonded to four bridging azides

---

[a] M. D. Brown, M. F. Davis, Prof. J. M. Dyke, Prof. W. Levason,
J. S. Ogden, M. Webster
School of Chemistry
University of Southampton
Southampton SO17 1BJ (UK)
E-mail: jmdyke@soton.ac.uk
wxl@soton.ac.uk

[b] F. Ferrante
Dipartimento di Chimica Fisica "F.Accascina"
Università degli Studi di Palermo
90128 Palermo (Italy)

and two water molecules and the azamacrocycle lies between the layers.[11] Alkaline-earth metal complexes of crown ether ligands are well established, although less thoroughly studied than their alkali metal analogues.[12,13]

The overall aim of this work was to see if nitrogen clusters could be stabilised between alkaline-earth crown ethers and to investigate the geometric and electronic structures of the alkaline-earth metal azide-crown ether complexes synthesized.

Experimental Section

General: Physical measurements were made as described previously.[8] The crown ethers were obtained from Aldrich and used as received.

CAUTION: HN_3 is dangerously explosive when concentrated and is also highly toxic. In this work dilute solutions (~5–10%) were prepared as described by Audrieth and Gibbs[14] with the preparation conducted in a good fume cupboard behind a polycarbonate blast screen. The alkaline-earth azides were made by modifications of the method of Gray and Waddington.[15] Although no problems were experienced in this work, the alkaline-earth azides can explode under some conditions and their crown complexes were made on a small scale with appropriate precautions.

$Ca(N_3)_2$: This was made by adding 40% H_2SO_4 (25 mL) dropwise to a refluxing solution of NaN_3 (3.5 g) in water (30 mL) and distilling the HN_3 produced directly into a suspension of $CaCO_3$ (2.5 g) in water. When all the carbonate had reacted, the clear solution was concentrated on a water bath until solid began to precipitate, then more HN_3 solution (ca. 5 mL) was added to convert any hydrolysis products to the binary azide. The solution was evaporated until solid began to separate, cooled and the product precipitated by adding ethanol. The white powder was dried in vacuo. Yield: 1.5 g (48%). IR (Nujol): $\tilde{\nu}=2145$ (sh), 2115, 633 cm^{-1}.

$Sr(N_3)_2$ and $Ba(N_3)_2 \cdot H_2O$: These were made similarly using the appropriate hydroxides. Yields 60–70%; IR (Nujol): $Sr(N_3)_2$: $\tilde{\nu}=2098$ (vbr), 633 cm^{-1}; $Ba(N_3)_2 \cdot H_2O$: $\tilde{\nu}=\sim 3300$, 2123 (sh), 2053, 649, 620 cm^{-1}.

$[Ba([18]crown\text{-}6)(N_3)_2(MeOH)] \cdot H_2O$: Barium azide (0.22 g, 1.0 mmol) and [18]crown-6 (0.26 g, 1.0 mmol) were added to methanol (20 mL) and the mixture heated to reflux, then evaporated to about 5 mL by heating. The solution was cooled and diethyl ether added dropwise until turbidity was observed. The solution was refrigerated for 12 h and the white powder which deposited filtered off and dried in vacuo. Yield: 0.40 g (77%). Elemental analysis calcd (%) for $C_{13}H_{30}BaN_6O_8$ (535.6): C 29.1, H 5.6, N 15.7; found: C 29.1, H 5.4, N 16.0; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta=3.8$ (s, 24H; CH_2), 3.2 (s, H; OH (MeOH)), 2.8 (s, 3H; CH_3), 2.2 ppm (s, 2H; H_2O); IR (Nujol): $\tilde{\nu}=3300$ (br, m), 2072 (s), 2032 (s), 1995 (sh), 1630 (w), 1291 (m), 1138 (w), 1092 (s), 1020 (m), 960 (m), 828 (w), 633 (m), 620 (m), 526 (w) cm^{-1}.

$[Sr([15]crown\text{-}5)(N_3)_2(H_2O)]$: $Sr(N_3)_2$ (0.34 g, 2.0 mmol) was suspended in methanol (20 mL), a solution of [15]crown-5 (0.44 g, 1.0 mmol) in methanol (15 mL) added and the mixture heated to boiling. The solution was evaporated to about 10 mL, cooled and diethyl ether (10 mL) added dropwise with stirring. The solution was refrigerated for 48 h and the white polycrystalline product filtered off, rinsed with diethyl ether (5 mL) and dried in vacuo. Yield: 0.54 g (65%). Further material was obtained by refrigerating the filtrate for some days. Elemental analysis calcd (%) for $C_{10}H_{22}N_6O_6Sr$ (409.9): C 29.3, H 5.4, N 20.5; found: C 29.4, H 5.4, N 20.8; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta=3.62$ (s, 20H; CH_2), 1.6 ppm (s, 2H; H_2O); IR (Nujol): $\tilde{\nu}=3300$ (br), 2068 (sh), 2038 (s), 1996 (s), 1626 (m), 1355 (m), 1287 (m), 1255 (m), 1175 (s), 1070 (s), 1036 (s), 948 (s), 923 (m), 875 (s), 828 (m), 637 (m), 625 (m), 552 (w), 523 (w) cm^{-1}.

$[Sr([15]crown\text{-}5)(N_3)(NO_3)]$: This was obtained as a small number of colourless crystals from a solution of $[Sr([15]crown\text{-}5)(N_3)_2]$ adventitiously contaminated with nitrate in MeOH-diethyl ether (see text). Elemental analysis calcd (%) for $C_{10}H_{20}N_4O_8Sr$: C 29.2, H 4.9, N 13.6; found: C 29.6, H 5.3, N 13.2; IR (Nujol): $\tilde{\nu}=2045$ (s), 1340 (sh), 1295 (m), 1108 (m), 1080 (s), 1036 (m), 956 (m), 926 (w), 862 (m), 832 (w), 620 (m), 625 (w), 560 (w) cm^{-1}.

$[Ca([15]crown\text{-}5)(N_3)_2(H_2O)]$: Method 1: $[Ca([15]crown\text{-}5)(NO_3)_2(H_2O)]$ (0.4 g, 1.0 mmol) was dissolved in boiling methanol (15 mL) and a solution of CsN_3 (0.36 g, 2.0 mmol) in methanol (10 mL) added, resulting in an instant white precipitate. The mixture was heated and stirred for 5 min, cooled and the white solid (identified as predominantly $CsNO_3$ by its IR spectrum) filtered off and discarded. The solution was allowed to stand for 5 h and a further small amount of white solid which separated, filtered off and discarded (This was a mixture of some $CsNO_3$ and the desired complex). The clear filtrate was treated dropwise with anhydrous diethyl ether (20 mL) and the mixture refrigerated overnight. The fine white powder which separated was filtered off and dried in vacuo. Yield: 0.15 g (41%). Elemental analysis calcd (%) for $C_{10}H_{22}CaN_6O_6$ (362.4): C 33.1, H 6.1, N 23.2; found: C 33.6, H 5.8, N 24.7; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta=3.65$ (s, 20H; CH_2), 1.5 ppm (s, 2H; H_2O); IR (Nujol): $\tilde{\nu}=3340$ (br), 2094 (vs), 2051 (sh), 1648 (w), 1250 (w), 1084 (vs), 1041 (vs), 950 (s), 870 (m), 833 (w), 616 (m) cm^{-1}.

Method 2: $[Ca(N_3)_2]$ (0.14 g, 1.1 mmol) was suspended in methanol (20 mL), a solution of [15]crown-5 (0.22 g, 1.0 mol) in methanol (15 mL) added and the mixture heated to boiling, when the salt dissolved to give a clear solution. The solution was evaporated to about 10 mL, cooled and diethyl ether (10 mL) added dropwise with stirring. The white powder was filtered off, rinsed with diethyl ether (5 mL) and dried in vacuo. Yield: 0.13 g (34%). Elemental analysis calcd (%) for $C_{10}H_{22}CaN_6O_6$ (362.4): C 33.1, H 6.1, N 23.2; found: C 32.6, H 5.8, N 24.0. IR and NMR spectra were as for Method 1 above.

