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The Crystal Structures of the Complexes Formed by Benzo-18-crown-6 with Barium Perchlorate and with Strontium Perchlorate, Bisperchloratobisaquo(6, 7, 9, 10, 12, 13, 15, 16, 18, 19 decahydro benzo[b]-1, 4, 7, 10, 13, 16 hexaoxacyclooctadecin)-barium and Trisaquo(6, 7, 9, 10, 12, 13, 15, 16, 18, 19 decahydrobenzo[b]-1, 4, 7, 10, 13, 16 hexaoxacyclooctadecin)Strontium Diperchlorate

D. L. HUGHES, C. L. MORTIMER and M. R. TRUTER

Molecular Structures Department, Rothamsted Experimental Station, Harpenden, Herts. AL5 2JQ, U.K.

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The crystal structures of the title compounds have been determined by X-ray diffraction. In the barium compound the cation is coordinated by 10 oxygen atoms, six from the crown ether ring (Ba–O 2.802–2.846 Å), two water molecules (Ba–O 2.780, 2.843 Å) and one oxygen atom from a perchlorate ion (Ba–O 2.937 Å) on one side of the ring and one oxygen atom from the second perchlorate ion on the other side of the ring (Ba–O 2.794 Å). The neutral complexes are held in the ab *plane by water···perchlorate hydrogen bonds.*

In the strontium compound there are separate perchlorate ions, and complex cations having strontium in 9 coordination by six oxygen atoms from the crown ether ring (Sr–O 2.662–2.723 Å), two water molecules on one side of the ring (Sr–O 2.578, 2.574 Å) and one water molecule on the other (Sr–O 2.553 Å). Each water molecule forms hydrogen bonds to two perchlorate ions; three of the four oxygen atoms of each anion (mean Cl–O 1.42 Å) accept one hydrogen bond, the fourth oxygen has a shorter Cl–O distance, mean 1.38 Å.

For the barium compound a = *14.030(5),* b = *18.828(7),* c = *9.844(7) Å, β = 99.08(2)°, space group* $P2_1/a$, Z = *4 Ba(benzo-18-crown-6)(ClO_4)$_2$(H_2O)$_2$. Observations were collected with Mo-K_α radiation on a 4-circle diffractometer: after full-matrix least-squares refinement, R = 0.059 for 2751 measured reflections. For the strontium compound* a = *11.237(3),* b = *21.487(6),* c = *10.908(3) Å, β = 93.68(2)°, space group* $P2_1/n$, Z = *4 Sr(benzo-18-crown-6)(ClO_4)$_2$(H_2O)$_3$. Observations were collected with Cu-K_α radiation on a kappa geometry diffractometer; after full-matrix least-squares refinement R = 0.079 for 3899 observed reflections.*

Introduction

As originally noted by Pedersen [1] the macrocyclic crown ethers form complexes with alkaline earth metal cations. A series of such compounds has been reported with perchlorate [2, 3], thiocyanate [2], picrate [3] and tetraphenylborate [2] as the counter ions. As with several of the alkali metal salt complexes crystalline derivatives are obtained only with some solvent of crystallisation, possibly but not necessarily coordinated to the cation.

With benzo-18-crown-6, L, strontium and barium perchlorates form complexes having general formulae $M(ClO_4)_2L, nH_2O$. The infra red spectra in the 630 cm^{-1} region indicated that the perchlorate anions were not coordinated in the strontium complex and that one or both were coordinated in the barium complex [2]. Elemental analysis indicated n = 2 for M = Ba and n = 2 or 3 for M = Sr; the exact value was established from accurate unit cell dimensions obtained from a powder photograph.

Experimental

For both compounds preliminary photographic measurements established the unit cell dimensions and space groups, and, from the measurement of the density, that the asymmetric unit consisted of one chemical formula unit. The numbering scheme of L is shown in Figure 1, the water molecules are O(23), O(24) and (in the strontium complex) O(25), perchlorate ions are numbered Cl(1) with O(26)–O(29) and Cl(2) with O(30)–O(33). For both, observations were collected on diffractometers and the phase problem solved by conventional Patterson and Fourier syntheses but in other respects the treatments differed so they are described separately.

Crystal Structure of Ba(ClO_4)$_2$(H_2O)$_2$L

Crystal data

$C_{16}H_{28}BaCl_2O_{16}$, M = 684.6, Monoclinic, a = 14.030(5), b = 18.828(7), c = 9.844(7) Å, β = 99.08(2)°, U = 2567.6 Å^3, D_m (flotation) 1.76, Z = 4, D_c = 1.77. Space group $P2_1/a$ with equivalent positions

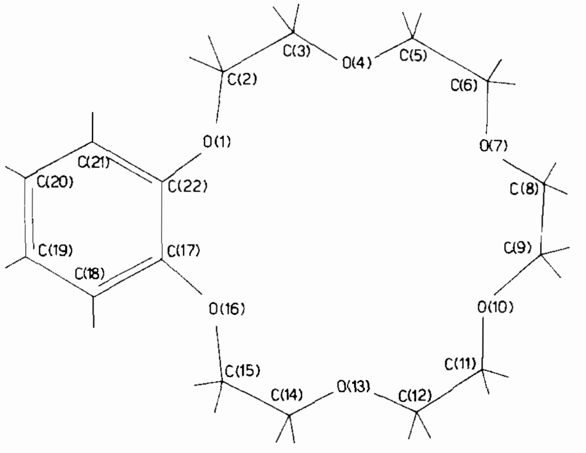

Figure 1. The designations of the carbon and oxygen atoms in the benzo-18-crown-6 molecule. Hydrogen atoms attached to C(n) are designated H(n) or H(nA) and H(nB).

±(*x*, *y*, *z*; ½ + *x*, ½ − *y*, *z*) uniquely determined. *F*(000) = 1368. Zr filtered Mo-K_α radiation, λ = 0.71069 Å (1 Å ≡ 10^{-10}m); $\mu = 18.24$ cm^{-1}.

An approximately equant crystal 0.22 mm was centred on a Picker diffractometer and accurate unit cell dimensions were obtained from optimised settings of 20 reflections. Observations were collected in the range $3° < 2\theta < 42°$ scanning from 0.5° in 2θ below α_1 to +0.5° above the α_2 peak, in the $\omega/2\theta$ scan mode at 0.5°/min. Of 2769 measurements 2314 had values greater than 2 σ_I; $\sigma_I^2 = I + (b_1 + b_2)(t_s/50)^2$, where I is the scan count, b_1 and b_2 are background counts for 25 s each and t_s the scan time. A standard reflection (731) was measured every 20 reflections and fell by 14% over the period of collection, and all the measured structure amplitudes were scaled to allow for this.

Coordinates for barium were obtained from the Patterson synthesis computed with the 2314 stronger reflections. The coordinates, temperature factor, and the overall scale were refined with the program RBLS [4] to an R value of 0.37. Successive Fourier syntheses and difference electron density maps revealed all but two of the non-hydrogen atoms and the positions of these, a perchlorate oxygen atom and a benzene ring carbon atom could be deduced. Isotropic refinement led, in two cycles, to R = 0.095. A difference electron density map showed as the main feature peaks round the barium ion indicative of anisotropic vibration. Probable positions for hydrogen atoms were calculated, and some corresponded to positive peaks in this map.

Full-matrix refinement was carried out with the program NUCLS [5] and 18 mis-measured reflections were omitted at this stage. Non-hydrogen atoms were allowed anisotropic vibration parameters, hydrogen atoms (except those of the water molecules) were assigned isotropic vibration parameters with a B value 1 Å^2 greater than the isotropic value of the carbon atoms to which they are attached. For refinement the hydrogen atoms were treated as a fixed contribution and the parameters of the other atoms were refined in two groups alternatively, barium and the macrocyclic ether in one cycle, the perchlorate ions and water molecules in the other. Scattering factors for Ba^{2+}, O, Cl, C and H and the anomalous contributions for barium were taken from ref. 6.

The function minimised was $\Sigma\, W(|F_o| - |F_c|)^2$ with the weighting scheme $W = 1/\sigma_F^2(4.48 - 0.001|F_o| + 0.00986|F_o|^2)$. Refinement concluded when the largest shift/e.s.d. was 0.5 (for the scale factor) and others were less than 0.3 R was 0.0588 for 2751 reflections.

Crystal Structure of $Sr(ClO_4)_2(H_2O)_3L$

Crystal data

$C_{16}H_{30}Cl_2O_{17}Sr$, M = 652.93, Monoclinic, *a* = 11.237(3), *b* = 21.487(6), *c* = 10.908(3) Å, β = 93.68(2), *U* = 2628.3 Å^3, D_m (flotation) = 1.633, *Z* = 4, D_c = 1.650, *F*(000) = 1336. Space group $P2_1/n$, determined from absences 0*k*0 with *k* = 2n + 1 and *h*0*l* with *h* + *l* = 2n + 1; non standard setting of C_{2h}^5 with equivalent positions ±(*x*, *y*, *z*; ½ + *x*, ½ − *y*, ½ + *z*).

Cu-K_α radiation (monochromated), λ(Cu-K_α) = 1.5418 Å; μ(Cu-K_α) = 54.66 cm^{-1}. (No molecular symmetry required).

Preliminary photographic measurements established unit cell dimensions and the space group. A crystal 0.3 × 0.2 × 0.2 mm was centred on an Enraf Nonius CAD-4 diffractometer, the orientation matrix and the quoted unit cell dimensions were determined from 25 reflections. Automatic collection of intensities was carried out under the following conditions:

Omega/2θ scan was used and 3902 unique reflections between θ = 1.5 and 60° were collected, the scan-range being 0.4° either side of the centre of the α_1 and α_2 peaks. Pre-scan was set at 20° in ω per minute. If the net intensity was below 10 counts the reflection was labelled as weak and not re-measured. 1210 reflections were in this category, the remainder were re-measured at a scan speed such that the net intensity of the majority of reflections was approximately 3000 counts. The three intensity control reflections (320, 023 and $23\bar{2}$) were measured every 48 reflections. There was no significant fall in any of their intensities so no scaling was required.

Reduction from intensity measurements to structure amplitudes and computation of the three dimensional Patterson synthesis were undertaken in Queen Mary College with programs CAD4 [7] and SHEL-X [8]. From the Patterson synthesis the strontium and chlorine atoms were located. Successive Fourier and difference Fourier syntheses with X-RAY ARC [4] programs revealed the remaining non-hydrogen atoms. Hydrogen atoms were added in calculated positions at 1.0 Å from, and completing trigonal or tetrahedral coordination about, the carbon atoms and were assigned temperature factors 0.01 Å^2 greater than U_{iso} for the carbon atom. The hydrogen atoms on the water molecules could not be located in difference syntheses.