$[Ca([15]crown\text{-}5)(NO_3)_2]$: $Ca(NO_3)_2 \cdot 4H_2O$ (0.69 g, 3.0 mmol) was dissolved in hot methanol (20 mL) and [15]crown-5 (0.66 g, 3.0 mmol) in methanol (15 mL) added. The solution was briefly refluxed, cooled and concentrated to 10 mL. Cooling overnight in a refrigerator gave white crystals. Yield: 0.80 g (69%) Elemental analysis calcd (%) for $C_{10}H_{20}CaN_2O_{11}$ (384.5): C 31.3, H 5.2, N 7.3; found: C 31.4, H 5.2, N 7.2; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta=3.7$ ppm (s, CH_2); IR (Nujol): $\tilde{\nu}=1570$ (m), 1350 (br), 1251 (m), 1084 (vs), 1034 (vs), 949 (s), 919 (sh), 868 (m), 823 (m), 526 (w) cm^{-1}.

$[Sr([15]crown\text{-}5)(NO_3)_2(H_2O)]$: This was made by using $Sr(NO_3)_2$ following the method used for the above calcium complex. Yield: 65%. Elemental analysis calcd (%) for $C_{10}H_{22}N_2O_{12}Sr$ (449.9): C 26.7, H 4.9, N 6.2; found: C 26.8, H 4.8, N 6.0; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta=3.7$ (s, 20H; CH_2), 1.8 ppm (s, 2H; H_2O); IR (Nujol): $\tilde{\nu}=3430$ (br), 1646 (w), 1350 (m), 1127 (w), 1114 (w), 1082 (s), 1037 (s), 949 (s), 933 (sh), 868 (m), 824 (m), 730 (sh), 516 (w) cm^{-1}.

$[Ba([18]crown\text{-}6)(NO_3)_2(H_2O)_2]$: This was made following the method for the above calcium nitrate complex from barium nitrate and [18]crown-6 in aqueous methanol. Colourless crystals. Yield: 65%. Elemental analysis calcd (%) for $C_{12}H_{28}BaN_2O_{14}$ (561.7): C 25.7, H 5.0, N 5.0; found: C 26.0, H 4.5, N 5.2; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta=3.7$ (s, 24H; CH_2), 1.6 ppm (s, 4H; H_2O); IR (Nujol): $\tilde{\nu}=3460$ (br), 1608 (w), 1350 (br), 1091 (vs), 1023 (sh), 960 (s), 834 (m), 801 (w), 522 (w), 480 (w) cm^{-1}.

Simple impact tests on the alkaline-earth metal azide-crown ether complexes prepared did not result in any explosions.

X-ray crystallography: Crystals of $(C_{10}H_{20}O_5)(N_3)_2Sr \cdot 1/2\,H_2O$ were isolated from the preparation by storing the filtrate in a freezer for a few weeks. All other crystals were obtained by vapour diffusion of diethyl ether into a methanol solution of the compound. Brief details of the data collection and refinement are presented in Table 1. Data collection used a Bruker-Nonius Kappa CCD diffractometer with the crystal held at 120 K in a cold nitrogen stream. Structure solution[16] and refinement[17] were routine with H atoms of the crowns added in calculated positions. Any less common features are commented on below. $(C_{10}H_{20}O_5)(N_3)_2Sr \cdot 1/2\,H_2O$ gave no evidence for H atoms bonded to O6 and the adp ellipsoids indicated disorder in the crown ring most marked at C9 and C10. This was modelled with two conformations of the ring at these atoms (A and B) using isotropic C atoms and Shelxl DFIX commands on associated C−C and C−O bonds. For $(C_{12}H_{24}O_6)(N_3)_2Ba \cdot 4/$

Table 1. Crystallographic data and refinement details.[a]

compound	$(C_{10}H_{20}O_5)(N_3)_2Sr\cdot 1/2H_2O$	$[(C_{10}H_{20}O_5)(N_3)(NO_3)Sr]$	$[(C_{12}H_{24}O_6)(NO_3)_2Ba]$	$(C_{12}H_{24}O_6)(N_3)_2Ba\cdot 4/3\,MeOH$
formula	$C_{10}H_{21}N_6O_{5.5}Sr$	$C_{10}H_{20}N_4O_8Sr$	$C_{12}H_{24}BaN_2O_{12}$	$C_{26.67}H_{58.67}Ba_2N_{12}O_{14.67}$
M_r	400.95	411.92	525.67	1056.87
crystal system	monoclinic	orthorhombic	monoclinic	triclinic
space group	$P2/c$ (no. 13)	$P2_12_12_1$ (no. 19)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
a [Å]	12.7961(11)	8.437(2)	8.300(2)	8.8449(10)
b [Å]	9.4865(10)	12.291(3)	15.540(4)	17.3250(10)
c [Å]	13.1647(11)	15.198(4)	7.6191(12)	20.969(2)
α [°]	90.0	90.0	90.0	83.789(4)
β [°]	94.676(5)	90.0	106.316(12)	86.470(4)
γ [°]	90.0	90.0	90.0	88.953(5)
U [Å^3]	1592.7(3)	1576.1(7)	943.2(4)	3188.1(5)
Z	4	4	2	3
μ [mm^{-1}]	3.42	3.47	2.17	1.92
$F(000)$	820	840	524	1596
total no. of obsns (R_{int})	16727 (0.143)	7146 (0.055)	10316 (0.038)	65178 (0.051)
unique obsns.	2807	3412	2158	14592
no. of parameters, restraints	217, 6	209, 0	125, 0	781, 3
goodness-of-fit on F^2	1.034	0.977	1.032	1.034
resid. electron density [eÅ^{-3}]	−0.72 to +0.52	−0.71 to +0.48	−0.58 to +0.44	−2.39 to +2.45
$R1$, $wR2$ ($I > 2\sigma(I)$)[b]	0.055, 0.102	0.046, 0.084	0.024, 0.043	0.040, 0.089
$R1$, $wR2$ (all data)	0.099, 0.118	0.058, 0.089	0.041, 0.048	0.061, 0.098

[a] Common items: temperature = 120 K; wavelength ($Mo_{K\alpha}$) = 0.71073 Å. [b] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$.

3MeOH the intensity data from the initial triclinic unit cell from the diffractometer (ca. $a = 17.32$; $b = 17.69$; $c = 20.97$ Å) failed to give a solution using the TREF command in Shelxl although there were recognisable crown ring fragments. Inspection of the measured intensities using the Layer program[18] showed that all zones with k odd were extremely weak but that the diffractometer software had found enough to force the use of a larger supercell. With a sequential (non-area detector) diffractometer this larger cell would in all probability not have been found. Transforming the data to this smaller cell gave a convincing solution with six Ba atoms in the unit cell in the space group $P\bar{1}$ which refined well. On making the C atoms anisotropic, several of the crown C atoms associated with Ba3 became elongated indicative of disorder. No attempt was made to model this, and H atoms associated with the MeOH were not included in the model. It should be noted that in halving b, the resulting cell is not in the reduced form and it is necessary to transform to the standard setting ($a < b < c$). The origin of the weak zones of reflections is not clear: it may arise from the disorder associated with the Ba3 containing cation. In principle a doubled cell could remove the disorder required in the present model but would also require translational symmetry that is half of the crystallographic translational symmetry of the larger cell.

CCDC-634502 (Sr/N_3), CCDC-634503 ($Sr/N_3/NO_3$), CCDC-634504 (Ba/N_3), CCDC-634505 (Ba/NO_3) 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, by using the Becke–Perdew BP86 generalised gradient functional[19] in conjunction with the Resolution of Identity (RIDFT) approximation.[20] The Pople-style valence triple zeta plus polarization 6–311G(d,p) basis set was used for all atoms, except for strontium and barium where the Stuttgart '97 relativistic effective small core potentials (ECPS[21]) were used.[22] For the Sr atom the ECP describes 28 core electrons and uses the basis set contraction Scheme (6s6p5d)/[4s4p2d] for the valence electrons; for Ba, 46 electrons are described by the ECP and one f function is added to the valence basis set, for the resulting contraction Scheme (6s6p5d1f)/[4s4p2d1f]. The auxiliary basis sets needed for the RIDFT method were 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 according to the harmonic approximation. All calculations were performed by using the Gaussian 03 package.[23] All optimized structures gave real frequencies.