Refinement was carried out by the program SHEL-X [8] on an ICL 4-70 computer; in the full-matrix least-squares refinement the non-hydrogen atoms were allowed anisotropic vibration. Three planes, with $|F_c| \gg |F_o|$, 002, $\bar{2}02$, and 210 were omitted from the final cycles of refinement. The scattering factors for all atoms were of the analytical form ref. [9a] and anomalous dispersion for all atoms was included [9b]. The weighting scheme, $w = 0.0472/(\sigma_F^2 + 0.1050\ F^2)$ was not entirely satisfactory as judged by variation of R with the average value of $|F_o|$. For all 3899 planes the value of R was 0.079.

Results

The atomic coordinates and vibration parameters for the two structures are given in Tables I and II. Bond lengths and angles with standard deviations

TABLE IA. Fractional Atomic Coordinates (×10^4) for Bisperchloratobisaquo(benzo-18-crown-6)barium with Isotropic Vibration Parameters (×10^3) Å^2 for Hydrogen atoms. Numbers in parentheses are the standard deviations in the least significant digits.

	x	y	z	U_{iso}
Ba	2542.7(3)	1645.0(3)	2209.4(5)	–
Cl(1)	2569(2)	–174(1)	–180(2)	–
O(26)	2638(5)	355(3)	835(7)	–
O(27)	3503(6)	–206(5)	–578(9)	–
O(28)	2396(7)	–849(4)	367(7)	–
O(29)	1938(6)	–16(4)	–1387(8)	–
Cl(2)	3902(2)	3103(1)	5070(2)	–
O(30)	3857(5)	2521(3)	4139(7)	–
O(31)	3363(7)	3650(4)	4340(9)	–
O(32)	4858(6)	3354(5)	5417(10)	–
O(33)	3523(10)	2975(6)	6203(10)	–
O(23)	2396(4)	3105(3)	1802(6)	–
O(24)	1666(5)	2142(3)	4444(6)	–
O(1)	3099(4)	638(3)	4314(5)	–
C(2)	2347(7)	285(5)	4923(10)	–
C(3)	1557(7)	95(5)	3795(10)	–
O(4)	1184(4)	721(3)	3115(6)	–
C(5)	293(7)	591(6)	2194(11)	–
C(6)	–42(7)	1300(7)	1591(11)	–
O(7)	634(4)	1626(4)	840(7)	–
C(8)	438(7)	1580(6)	–551(11)	–
C(9)	1098(8)	1979(7)	–1249(10)	–
O(10)	2053(4)	1911(4)	–615(6)	–
C(11)	2777(7)	2237(6)	–1314(10)	–
C(12)	3668(8)	1820(5)	–959(10)	–
O(13)	3989(4)	1821(3)	509(5)	–
C(14)	4807(6)	1368(5)	849(9)	–
C(15)	5182(6)	1409(5)	2336(9)	–
O(16)	4443(4)	1158(3)	3068(5)	–
C(17)	4726(7)	1025(4)	4458(9)	–
C(18)	5645(6)	1152(5)	5169(9)	–
C(19)	5838(7)	963(6)	6572(10)	–
C(20)	5134(8)	671(6)	7189(9)	–
C(21)	4220(7)	551(5)	6499(9)	–
C(22)	3994(7)	729(4)	5126(8)	–
H(2A)	2610	–0154	5417	079
H(2B)	2098	0610	5588	079
H(3A)	1812	–0226	3128	087
H(3B)	1033	–0156	4185	087
H(5A)	–0199	0385	2709	094
H(5B)	0406	0256	1448	094
H(6A)	–0153	1623	2356	096

TABLE IA (continued)

H(6B)	−0666	1229	0958	096
H(8A)	−0230	1764	−0860	095
H(8B)	0467	1070	−0818	095
H(9A)	0912	2491	−1262	106
H(9B)	1041	1802	−2216	106
H(11A)	2890	2739	−1002	092
H(11B)	2560	2230	−2330	092
H(12A)	4182	2030	−1431	081
H(12B)	3544	1320	−1281	081
H(14A)	5323	1519	0316	077
H(14B)	4616	0868	0600	077
H(15A)	5351	1912	2603	067
H(15B)	5772	1107	2560	067
H(18)	6155	1371	4703	065
H(19)	6494	1044	7112	079
H(20)	5286	0539	8183	081
H(21)	3718	0336	6991	076

TABLE IB. Anisotropic Vibration Parameters ($\times 10^4$) Å^2 of the Form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba	421(4)	−363(4)	412(4)	18(3)	49(3)	15(2)
Cl(1)	662(17)	502(16)	568(16)	11(13)	−21(14)	−113(13)
O(26)	1528(71)	566(46)	779(49)	−6(45)	261(47)	−390(40)
O(27)	1195(77)	1904(104)	1628(88)	382(71)	582(67)	−167(77)
O(28)	2222(102)	634(54)	875(57)	−510(60)	−63(59)	131(45)
O(29)	1276(71)	1243(73)	1061(66)	−14(58)	−551(59)	74(56)
Cl(2)	745(19)	619(18)	558(17)	−20(15)	59(14)	−85(14)
O(30)	1109(60)	538(46)	935(53)	135(41)	−173(45)	−295(40)
O(31)	1978(100)	922(67)	1371(81)	563(69)	−562(73)	−561(62)
O(32)	972(70)	1797(100)	1391(87)	−394(62)	48(60)	−600(67)
O(33)	3591(174)	2194(124)	1242(85)	−1006(118)	1639(106)	−240(85)
O(23)	718(44)	382(36)	742(44)	19(32)	40(34)	95(34)
O(24)	1076(56)	708(49)	759(48)	−3(42)	404(42)	−91(39)
O(1)	571(42)	520(41)	503(39)	55(34)	57(35)	124(32)
C(2)	845(82)	621(71)	783(77)	83(63)	334(68)	348(61)
C(3)	726(78)	705(82)	916(86)	−140(65)	240(66)	261(67)
O(4)	518(42)	446(40)	872(49)	−100(34)	147(37)	97(37)
C(5)	477(72)	782(87)	1214(100)	−172(63)	105(68)	−163(75)
C(6)	488(71)	1260(112)	834(83)	−52(74)	137(62)	102(82)
O(7)	427(45)	1719(87)	637(54)	−163(45)	−23(39)	188(50)
C(8)	572(76)	1227(109)	705(88)	−85(70)	−102(65)	25(74)
C(9)	672(83)	1490(120)	620(77)	246(82)	−29(66)	251(78)
O(10)	661(50)	1140(61)	536(46)	−89(45)	−117(39)	228(43)
C(11)	778(82)	1174(103)	590(74)	−52(76)	167(63)	329(69)
C(12)	914(87)	815(83)	556(75)	−16(67)	232(64)	118(59)
O(13)	594(43)	611(43)	437(41)	−34(35)	137(32)	57(32)
C(14)	585(68)	596(67)	684(75)	54(56)	268(56)	32(56)
C(15)	501(63)	525(62)	677(73)	13(51)	128(55)	36(54)
O(16)	373(36)	513(39)	483(40)	52(30)	44(30)	80(31)
C(17)	705(76)	366(60)	529(68)	193(53)	26(61)	−77(50)
C(18)	507(68)	592(69)	657(73)	144(53)	−178(56)	−127(55)
C(19)	754(89)	831(92)	800(98)	358(72)	−283(73)	−266(73)
C(20)	1167(113)	888(96)	397(68)	532(87)	−129(77)	−156(64)
C(21)	943(89)	589(70)	482(69)	294(63)	85(63)	77(55)
C(22)	826(82)	348(57)	441(64)	188(55)	71(62)	23(47)

TABLE IIA. Fractional Atomic Coordinates ($\times 10^4$) for Trisaquo(benzo-18-crown-6)strontium Diperchlorate, and Isotropic Vibration Parameters ($\times 10^3$) Å^2 for Hydrogen Atoms. Standard deviations in parentheses refer to the least significant figures.

	x	*y*	*z*	U_{iso}
Sr	3638.2(5)	1513.3(3)	2288.8(5)	–
Cl(1)	3360(1)	4178(1)	–2686(1)	–
O(26)	2550(7)	4559(4)	–2089(8)	–
O(27)	3482(8)	4387(4)	–3874(6)	–
O(28)	4497(5)	4177(4)	–2023(6)	–
O(29)	2870(8)	3556(3)	–2737(9)	–
Cl(2)	304(2)	3290(1)	2343(1)	–
O(30)	994(6)	3391(3)	3457(5)	–
O(31)	998(6)	3367(4)	1316(6)	–
O(32)	–637(6)	3706(4)	2264(6)	–
O(33)	–91(8)	2667(3)	2359(7)	–
O(23)	1368(5)	1601(3)	2090(6)	–
O(24)	5550(5)	1672(3)	1142(5)	–
O(25)	5441(5)	1256(3)	3778(5)	–
O(1)	3331(4)	2609(2)	1054(4)	–
C(2)	3069(7)	2601(4)	–251(6)	–
C(3)	2409(7)	2026(4)	–603(7)	–
O(4)	3112(5)	1523(2)	–126(5)	–
C(5)	2745(8)	926(4)	–638(8)	–
C(6)	3690(7)	470(3)	–211(8)	–
O(7)	3797(5)	430(2)	1100(5)	–
C(8)	3099(8)	–73(4)	1542(8)	–
C(9)	3311(8)	–83(3)	2897(8)	–
O(10)	2903(5)	482(2)	3379(5)	–
C(11)	2907(8)	488(4)	4658(7)	–
C(12)	2342(9)	1076(5)	5037(8)	–
O(13)	3007(5)	1579(2)	4615(5)	–
C(14)	2548(7)	2170(4)	5015(6)	–
C(15)	3392(8)	2671(4)	4692(7)	–
O(16)	3551(5)	2629(2)	3385(4)	–
C(17)	3956(6)	3156(3)	2813(7)	–
C(18)	4366(7)	3678(4)	3427(8)	–
C(19)	4729(8)	4191(4)	2770(10)	–
C(20)	4616(8)	4176(4)	1492(12)	–
C(21)	4189(7)	3661(4)	928(8)	–
C(22)	3817(7)	3152(3)	1563(7)	–
H(2A)	2531	3001	–517	71
H(2B)	3892	2615	–711	71
H(3A)	2287	1991	–1590	70
H(3B)	1550	2025	–212	70
H(5A)	1895	791	–310	75
H(5B)	2674	949	–1629	75
H(6A)	4534	617	–536	70
H(6B)	3461	17	–584	70
H(8A)	2165	4	1293	74
H(8B)	3376	–508	1156	74
H(9A)	4253	–136	3137	79
H(9B)	2832	–467	3271	79
H(11A)	2408	95	4969	80
H(11B)	3813	465	5052	80
H(12A)	2336	1094	6026	81
H(12B)	1438	1101	4639	81
H(14A)	1682	2255	4560	70
H(14B)	2473	2163	5997	70
H(15A)	4239	2607	5203	78
H(15B)	3030	3120	4905	78
H(18A)	4406	3691	4419	70