Calculations were performed on the following alkaline-earth complexes.

i) calcium: $[Ca([15]crown\text{-}5)(N_3)_2]$

ii) strontium: $[Sr([15]crown\text{-}5)(N_3)_2]$; $[Sr([15]crown\text{-}5)(N_3)_2(H_2O)]$; $[Sr([15]crown\text{-}5)(N_3)(NO_3)]$

iii) barium: $[Ba_2([18]crown\text{-}6)_2(N_3)_3(MeOH)_2]^+$; $[Ba([18]crown\text{-}6)(NO_3)_2]$; $[Ba([15]crown\text{-}5)(N_3)_2]$; $[Ba([18]crown\text{-}6)(N_3)_2]$

Results and Discussion

The alkaline-earth metal azides $Ca(N_3)_2$, $Sr(N_3)_2$ and $Ba(N_3)_2\cdot H_2O$ were made[14] by distilling excess dilute aqueous HN_3 directly onto slurries of MCO_3 or $M(OH)_2$ in water (see Experimental Section). The strontium and barium compounds were readily obtained, but as previously reported,[14] the calcium compound is prone to hydrolysis and excess HN_3 and cautious precipitation with alcohol is necessary to obtain a reasonably pure sample and the yield is poorer.

The reaction of $Ba(N_3)_2$ and [18]crown-6 in a 1:1 mol. ratio in methanol produced a white powder, identified by analysis, ^{1}H NMR and IR spectroscopy as $[Ba([18]crown\text{-}6)(N_3)_2(MeOH)]\cdot H_2O$, in particular the water and methanol were both evident in the spectroscopic data. Vapour diffusion of diethyl ether into a solution of the complex in methanol produced colourless crystals which were identified as $[Ba([18]crown\text{-}6)(N_3)_2(MeOH)]\cdot 1/3\,MeOH$ (see below). Apart from the absence of features due to water in the IR and ^{1}H NMR spectra, the data, most notably the azide modes in the region of 2100–1950 cm^{-1} were very similar to those of the bulk solid and it seems certain that the same barium environment is present. The structure consists of dimeric units of two types. Each ten-coordinate Ba is bonded to the six O atoms of the crown and on an "axial" position is a coordinated MeOH ligand. The first type of dimer formed from Ba1 and Ba2 has three bridging azides (Figure 1a, Table 2) with Ba–N distances of 2.804(4)–2.856(4) Å. The second type of dimer (Ba3/Ba3a) is centrosymmetric with necessarily disordered azides (Figure 2a) and in total

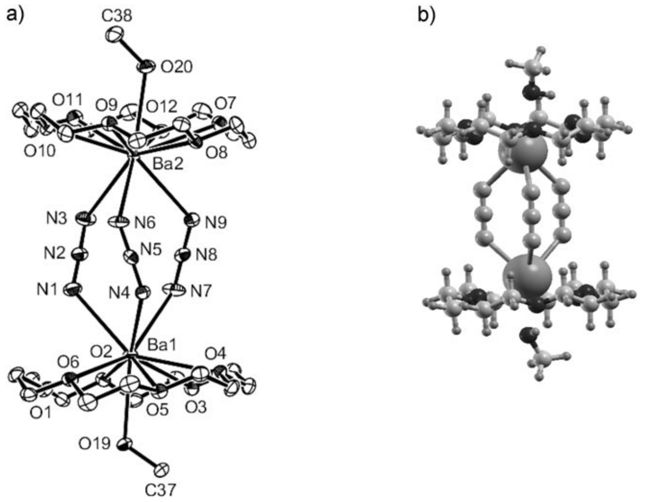

Figure 1. a) Structure of one dimeric unit involving Ba1 and Ba2 in $[Ba([18]crown\text{-}6)(N_3)_2(MeOH)]\cdot 1/3\,MeOH$ showing the atom labelling Scheme for the non-C atoms. This species has no crystallographic symmetry. Ellipsoids are drawn at the 50 % probability level and H atoms of the crown omitted for clarity. b) Calculated structure of $[Ba_2([18]crown\text{-}6)_2(N_3)_3(MeOH)_2]^+$.

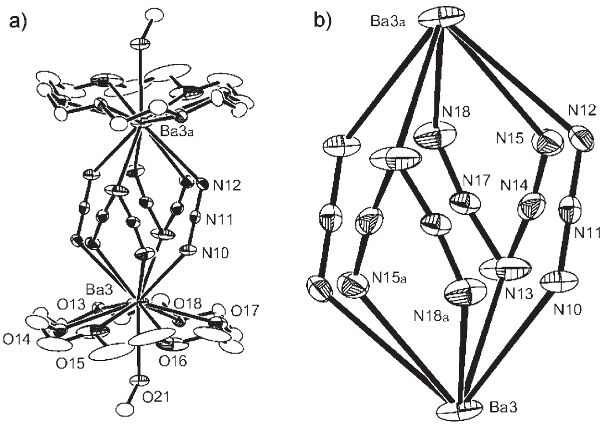

Figure 2. a) Structure of one dimeric unit involving Ba3 and Ba3a in $[Ba([18]crown\text{-}6)(N_3)_2(MeOH)]\cdot 1/3\,MeOH$ showing the atom labelling Scheme for the non-C atoms. This species has a centre of symmetry and disorder involving the three bridging azide groups. Ellipsoids are drawn at the 50 % probability level with boundary ellipsoids for C atoms. H atoms of the crown are omitted for clarity. Symmetry operation: $a=3-x, 1-y, -z$. b) The bridging disordered azide ligands involved in the Ba3–Ba3a unit showing the atom-labelling scheme. N13 and N16 (unlabelled) occupy the same position in the model and all N atoms have a site occupation factor of 0.5. Details as Figure 2a.

Table 2. Selected bond lengths [Å] and angles [°] for $[Ba([18]crown\text{-}6)(N_3)_2(MeOH)]\cdot 1/3\,MeOH$.[a]

Ba1–O1	2.904(3) (2.948)	Ba2–O7	2.909(3) (2.947)
Ba1–O2	2.863(3) (2.916)	Ba2–O8	2.876(3) (2.921)
Ba1–O3	2.935(3) (2.998)	Ba2–O9	2.939(3) (2.996)
Ba1–O4	2.908(3) (2.968)	Ba2–O10	2.920(3) (2.969)
Ba1–O5	2.953(3) (3.005)	Ba2–O11	2.942(3) (2.997)
Ba1–O6	2.972(3) (3.146)	Ba2–O12	2.926(3) (3.149)
Ba1–O19	2.810(3) (2.917)	Ba2–O20	2.797(3) (2.902)
Ba1–N1	2.819(4) (2.820)	Ba2–N3	2.856(4) (2.817)
Ba1–N4	2.811(4) (2.814)	Ba2–N6	2.811(3) (2.816)
Ba1–N7	2.804(4) (2.794)	Ba2–N9	2.825(4) (2.793)
N1–N2	1.178(5) (1.189)	N2–N3	1.186(5) (1.186)
N4–N5	1.177(5) (1.188)	N5–N6	1.174(5) (1.188)
N7–N8	1.176(5) (1.187)	N8–N9	1.180(5) (1.188)
O_c-Ba1-O_c (ca. 60°)	55.80(8)-59.17(8) (55.1–58.0)	O_c-Ba2-O_c (ca. 60°)	56.23(8)-58.29(8) (54.9–57.9)
O19-Ba1-O_c	64.04(8)-83.40(8) (53.7–86.5)	O20-Ba2-O_c	62.62(9)-80.52(9) (53.7–86.3)
N1-Ba1-N4	74.40(11) (78.9)	N3-Ba2-N6	71.79(11) (79.1)
N1-Ba1-N7	70.87(12) (78.6)	N3-Ba2-N9	73.10(13) (78.4)
N4-Ba1-N7	75.57(11) (79.1)	N6-Ba2-N9	74.73(11) (79.2)
Ba1-N1-N2	129.3(3) (133.8)	Ba2-N3-N2	127.3(3) (130.7)
Ba1-N4-N5	124.3(3) (130.9)	Ba2-N6-N5	132.4(3) (133.4)
Ba1-N7-N8	131.5(3) (132.4)	Ba2-N9-N8	125.5(3) (132.9)
N1-N2-N3	178.8(5) (179.0)	N4-N5-N6	177.5(4) (178.9)
N7-N8-N9	178.0(4) (179.1)		

[a] Data are given for the Ba1/Ba2 dimer unit. O_c refers to a crown O atom. Values in brackets are computed values for $[Ba_2([18]crown\text{-}6)_2(N_3)_3(MeOH)_2]^+$ (see Figure 1b).

there are three azide ligands. Label N13 is the site of atom N13 and N16 (not labelled) and each of the nine atoms N10–N18 have a site-occupation factor (sof) of 0.5 (Figure 2b, Ba–N 2.711(7)–3.001(7) Å). There are three of these moieties in the unit cell whose charges are balanced by three uncoordinated azide anions. There are also uncoordinated MeOH solvate molecules. The $Ba-O_{crown}$ distances 2.863(3)–2.972(3) Å may be compared with those in $[Ba([18]crown\text{-}6)(NCS)_2(H_2O)]$[24] 2.808(6)–2.875(5) Å. The latter structure is mononuclear with nine-coordinate barium, but has a similar barium environment with barium coordinated to six crown oxygens with two terminal thiocyanates on one side of the molecule and a coordinated water molecule on the other. In the present complex the coordinated methanol takes the place of the water, and three azide bridges (Ba–N = 2.804(4)–2.856(4) Å) replace the terminal thiocyanates (Ba–N = 2.779(12), 2.839(11) Å).