TABLE IIA (continued)

H(19A)	5095	4596	3245	75
H(20A)	4869	4574	963	82
H(21A)	4134	3646	−64	74

TABLE IIB. Anisotropic Vibration Parameters (× 10^4) Å^2 of the form exp $[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sr	359(4)	372(4)	379(4)	−9(2)	50(3)	37(2)
Cl(1)	478(9)	531(10)	467(9)	16(7)	71(7)	−3(7)
O(26)	1055(59)	1590(81)	1257(68)	641(55)	165(51)	−535(58)
O(27)	1575(76)	1527(72)	565(41)	287(62)	242(44)	363(44)
O(28)	554(35)	1263(59)	887(47)	−54(35)	−5(32)	−39(40)
O(29)	954(57)	795(47)	1483(76)	−208(38)	−392(54)	216(43)
Cl(2)	526(10)	470(9)	446(9)	34(7)	27(7)	−28(7)
O(30)	700(39)	910(43)	543(35)	0(30)	−141(29)	−33(28)
O(31)	692(42)	1398(64)	658(42)	70(39)	159(33)	−7(37)
O(32)	797(44)	1256(59)	801(45)	462(42)	−8(36)	−139(41)
O(33)	1522(69)	799(46)	984(51)	−619(48)	−19(47)	−150(39)
O(23)	475(31)	723(36)	796(42)	−14(24)	37(28)	−19(28)
O(24)	443(28)	963(40)	498(30)	−37(27)	59(23)	127(27)
O(25)	531(31)	1075(45)	482(29)	89(31)	11(24)	4(30)
O(1)	659(31)	366(24)	393(25)	89(21)	89(22)	81(19)
C(2)	749(51)	625(47)	231(31)	223(38)	23(31)	139(30)
C(3)	639(48)	781(54)	426(42)	231(42)	−117(34)	−35(37)
O(4)	502(31)	544(31)	543(32)	25(20)	−40(25)	−109(21)
C(5)	705(53)	673(51)	570(48)	−198(42)	28(41)	−128(39)
C(6)	586(44)	476(42)	775(57)	−85(36)	49(40)	−209(39)
O(7)	651(31)	396(25)	726(36)	−121(23)	146(26)	−88(24)
C(8)	765(53)	430(41)	822(59)	−166(38)	116(44)	8(38)
C(9)	707(51)	450(42)	870(62)	−24(38)	185(44)	218(41)
O(10)	605(30)	466(28)	743(37)	−61(24)	119(26)	187(25)
C(11)	805(55)	682(53)	541(48)	−144(44)	−33(41)	379(42)
C(12)	712(56)	1147(80)	519(50)	−253(56)	229(43)	277(49)
O(13)	537(33)	705(36)	557(32)	73(24)	163(26)	101(24)
C(14)	746(51)	692(51)	327(37)	223(42)	139(33)	50(33)
C(15)	830(56)	584(47)	468(42)	127(40)	−44(39)	−97(35)
O(16)	715(32)	413(26)	384(25)	18(22)	79(22)	33(19)
C(17)	389(34)	328(34)	699(47)	29(27)	−28(32)	−31(32)
C(18)	600(47)	456(42)	749(53)	53(35)	12(41)	12(38)
C(19)	558(47)	506(47)	984(69)	122(35)	98(46)	−58(44)
C(20)	673(57)	317(41)	1701(119)	51(36)	414(68)	191(53)
C(21)	609(47)	453(40)	780(56)	44(37)	255(42)	193(40)
C(22)	525(41)	539(43)	492(42)	167(33)	161(33)	144(32)

allowing for the correlation coefficients given by the full-matrix least-squares were calculated by the program ORFFE [5] (barium compound) or SHEL-X [8] (strontium compound); torsion angles and their standard deviations were obtained from the program TORSN [4]. Figures 2 and 3 show stereo diagrams of the complexes.

In the barium compound the perchlorate ions are coordinated to the metal (through O(26) and O(30)) as are the two water molecules and the six ether oxygen atoms. Bond lengths and angles for the coordination around barium and for the perchlorate ions are given in Table III. In the strontium compound the crown ether and the water molecules are coordinated to the metal at distances and angles given in Table IV which also shows the dimensions of the perchlorate ions. Bond lengths, bond angles and torsion angles in both cyclic ether molecules are in Table V; mean planes through various groups of atoms are in

TABLE III. Barium Complex.

(a) Distances (Å), with Standard Deviations in Parentheses, for the Coordination about the Barium Ion

Ba–O(1)	2.826(5)	Ba–O(23)	2.780(6)
Ba–O(4)	2.827(5)	Ba–O(24)	2.843(6)
Ba–O(7)	2.802(6)	Ba–O(26)	2.794(6)
Ba–O(10)	2.802(6)	Ba–O(30)	2.937(6)
Ba–O(13)	2.846(5)		
Ba–O(16)	2.820(5)		

(b) Angles Subtended at the Barium Ion O(A)–Ba–O(B). Standard Deviations are 0.15–0.20°

(A)	(B) : (4)	(7)	(10)	(13)	(16)	(23)	(24)	(26)	(30)
(1)	58.5	118.5	147.5	111.7	54.8	140.8	75.9	75.1	80.2
(4)	–	60.2	110.6	146.7	111.0	128.0	64.1	72.8	121.8
(7)		–	57.2	115.8	157.9	84.2	83.1	82.6	140.6
(10)			–	58.8	115.3	71.3	129.8	72.4	124.9
(13)				–	59.1	81.0	148.4	73.9	83.2
(16)					–	114.2	112.3	75.3	61.4
(23)						–	75.8	142.9	64.1
(24)							–	136.1	67.6
(26)								–	136.7

Ba–O(26)–Cl(1)	163.5(4)
Ba–O(30)–Cl(2)	143.9(4)

(c) Bond Lengths and Angles in the Perchlorate Ions

Cl(1)–O(26)	1.404(6)	Cl(2)–O(30)	1.424(6)
Cl(1)–O(27)	1.428(8)	Cl(2)–O(31)	1.405(8)
Cl(1)–O(28)	1.416(7)	Cl(2)–O(32)	1.412(8)
Cl(1)–O(29)	1.397(7)	Cl(2)–O(33)	1.331(8)

	O(A)–Cl(1)–O(B)				O(C)–Cl(2)–O(D)		
(A)	(B): (27)	(28)	(29)	(C)	(D): (31)	(32)	(33)
(26)	105.1(5)	111.3(5)	114.7(5)	(30)	105.6(4)	110.9(5)	114.6(6)
(27)	–	106.6(6)	105.1(6)	(31)	–	107.1(6)	107.9(8)
(28)		–	113.1(5)	(32)		–	110.3(7)

Figures 4 and 5 and selected intermolecular distances in Tables VII and VIII.

Discussion

The crystals of the barium compound contain neutral entities, the coordinated ion pairs, while those of the strontium compound contain complex cations and perchlorate anions. This difference is in agreement with deductions from the i.r. spectra [2]; the spectra in the 'finger print' region did not indicate whether the conformations of the ligands would be significantly different.

As shown in Tables III–V the apparent standard deviations in the corresponding dimensions are approximately the same for both structures. This is because the higher R value for the strontium compound approximately compensates for the improvement to be expected from the larger number of measured structure amplitudes and the smaller scattering power of the strontium as compared with the barium ion. The agreement between chemically indistinguishable bonds within the entities can be used as a check on the reliability of the standard deviations which, as quoted, assume that ΔF is random. Two sets of bonds were used, C_{sp^3}–O and C–C in benzene which are shown in Table V to

TABLE IV. Strontium Complex.

(a) Distances (Å) with Standard Deviations in Parentheses for the Coordination About the Strontium Ion

Sr–O(1)	2.723(4)	Sr–O(23)	2.553(5)
Sr–O(4)	2.662(5)	Sr–O(24)	2.578(5)
Sr–O(7)	2.675(5)	Sr–O(25)	2.574(5)
Sr–O(10)	2.670(5)		
Sr–O(13)	2.682(6)		
Sr–O(16)	2.683(5)		

(b) Angles Subtended at Strontium in the Form O(A)–Sr–O(B)°, Standard Deviations 0.2°

(A)	(B): O(4)	O(7)	O(10)	O(13)	O(16)	O(23)	O(24)	O(25)
O(1)	59.4	121.5	154.8	113.0	56.0	78.5	74.2	124.6
O(4)	–	62.9	113.0	151.7	114.9	76.0	70.0	137.9
O(7)		–	61.7	122.3	176.8	96.9	78.2	92.5
O(10)			–	60.9	121.4	76.3	128.1	78.1
O(13)				–	60.8	75.7	137.0	70.1
O(16)					–	84.7	98.8	87.7
O(23)						–	143.9	144.2
O(24)							–	71.8

(c) Bond Lengths and Angles in the Perchlorate Ions

Cl(1)–O(26)	1.414(9)	Cl(2)–O(30)	1.415(6)
Cl(1)–O(27)	1.386(7)	Cl(2)–O(31)	1.416(7)
Cl(1)–O(28)	1.427(6)	Cl(2)–O(32)	1.383(8)
Cl(1)–O(29)	1.446(7)	Cl(2)–O(33)	1.411(7)

	O(A)–Cl(1)–O(B)				O(C)–Cl(2)–O(D)		
(A)	(B): (27)	(28)	(29)	(C)	(D): (31)	(32)	(33)
(26)	110.4	110.5	107.3	(30)	111.2	109.2	106.9
(27)	–	109.6	108.9	(31)	–	109.5	108.0
(28)		–	110.1	(32)		–	112.0

Estimated standard deviations in the angles are in the range 0.4–0.6°.