The combination of $Sr(N_3)_2$ and [15]crown-5 in methanol produced a colourless microcrystalline solid $[Sr([15]crown\text{-}5)(N_3)_2(H_2O)]$ that showed spectroscopic features in the ^1H and IR spectra consistent with the presence of the crown, water and azide ligands. The azide stretching region showed several bands, but it is not possible to deduce the structural unit present from the spectrum. Colourless crystals were obtained directly from the reaction solution and the structure consists of Sr1 coordinated by the five O atoms of the crown and linked into dimers through a bridging azide (see Table 3 and Figure 3a and 4). N2 is positioned on a two-fold axis and the azide N1-N2-N1a bonds to Sr1 and Sr1a (Sr1–N1 2.626(5) Å). A second terminal azide (N3-N4-N5) is bonded to Sr1 (Sr1-N3 2.547(7) Å) and the dimers are linked into a chain through a disordered H-bonded azide. The O6 of a water molecule and the azide N6-N7-N8 are disordered with N8 on a two-fold axis common to the two azides (N6-N7-N8 and N8-N7b-N6b) (see Figure 4). The linking into a chain is thus of the type Sr–O6···N8-N7b-N6b-Sr′ where the O6···N8 distance is 2.921(11) Å and the Sr1–N6 distance is 2.561(10) Å resulting in an eight-coordinate Sr atom. The Sr–O and Sr–N distances are unexceptional and similar to those in $[Sr([12]crown\text{-}4)(NCS)_2(H_2O)_2]$,

Table 3. Selected bond lengths [Å] and angles [°] for [Sr([15]crown-5)$(N_3)_2$]·1/2 H_2O.[a]

Sr1−N1	2.626(5) (2.518)	Sr1−N6	2.561(10) (–)
Sr1−N3	2.547(7) (2.383)	Sr1−O6	2.606(9) (2.644)
Sr1−O1	2.720(4) (2.931)	Sr1−O4	2.709(4) (2.709)
Sr1−O2	2.653(4) (3.295)	Sr1−O5	2.696(4) (2.689)
Sr1−O3	2.632(4) (2.853)	N1−N2	1.179(5) (1.212)
N3−N4	1.170(9) (1.211)	N6−N7	1.150(14) (–)
N4−N5	1.190(9) (1.168)	N7−N8	1.046(12) (–)
N1-N2-N1a	179.7(8) (178.9)	N1-Sr1-N3	85.3(2) (102.3)
N3-N4-N5	178.8(7) (179.3)	N1-Sr1-N6	88.2(3) (–)
N6-N7-N8	172.9(11) (–)	N3-Sr1-N6	80.5(3) (–)
N1-Sr1-O6	78.2(2) (64.0)	N6-Sr1-O6	27.1(3) (–)
Sr1-N1-N2	167.3(5) (151.1)	N3-Sr1-O6	104.6(3) (107.1)
Sr1-N6-N7	151.9(10) (–)	Sr1-N3-N4	164.1(5) (169.8)
O1-Sr1-O2	62.40(12) (53.2)	O4-Sr1-O5	61.99(14) (62.2)
O2-Sr1-O3	61.03(12) (52.7)	O5-Sr1-O1	60.66(12) (58.6)
O3-Sr1-O4	60.82(12) (58.4)		

[a] N6, N7, N8 and O6 are disordered atoms (see text). Symmetry operation: *a*=2−*x*, *y*, 1/2−*z*. Values in brackets are computed values for [Sr([15]crown-5)$(N_3)_2(H_2O)$] (see Figure 3b). The calculated parameters have been compared with the experimental parameters of Figure 3a including O6 and azides N1, N2 and N1a and N3, N4 and N5, but omitting N6, N7 and N8.

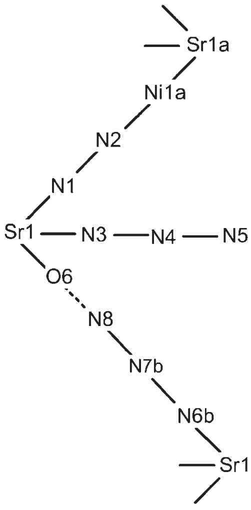

Figure 4. A schematic diagram of the disordered chain in [Sr([15]crown-5)$(N_3)_2$]·1/2 H_2O in the *a* direction linking the residues. The dashed line identifies the O6···N8 H-bond in one of the disordered arrangements (see text). Symmetry operations: *a*=2−*x*, *y*, 1/2−*z*; *b*=1−*x*, *y*, 1/2−*z*. The crown ether unit associated with each strontium atom is not shown.

which is mononuclear with eight-coordinate strontium.[25] The reason for the different structural motifs observed between the mononuclear thiocyanate complexes and the dinuclear or polymeric azide complexes presumably lies in the diminished affinity of the s-block metal for the thiocyanate sulfur (a few examples of *S*-CN coordinated thiocyanates are known for s-block metals, but they are very rare[13]).

The synthesis of the strontium azide-([15]crown-5) complex was carried out on a number of occasions and gave the same product (IR evidence), but one sample gave a few clear crystals with a quite different unit cell. The structure solution showed these crystals to be the azide-nitrate complex [Sr([15]crown-5)$(N_3)(NO_3)$], and sufficient crystals were obtained from this batch to allow microanalytical data to be obtained and the IR spectrum recorded. The latter shows clear differences in the azide stretching region from that of [Sr([15]crown-5)$(N_3)_2(H_2O)$] and weak features due to nitrate groups (see Experimental Section). The structure consists of Sr1 coordinated by the five oxygen atoms of the crown and linked into a chain through a bridging azide (see Table 4 and Figure 5a and 6). The two Sr1−N distances are similar (Sr1−N1 2.589(4), Sr1−N3a 2.577(4) Å) and in addition there is a symmetrically bonded bidentate nitrate ligand coordinated to the Sr atom completing the nine-coordination. Spot tests on the reagents for nitrate proved negative, and the serendipitous presence of nitrate is believed to have arisen in this sample from a contaminated glass sinter cleaned with HNO_3 and insufficiently rinsed with water. The

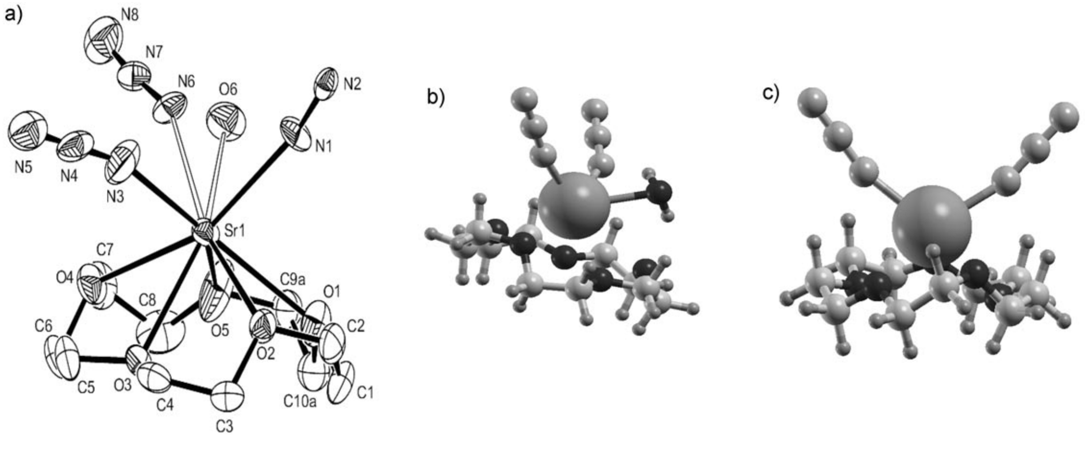

Figure 3. a) The asymmetric unit in [Sr([15]crown-5)$(N_3)_2$]·1/2 H_2O showing the atom numbering scheme. N2 and N8 are lying on twofold axes and the open bonds show the links to the disordered O6 and N6, N7, N8 azide from Sr1. There is disorder in the crown particularly at C9 and C10 and the diagram shows C9a and C10a and omits C9b and C10b. Ellipsoids are drawn at the 50% probability level and H atoms omitted for clarity. b) Calculated structure of [Sr([15]crown-5)$(N_3)_2(H_2O)$]. c) Calculated structure of [Sr([15]crown-5)$(N_3)_2$].