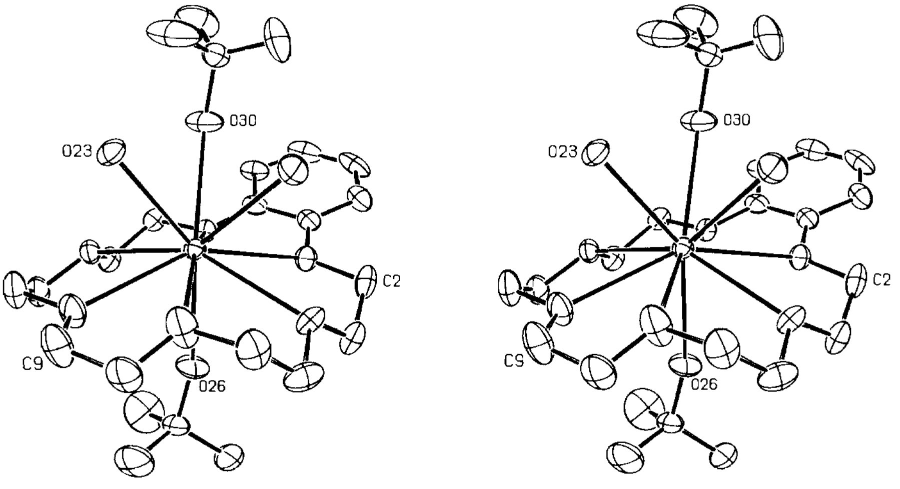

Figure 2. Stereo diagram of the bisperchloratobisaquo(benzo-18-crown-6)barium, calculated by the program ORTEP [5] showing the ellipsoids of vibration at the 50% confidence level.

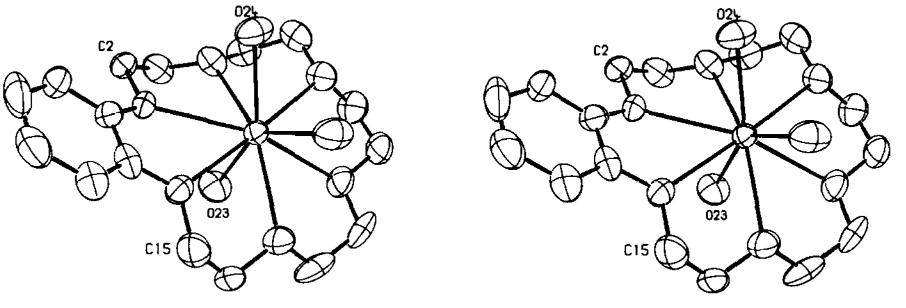

Figure 3. Stereo diagram of the complex cation of trisaquo(benzo-18-crown-6)strontium, calculated by the program ORTEP [5] showing the ellipsoids of vibration at the 50% confidence level.

TABLE V. Bond Lengths, Å, Angles, °, Torsion Angles in Benzo-18-crown-6 in the two Complexes.

	Bond Lengths (Å), Standard Deviations in Parentheses	
	M = Ba	M = Sr
O(1)–C(2)	1.454(10)	1.435(7)
C(2)–C(3)	1.484(13)	1.479(11)
C(3)–O(4)	1.414(10)	1.418(10)
O(4)–C(5)	1.445(10)	1.448(10)
C(5)–C(6)	1.505(14)	1.498(12)
C(6)–O(7)	1.430(11)	1.431(10)
O(7)–C(8)	1.356(11)	1.437(10)
C(8)–C(9)	1.448(14)	1.481(12)
C(9)–O(10)	1.392(10)	1.412(9)
O(10)–C(11)	1.449(11)	1.396(10)
C(11)–C(12)	1.471(13)	1.485(13)
C(12)–O(13)	1.445(11)	1.407(11)
O(13)–C(14)	1.428(10)	1.449(10)
C(14)–C(15)	1.477(12)	1.491(12)
C(15)–O(16)	1.433(9)	1.451(9)
O(16)–C(17)	1.386(9)	1.384(8)
C(17)–C(18)	1.387(11)	1.370(10)
C(18)–C(19)	1.410(12)	1.391(12)
C(19)–C(20)	1.355(14)	1.392(17)
C(20)–C(21)	1.372(13)	1.340(12)
C(21)–C(22)	1.381(11)	1.376(11)
C(22)–O(1)	1.389(9)	1.389(9)
C(17)–C(22)	1.419(11)	1.363(10)

	Bond Angles (°)	
Ranges of Standard Deviations:	0.6–1.0°	0.4–0.9°
C(22)–O(1)–C(2)	117.9	117.2
O(1)–C(2)–C(3)	107.9	109.5
C(2)–C(3)–O(4)	109.3	106.5
C(3)–O(4)–C(5)	112.0	113.3
O(4)–C(5)–C(6)	106.5	106.3
C(5)–C(6)–O(7)	113.1	111.2
C(6)–O(7)–C(8)	116.7	111.5
O(7)–C(8)–C(9)	113.8	106.8
C(8)–C(9)–O(10)	112.5	108.9
C(9)–O(10)–C(11)	116.5	113.6
O(10)–C(11)–C(12)	107.1	108.2