Table 4. Selected bond lengths [Å] and angles [°] for [Sr([15]crown-5)(N_3)(NO_3)].[a]

Sr1−N1	2.589(4) (2.422)	Sr1−N3a	2.577(4) (–)
Sr1−O1	2.715(3) (2.792)	Sr1−O5	2.695(3) (2.704)
Sr1−O2	2.647(3) (2.724)	Sr1−O6	2.644(4) (2.544)
Sr1−O3	2.801(3) (2.854)	Sr1−O7	2.688(4) (2.583)
Sr1−O4	2.777(3) (2.701)	N1−N2	1.179(5) (1.214)
N2−N3	1.168(5) (1.167)	N4−O6	1.260(5) (1.308)
N4−O7	1.286(5) (1.308)	N4−O8	1.241(5) (1.287)
N1-N2-N3	178.0(5) (179.1)	N1-Sr1-N3a	77.79(14) (–)
N1-Sr1-O6	99.91(14) (96.4)	N1-Sr1-O7	76.18(13) (116.1)
N3a-Sr1-O6	88.17(12) (–)	N3a-Sr1-O7	122.07(12) (–)
Sr1-N1-N2	153.3(4) (159.8)	Sr1-N3a-N2a	162.7(4) (–)
O1-Sr1-O2	60.86(10) (59.9)	O4-Sr1-O5	60.83(9) (61.9)
O2-Sr1-O3	58.60(10) (58.5)	O5-Sr1-O1	63.02(9) (60.6)
O3-Sr1-O4	60.32(9) (59.9)	O6-Sr1-O7	47.82(12) (51.0)
O6-N4-O7	116.2(4) (116.4)	O6-N4-O8	122.5(4) (122.5)
O7-N4-O8	121.2(4) (121.0)		

[a] Symmetry operation: a = $x-1/2$, $1/2-y$, $1-z$. Computed values of [Sr([15]crown-5)(N_3)(NO_3)] in brackets (see Figure 5b).

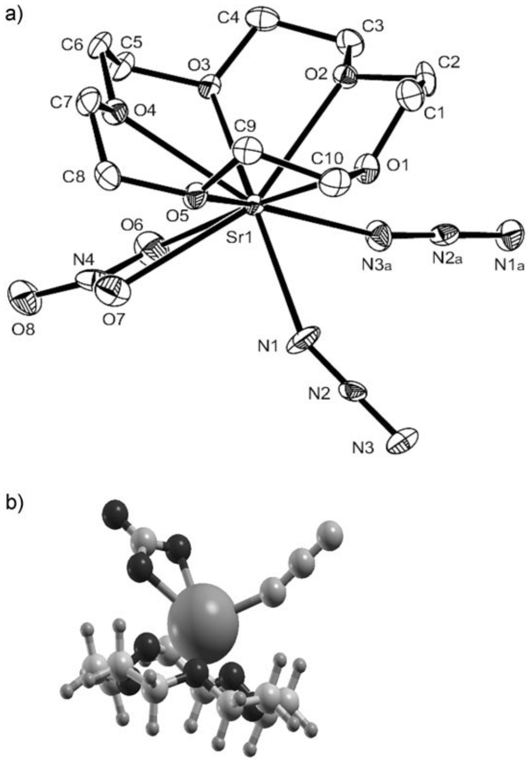

Figure 5. a) Coordination around Sr1 in [Sr([15]crown-5)(N_3)(NO_3)] showing the atom labelling scheme. Ellipsoids are drawn at the 50% probability level and H atoms omitted for clarity. Symmetry operation: $a = x-1/2$, $1/2-y$, $1-z$. b) Calculated structure of [Sr([15]crown-5)(N_3)(NO_3)].

formation of this complex is significant in respect of the metathesis reactions described below.

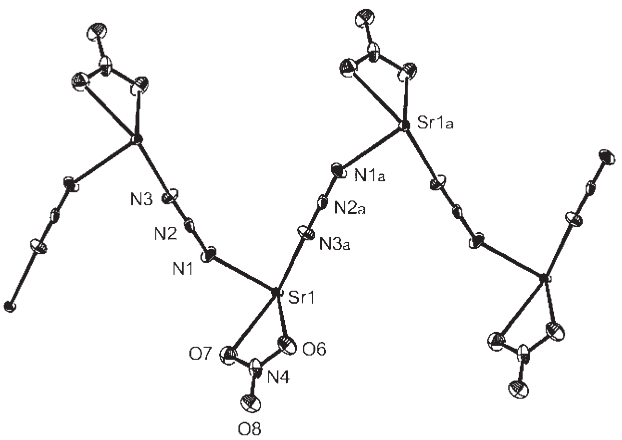

Figure 6. [Sr([15]crown-5)(N_3)(NO_3)] showing part of the chain structure arising from a 2_1 screw axis in the *a* direction where the azide acts as a bridging ligand. The crown moiety has been omitted for clarity. Details as in Figure 5a.

Table 5. Selected bond lengths [Å] and angles [°] for [Ba([18]crown-6)(NO_3)$_2$].[a]

Ba1−O1	2.7591(16) (2.815)	Ba1−O4	2.811(2) (2.880)
Ba1−O2	2.8195(17) (2.872)	Ba1−O5	2.841(2) (2.878)
Ba1−O3	2.7979(18) (2.872)	N1−O4	1.254(3) (1.295)
N1−O5	1.257(3) (1.294)	N1−O6	1.239(3) (1.231)
O1-Ba1-O2	59.66(5) (61.5)	O3-Ba1-O1a	60.74(5) (59.8)
O2-Ba1-O3	60.71(5) (61.8)	O4-Ba1-O5	44.61(6) (46.7)
O4-N1-O5	117.4(2) (116.8)	O4-N1-O6	121.6(2) (121.7)
O5-N1-O6	121.0(2) (121.5)		

[a] Symmetry operation: a = 1−x, $-y$, $2-z$. Computed values of [Ba([18]-crown-6)(NO_3)$_2$] in brackets (see Figure 7b).

In view of the production of the novel strontium structure, we attempted to obtain a barium nitrate-azide complex by allowing a very dilute solution of NH_4NO_3 in methanol to diffuse into a solution of [Ba([18]crown-6)(N_3)$_2$(MeOH)] in the same solvent. After a few days some block crystals had formed, but the structure of these showed them to be the dinitrate [Ba([18]crown-6)(NO_3)$_2$]. This structure consists (Table 5, Figure 7a) of a discrete centrosymmetric molecule with ten-coordinate Ba1 lying in the centre of the [18]-crown-6. The symmetrically bonded bidentate nitrate ligands (Ba1−O4 2.811(2), Ba1−O5 2.841(2) Å) complete the Ba1 coordination. This result does not of course prove that barium-azide-nitrate species do not form, but it does illustrate both the affinity of barium for the O-donor nitrate and that crystals form easily in alkaline-earth nitrate-crown ether systems. The latter point has been noted by others.[26] The structure of the related hydrate [Ba([18]crown-6)-(NO_3)$_2$(H_2O)] has been reported previously.[26] It contains an eleven-coordinate barium with two chelating nitrates on one side of the Ba-crown plane and a water molecule coordinated on the other. In the hydrate the Ba−O distances are slightly longer ($Ba-O_{crown} = 2.83(1)-2.908(8)$ Å and $Ba-O_2NO = 2.845(9)-2.98(1)$ Å) than in the present structure reflecting the higher coordination number in the former.

Combination of $Ca(N_3)_2$ and [15]crown-5 in methanol was carried out on a number of occasions with minor modifications and seemed to give the same basic complex based upon the IR spectra obtained. Analytical data on these samples was rather variable and some samples turned yellow on

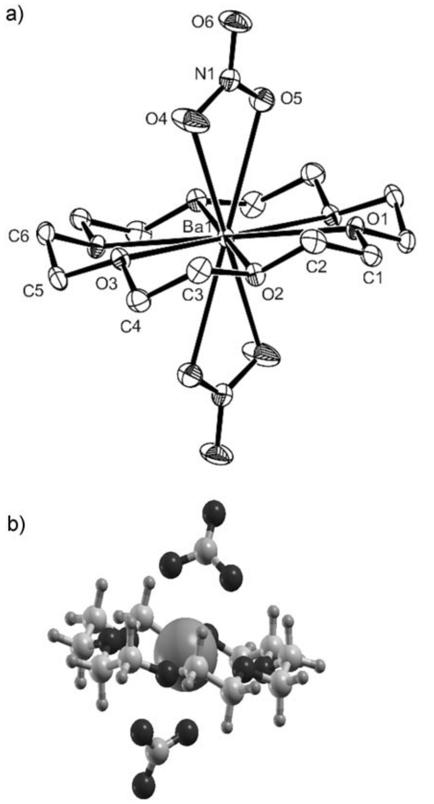

Figure 7. a) The structure of $[Ba([18]crown\text{-}6)(NO_3)_2]$ showing the atom-labelling scheme. The Ba1 atom is on a centre of symmetry. Ellipsoids are drawn at the 50% probability level and H atoms omitted for clarity. b) Calculated structure of $[Ba([18]crown\text{-}6)(NO_3)_2]$.

keeping over a period of a few days. By using a slight excess of $Ca(N_3)_2$:(crown) (ca. 1.1:1) and rapidly isolating the product, we obtained a white powder which did not yellow on keeping and analysed as $[Ca([15]crown\text{-}5)(N_3)_2(H_2O)]$. The IR spectrum shows the presence of crown, water and coordinated azide, but the structure present cannot be deduced from the data. Despite many attempts we have been unable to grow suitable crystals of this substance for an X-ray study; the complex appears to decompose slowly in solution. The complex $[Ca([15]crown\text{-}5)(NCS)_2(H_2O)]$ has been structurally characterised and contains an eight-coordinate calcium centre.[27]

Since alkaline-earth metal azides are not commercially available, we also sought a metathetical route to introduce the azide groups. Metathesis is rarely used to produce crown ether complexes since the likelihood of forming mixtures is obvious, but a few cases of the successful isolation of a single species from a mixture of cations/anions and crown have been reported.[28] After some preliminary work, the anion exchange between $[M(crown)(NO_3)_2]$ and either NaN_3 or CsN_3 in methanol was selected, which it was hoped would be driven by the insolubility of alkali metal nitrates, (always assuming the crown ether would bond to the alkaline-earth cation). Samples of the $[Ca([15]crown\text{-}5)(NO_3)_2]$, $[Sr([15]crown\text{-}5)(NO_3)_2(H_2O)]$ and $[Ba([18]crown\text{-}6)(NO_3)_2(H_2O)_2]$ were made from the appropriate metal nitrate and crown in methanol and fully characterised (see Experimental Section). Solutions of the appropriate $[M(crown)(NO_3)_2(H_2O)_x]$ and CsN_3 or NaN_3 in methanol in a 1:2 mol. ratio were mixed, and the products which precipitated were filtered off; further products were precipitated on concentration of the solutions. All products were monitored by IR spectroscopy to identify the anions present. Taking the calcium system as an example, as described in the Experimental Section by using CsN_3 and $[Ca([15]crown\text{-}5)(NO_3)_2]$ the initial precipitate is $CsNO_3$ (which is poorly soluble in methanol) and typically amounts to about 95% of the theoretical yield. Further solid deposited proved to be a mixture of $CsNO_3$ and some CsN_3. Finally a white powder precipitated on concentration which was identified as $[Ca([15]crown\text{-}5)(N_3)_2(H_2O)]$ by analysis and comparison of its IR spectrum with that of a sample produced from $Ca(N_3)_2$. However reproducibility using this route is not good, and minor changes in the reaction conditions led on other occasions to products containing some residual nitrate evident in the IR spectrum. Attempts to prepare strontium or barium azide complexes by metathetical routes were unsuccessful, the IR spectra of the products varying from preparation to preparation, and usually showing substantial amounts of nitrate present. The ease with which the nitrate complexes form and crystallise (see above), and the formation of the strontium azide-nitrate from small amounts of nitrate show the preference of the alkaline-earth metals for nitrate over azide ligands, which is only partially offset by the very low solubility of the (crown-free) alkali metal nitrates in methanol. It was concluded that metathesis was not a generally useful route to the azide complexes. Attempts to isolate a magnesium azide-[12]crown-4 complex from CsN_3 and $[Mg([12]crown\text{-}4)(NO_3)_2]$ were also unsuccessful.

Computational Results and Comparison between Computed and Experimental Structures

Comparison between experimental and computed structures is shown in Figure 1, 3, 5 and 7, and comparison of the experimental and computed structural parameters is shown in Tables 2 to 5.

i) $[M([15]crown\text{-}5)(N_3)_2]$ (M = Ca, Sr or Ba) and $[Ba([18]crown\text{-}6)(N_3)_2]$: The geometries and harmonic vibrational frequencies of $[Ca([15]crown\text{-}5)(N_3)_2]$, $[Sr([15]crown\text{-}5)(N_3)_2]$, $[Ba([15]crown\text{-}5)(N_3)_2]$ and $[Ba([18]crown\text{-}6)(N_3)_2]$ have been calculated taking into account two possible positions of the two azide moieties. In the first (angular form), both azide ions, coordinated to the metal centre, lie on the same side of the crown ether unit; in the second (axial form) the two N_3 units lie on opposite sides. Zero point corrected energies reveal that the angular and axial forms of $[Ca([15]crown\text{-}5)(N_3)_2]$ have approximately the same energy (the axial form is ca. $1\,kJ\,mol^{-1}$ more stable than the angular one), while in the $[Sr([15]crown\text{-}5)(N_3)_2]$ and $[Ba([15]crown\text{-}5)(N_3)_2]$ cases the angular form is more stable than the axial form (by $37\,kJ\,mol^{-1}$ and $63\,kJ\,mol^{-1}$, respectively). When

$[Ba([18]crown\text{-}6)(N_3)_2]$ is considered, the axial form is the more stable (by 20 kJ mol^{-1}). This behaviour can be explained in terms of the structures of the isolated $M(N_3)_2$ and of the relative dimensions of the metal centre and the crown ether. For the alkaline-earth azides, $M(N_3)_2$, (M = Ca, Sr or Ba), only calcium azide possesses, at the level of calculation used in this work, a $D_{\infty h}$ minimum, while the strontium and barium azides have an angular C_{2v} geometry in their ground states. When coordinated to the crown ether, the $Ca(N_3)_2$ moiety would like to maintain its linear structure in an axial geometry, but the calcium atom cannot coordinate to the two azide groups with the same strength, being slightly above the crown ether plane. In fact, the two Ca−N distances are 2.226 and 2.514 Å and, as a result, the azide ion below the crown ether plane bends forming an angle N-N-Ca of 114° instead of about 180°. The axial form is thus destabilized.

Calculations on the $Sr(N_3)_2$ and $Ba(N_3)_2$ molecules show that they prefer angular geometries. When the barium atom is combined with the [18]crown-6 ether, its angular coordination is satisfied by the oxygen atoms and, since Ba fits well in the centre of [18]crown-6, a perfectly axial di-azide centrosymmetric structure results: the Ba−N distances are 2.609 Å and the N-N-Ba angles are 180° on both sides of the crown. The angular coordination should be satisfied also for Sr in $[Sr([15]crown\text{-}5)(N_3)_2]$, but now the metal is well outside the plane of the crown ether, so that it cannot have a strong interaction with the azide below the plane (Sr−N distances are 2.400 and 2.801 Å, respectively in an axial structure), which shows a M-N-N angle (N-N-Sr is 117°) similar to the one in $[Ca([15]crown\text{-}5)(N_3)_2]$. Therefore the angular form of $[Sr([15]crown\text{-}5)(N_3)_2]$, whose geometric parameters are reported in Table 6, is the most stable. Incidentally, for the same reason, enhanced by the size of the barium atom, the angular form of $[Ba([15]crown\text{-}5)(N_3)_2]$ is 63 kJ mol^{-1} more stable than the axial geometry.

Table 6. Selected calculated bond lengths [Å] and angles [°] for $[Sr([15]crown\text{-}5)(N_3)_2]$ (see Figure 3c).

Sr1−N3	(2.415)	Sr1−N6	(2.420)
Sr1−O1	(2.766)	Sr1−O4	(2.815)
Sr1−O2	(2.701)	Sr1−O5	(2.671)
Sr1−O3	(2.792)	N6−N7	(1.213)
N3−N4	(1.214)	N7−N8	(1.167)
N4−N5	(1.167)		
N3-N4-N5	(179.2)	N3-Sr1-N6	(111.3)
N6-N7-N8	(179.2)	Sr1-N3-N4	(163.9)
Sr1-N6-N7	(162.3)	O3-Sr1-O4	(59.3)
O1-Sr1-O2	(62.6)	O4-Sr1-O5	(59.3)
O2-Sr1-O3	(60.5)	O5-Sr1-O1	(61.4)

ii) Strontium complexes: $[Sr([15]crown\text{-}5)(N_3)_2]$, $[Sr([15]crown\text{-}5)(N_3)_2(H_2O)]$ and $[Sr([15]crown\text{-}5)(N_3)(NO_3)]$: The main difference between the experimental structure of the $[Sr([15]crown\text{-}5)(N_3)_2(H_2O)]$ unit and the calculated structure of the isolated complex with the same stoichiometry lies in the coordination of the metal centre to the crown ether (see Figure 5). This, in turn, seems to be heavily affected by the position of the water molecule. The calculated values of the distances between the strontium atom and the oxygen atoms of the crown ether disagree with the distances obtained in the experimental five-coordinate structure. In particular, from the calculated Sr−O distances, the Sr1 seems not coordinated to the O2, and perhaps also to the O1 atom, as revealed by rather large values of distances and small values of the corresponding angles. This disagrees also with the $Sr{-}O_{crown}$ values calculated for $Sr([15]crown\text{-}5)(N_3)_2]$ (Table 6) and for $[Sr([15]crown\text{-}5)(N_3)(NO_3)]$ (Table 4), which show a metal centre coordinated to all the oxygen atoms of the crown ether. The angles at the Sr1 involving the azide residues and O6 show, not surprisingly, rather larger differences between calculated and experimental values probably due the the bridging azide (N1, N2, N1a) and the disorder associated with O6 and the H-bonded azide (N6, N7, N8).

The only relevant difference between the experimental and calculated structures of $[Sr([15]crown\text{-}5)(N_3)(NO_3)]$ is the N1-Sr1-O7 angle, which differs by about 40°, and is probably due to a rearrangement caused by the absence of the azide group coordinated to the strontium atom in the extended solid state structure as seen in Figure 5a and 6.

iii) Barium complexes: $[Ba_2([18]crown\text{-}6)_2(N_3)_3(MeOH)_2]^+$ and $[Ba([18]crown\text{-}6)(NO_3)_2]$: The experimental characterization of the dimeric unit Ba1/Ba2 is well supported by the calculated structure of the model compound $[Ba_2([18]crown\text{-}6)_2(N_3)_3(MeOH)_2]^+$. The values listed in Table 2 show that the maximum deviations between the experimental and calculated values are about 6 % in bond lengths and 10 % in bond angles. In particular, the positions of the three azide moieties coordinated to the two barium atoms are well reproduced, with a maximum deviation less than 1.5 % for the six Ba−N bond lengths, while the distances between the metal centres and the oxygen atom belonging to CH_3OH are overestimated by only 4 %.

Taking into account that the comparison is made between a model compound in the isolated state and experimental data obtained by X-ray diffraction measurements on a crystalline compound, we can conclude that the computational approach used here clearly supports the experimentally obtained structure.

In the 2100 cm^{-1} region of the calculated harmonic vibrational spectrum of $[Ba_2([18]crown\text{-}6)_2(N_3)_3(MeOH)_2]^+$, three normal modes localized on the azide groups can be identified. These represent asymmetric stretching modes involving almost entirely the central nitrogen atom of the azide moieties, which lead to hardly any change of Ba−N distances on vibration. Following the atom-labelling scheme in Figure 1a, the quasi-degenerate modes at 2099 and 2101 cm^{-1} correspond to an in-phase movement of N2 and N8 with an out-of-phase movement of N5, and an out-of-phase movement of N2 and N8 with no movement of N5, respectively. The third mode at 2160 cm^{-1}, the most intense, is a synchronous all-in-phase movement of the central N atoms of the three azide ions. Taking into account the correction for anharmonicity effects (which give rise to a decrease of ca. 5% of the harmonic frequencies), the calculated range of these frequencies fits well inside the experimental range for these asymmetric stretching modes.

The comparison between the experimental and calculated structure of the $[Ba([18]crown\text{-}6)(NO_3)_2]$ species can be made by inspecting Table 5 and Figure 7. Although the agreement between the experimental and calculated values mirrors that found for $[Ba_2([18]crown\text{-}6)_2(N_3)_3(MeOH)_2]^+$, two major differences are present: the two NO_3 groups are not oriented along the axis perpendicular to the crown ether plane, but are bent by about 10° (exptl. Ba1···N1–O6 = 174.2°) compared to the calculated values of 175.8° (Ba1···N1–O6) and 167.1° (Ba1···N1a–O6a, where the label a indicates the second NO_3 group); furthermore the NO_3 groups are rotated in the computed structure with respect to each other by about 53° (the torsion angle O4–N1···N1a–O4a), a value which corresponds approximately to one -OCH_2O- period of the crown ether. This establishes that, although some symmetry is evident in the calculated structure, the computed structure of isolated $[Ba([18]crown\text{-}6)(NO_3)_2]$ is not centrosymmetric like the same unit in the crystal structure.

As in our earlier study of alkali metal azide-crown ether complexes, a comparison has been made between the calculated $M{-}N_{terminal}$ distances for the isolated $M(N_3)_2$ and $[Ca([15]crown\text{-}5)(N_3)_2]$, $[Sr([15]crown\text{-}5)(N_3)_2(H_2O)]$, $[Sr([15]crown\text{-}5)(N_3)_2]$, $[Ba([18]crown\text{-}6)(N_3)_2]$ and $[Ba_2([18]crown\text{-}6)_2(N_3)_3(MeOH)_2]^+$ as well as the computed Mulliken charges on the M and N centres in the $M{-}N_{terminal}$ bond in each case (Table 7). The effect of O→M electron transfer in reducing the metal and $N_{terminal}$ Mulliken charges in the crown ether complexes compared to the parent $M(N_3)_2$ is again evident. Also, the $M{-}N_{terminal}$ bond lengths are shorter in the $M(N_3)_2$ complexes than in the $M([m]crown\text{-}n)(N_3)_2$ complexes, although it must be remembered that on comparing computed $M{-}N_{terminal}$ bond lengths for isolated alkaline-earth azide complexes with $M{-}N_{terminal}$ bond lengths from X-ray crystallographic measurements the effects of the lattice and hydrogen bonding in the lattice have been neglected.

For the complexes $[M([15]crown\text{-}5)(N_3)_2]$, where M = Ca, Sr and Ba, and $[Ba([18]crown\text{-}6)(N_3)_2]$, the reaction enthalpy to give the alkaline earth crown ether plus $3N_2$ was calculated in each case. The reaction enthalpies obtained were 76, 22, 77 and 48 kJ mol^{-1} respectively indicating that in all four case production of N_2 from these complexes is endothermic (in comparing these values it should be borne in mind that an all electron basis set has been used for Ca and ECPs have been used for Sr and Ba).

Concluding Remarks

The work has successfully characterised the first examples of Ca, Sr and Ba azides with crown ethers and provided X-ray structural data. Their electronic structures have been investigated with DFT calculations. The various coordination modes of the azide ligand identified in our previous study on alkali metal azide-crown ether complexes[8] were observed here—specifically κ^1 in $[Sr([15]crown\text{-}5)(N_3)_2]\cdot 1/2H_2O$ and μ-1,3 in $[Sr([15]crown\text{-}5)(N_3)(NO_3)]$ and $[Ba([18]crown\text{-}6)(N_3)_2(MeOH)]$, whilst in $[Sr([15]crown\text{-}5)(N_3)_2]\cdot 1/2H_2O$ hydrogen bonding between water molecules and azide ligands assembles the chain structure. The triple azide bridges in the dibarium cations $[Ba_2([18]crown\text{-}6)_2(N_3)_3(MeOH)_2]^+$ are the first examples in s-block chemistry. The serendipitous formation of $[Sr([15]crown\text{-}5)(N_3)(NO_3)]$ and the problems encountered in the attempted metathetical syntheses show the marked preference of these hard metals for O donors such as nitrate, which are clearly preferred over N-coordinated azide. As shown in Tables 2 to 5 and Figure 1, 3, 5 and 7, the calculated structures for alkaline earth metal azide-crown ether complexes reproduce well the solid state structures derived from X-ray crystallographic measurements, apart from $[Sr([15]crown\text{-}5)(N_3)_2(H_2O)]$ and $[Sr([15]crown\text{-}5)(N_3)(NO_3)]$ where the local structure around the metal in the crystal cannot be represented as an isolated metal azide-crown ether complex. The bonding in all these complexes is believed to be pre-

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

Compound	Nearest M–N(terminal) [Å]	Mulliken Charges		Comments
		M	N(terminal)	
$[Ca([15]crown\text{-}5)(N_3)_2]$[a]	2.27, 2.28 (calcd)	1.13	−0.56, −0.56	
$Ca(N_3)_2$[b]	2.14 (calcd)	1.26	−0.58	DFT, linear
$[Sr([15]crown\text{-}5)(N_3)_2(H_2O)]$	2.54, 2.63 (exptl) 2.38, 2.52(calcd)	1.05	−0.59, −0.51	
$[Sr([15]crown\text{-}5)(N_3)_2]$[a]	2.41, 2.42 (calcd)	1.13	−0.53, −0.53	
$Sr(N_3)_2$[b]	2.29 (calcd)	1.32	−0.54	DFT, angular
$[Ba_2([18]crown\text{-}6)_2(N_3)_3(MeOH)_2]^+$	2.82, 2.81, 2.80, 2.85, 2.81, 2.82 (exptl)			
$[Ba_2([18]crown\text{-}6)_2(N_3)_3(MeOH)_2]^+$	2.82, 2.81, 2.79, 2.82, 2.82, 2.79 (calcd)	1.09, 1.09	−0.45, −0.45, −0.44 −0.44, −0.45, −0.45	
$[Ba([18]crown\text{-}6)(N_3)_2]$[a]	2.57, 2.57 (calcd)	1.16	−0.52, −0.52	
$Ba(N_3)_2$[b]	2.43 (calcd)	1.27	−0.53	DFT, angular

[a] This is the structure with the azide groups on the same side of the crown ether ring; it is termed the "angular" structure. For Ca, this is a higher energy structure than the structure with the two azide groups on opposite sides of the ring (the "axial" structure) (by 1.3 kJ mol^{-1} at the B3LYP level). For Sr and Ba, the angular structure is lower in energy than the axial structure. [b] Isolated $Ca(N_3)_2$ is computed to be linear in its ground state. $Sr(N_3)_2$ and $Ba(N_3)_2$ are computed to have a C_{2v} minimum energy geometry at the DFT level.

dominantly 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 replusions.

Acknowledgements

The authors gratefully acknowledge QinetiQ U.K. for providing support for this work, which was carried out as part of the Weapons, Platforms and Effectors domain of the MOD research programme. We also thank EPSRC for support (M.D.B. and M.F.D). Support from the EPSRC (UK) National Service for Computational Chemistry Software is also acknowledged.

---

[1] D. A. Dixon, D. Feller, K. O. Christe, W. W. Wilson, A. Vij, V. Vij, H. D. B. Jenkins, R. M. Olson, M. S. Gordon, *J. Am. Chem. Soc.* **2004**, *126*, 834.

[2] W. W. Wilson, A. Vij, V. Vij, E. Bernhardt, K. O. Christe, *Chem. Eur. J.* **2003**, *9*, 2840.

[3] R. Haiges, S. Schneider, T. Schroer, K. O. Christe, *Angew. Chem.* **2004**, *116*, 5027; *Angew. Chem. Int. Ed.* **2004**, *43*, 4919.

[4] M. T. Nguyen, *Coord. Chem. Rev.* **2003**, *244*, 93.

[5] C. Knapp, J. Passmore, *Angew. Chem.* **2004**, *116*, 4938; *Angew. Chem. Int. Ed.* **2004**, *43*, 4834.

[6] a) R. Haiges, J. A. Boatz, S. Schneider, T. Schroer, M. Yousufuddin, K. O. Christe, *Angew. Chem.* **2004**, *116*, 3210; *Angew. Chem. Int. Ed.* **2004**, *43*, 3148; b) R. Haiges, J. A. Boatz, R. Bau, S. Schneider, T. Schroer, M. Yousufuddin, K. O. Christe, *Angew. Chem.* **2005**, *117*, 1894; *Angew. Chem. Int. Ed.* **2005**, *44*, 1860; c) R. Haiges, J. A. Boatz, A. Vij, V. Vij, M. Gerken, S. Schneider, T. Schroer, M. Yousufuddin, K. O. Christe, *Angew. Chem.* **2004**, *116*, 6844; *Angew. Chem. Int. Ed.* **2004**. *43*, 6676; d) R. Haiges, J. A. Boatz, T. Schroer, M. Yousufuddin, K. O. Christe, *Angew. Chem.* **2006**, *118*, 4948; *Angew. Chem. Int. Ed.* **2006**. *45*, 4830.

[7] "Recent Developments in the Chemistry of Covalent Main Group Azides": W. Fraenke, T. Klapötke in *Inorganic Chemistry Highlights* (Eds.: G. Meyer, D. Naumann, L. Wesemann), Wiley-VCH, Weinheim, **2002**.

[8] M. D. Brown, J. M. Dyke, F. Ferrante, W. Levason, J. S. Ogden, M. Webster, *Chem. Eur. J.* **2006**, *12*, 2620.

[9] A. Taeb, H. Krischner, C. Kratky, *Z. Kristallogr.* **1986**, *177*, 263.

[10] A. Taeb, H. Krischner, C. Kratky, *Z. Anorg. Allg. Chem.* **1987**, *545*, 191.

[11] F. A. Mautner, H. Krischner, C, Kratky, *Z. Naturforsch. B* **1989**, *44*, 135.

[12] R. D. Rogers, C. B. Bauer in *Comprehensive Supramolecular Chemistry* (Eds.: J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle), Elsevier, Oxford, **1996**, *1*, 315.

[13] T. P. Hanusa in *Comprehensive Coordination Chemistry II, vol. 3* (Eds.: J. A. McCleverty, T. J. Meyer), Elsevier, Oxford, **2004**, p. 1.

[14] L. F. Audrieth, C. F. Gibbs, *Inorg. Synth.* **1939**, *1*, 77.

[15] P. Gray, T. C. Waddington, *Trans. Farad. Soc.* **1957**, *53*, 901.

[16] G. M. Sheldrick, SHELXS-97, Program for the solution of crystal structures, University of Göttingen, Germany, **1997**.

[17] G. M. Sheldrick, SHELXL-97, Program for the refinement of crystal structures, University of Göttingen, Germany, **1997**.

[18] L. J. Barbour, *J. Appl. Crystallogr.* **1999**, *32*, 351.

[19] J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822.

[20] a) B. I. Dunlap, *J. Chem. Phys.* **1983**, *78*, 3140; b) B. I. Dunlap, *J. Mol. Struct.* **2000**, *529*, 37.

[21] T. Leininger, A. Nicklass, W. Küchle, H. Stoll, M. Dolg, A. Bergner, *Chem. Phys. Lett.* **1996**, *255*, 274.

[22] Institut für Theoretische Chemie, Universität Stuttgart; ECPs and corresponding basis sets. http://www.theochem.uni-stuttgart.de/ Stuttgart RSC '97 effective core potentials are indicated as follows: ECP28MWB (Sr), ECP46MWB (Ba).

[23] Gaussian 03, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.

[24] Y. Y. Wei, B. Tinant, J.-P. Declercq, M. Van Meerssche, J. Dale, *Acta Crystallogr. Sect. C* **1988**, *44*, 77.

[25] Y. Y. Wei, B. Tinant, J.-P. Declercq, M. Van Meerssche, J. Dale, *Acta Crystallogr. Sect. C* **1988**, *44*, 68.

[26] P. C. Junk, J. W. Steed, *J. Chem. Soc. Dalton Trans.* **1999**, 407.

[27] Y. Y. Wei, B. Tinant, J.-P. Declercq, M. Van Meerssche, J. Dale, *Acta Crystallogr. Sect. C* **1988**, *44*, 73.

[28] D. G. Parsons, J. N. Wingfield, *Inorg. Chim. Acta* **1976**, *18*, 263.

Received: September 21, 2007