TABLE V. (continued)

C(11)–C(12)–O(13)	110.8	108.4
C(12)–O(13)–C(14)	110.2	111.6
O(13)–C(14)–C(15)	110.3	108.5
C(14)–C(15)–O(16)	108.0	108.0
C(15)–O(16)–C(17)	116.0	117.1
O(16)–C(17)–C(22)	114.4	115.1
O(16)–C(17)–C(18)	124.5	124.0
C(22)–C(17)–C(18)	121.1	120.6
C(17)–C(18)–C(19)	118.1	119.8
C(18)–C(19)–C(20)	120.0	119.1
C(19)–C(20)–C(21)	122.3	119.1
C(20)–C(21)–C(22)	119.8	122.5
C(21)–C(22)–O(1)	125.5	126.3
C(17)–C(22)–O(1)	115.9	115.1
C(21)–C(22)–C(17)	118.6	118.6

	Torsion Angles (°)	
Range of Standard Deviations:	0.7–1.2°	0.6–0.9°
C(22)–O(1)–C(2)–C(3)	−167	−172
O(1)–C(2)–C(3)–O(4)	−61	−55
C(2)–C(3)–O(4)–C(5)	−168	−166
C(3)–O(4)–C(5)–C(6)	178	171
O(4)–C(5)–C(6)–O(7)	60	61
C(5)–C(6)–O(7)–C(8)	102	95
C(6)–O(7)–C(8)–C(9)	174	178
O(7)–C(8)–C(9)–O(10)	42	62
C(8)–C(9)–O(10)–C(11)	174	172
C(9)–O(10)–C(11)–C(12)	−151	−174
O(10)–C(11)–C(12)–O(13)	−60	−60
C(11)–C(12)–O(13)–C(14)	175	−177
C(12)–O(13)–C(14)–C(15)	176	172
O(13)–C(14)–C(15)–O(16)	63	55
C(14)–C(15)–O(16)–C(17)	168	159
C(15)–O(16)–C(17)–C(22)	−176	−165
O(16)–C(17)–C(22)–O(1)	−2	−2
C(17)–C(22)–O(1)–C(2)	175	175

have apparent e.s.d.'s of 0.011 and 0.012 Å. Their values were calculated and the standard deviation in individual values derived from the spread about the mean. For the barium compound the two σ values were 0.030 and 0.024 Å, and for the strontium com-

TABLE VI. Mean Planes through Various Groups of Atoms. Equations of the planes are mX' + nY' + lZ' + d = 0 where X', Y' and Z' are distances in Å with reference to an orthogonal system of axes related to the crystallographic axes by $X' = ax + cz\cos\beta$, $Y' = by$, $Z' = cz\sin\beta$.

For the Barium Compound	m	n	l	d
Plane A	0.3205	−0.9139	−0.2488	0.9463
Plane B	0.1043	−0.8692	−0.4833	2.6725
Plane C	0.1500	−0.8756	−0.4589	2.4140
For the Strontium Compound				
Plane D	−0.9281	0.3718	0.0141	1.3578
Plane E	−0.9917	0.0223	−0.1261	3.7397
Plane F	−0.9886	0.1390	−0.0572	2.9885

Distances 10^3 Å of atoms from the planes, * marks an atom included in the calculation of the plane.

Benzene rings	M = Ba Plane A	M = Sr Plane D
C(17)*	8(8)	−21(7)
C(18)*	−4(9)	18(8)
C(19)*	−2(10)	−4(9)
C(20)*	5(11)	0(9)
C(21)*	1(9)	−12(8)
C(22)*	−6(8)	21(8)
O(1)	−16(5)	53(4)
O(16)	57(5)	27(5)

Ether Oxygen Atoms	Plane B	Plane E
O(1)*	−14(5)	82(5)
O(4)*	152(6)	353(6)
O(7)*	−304(7)	−546(6)
O(10)*	144(7)	298(6)
O(13)*	28(5)	152(6)
O(16)*	−63(5)	−321(6)
M^{2+}	−721(0.4)	−397(1)

Five Ether Oxygen Atoms	Plane C	Plane F
O(1)*	−11(5)	75(4)
O(4)*	12(6)	−15(6)
O(10)*	−16(7)	−69(6)
O(13)*	12(5)	151(6)
O(16)*	0(5)	−148(6)
O(7)	−528(8)	−1094(6)
M^{2+}	−800(0.4)	−585(1)

Angle between planes A and C = 15.7° and between planes D and F = 14.4°.

TABLE VII. Barium Complex.

(a) Possible Hydrogen Bonded Contacts and the Angles, °, Subtended at Water Molecules. (b) Intermolecular Distances, Å, less than 3.6 Å between Atoms Other than Hydrogen.

(a)			
O(23)···O(28^{I})	2.952	Ba–O(23)···O(28^{I})	138.6°
O(23)···O(31)	2.840	Ba–O(23)···O(31)	102.5
		O(28^{I})···O(23)···O(31)	107.9
O(24)···O(32^{II})	2.999	Ba–O(24)···O(32^{II})	129.5
O(24)···O(33)	3.289	Ba–O(24)···O(33)	99.3
		O(32^{II})···O(24)···O(33)	128.3

(b) Atom a	Atom b	a–b	a → b	b → a
O(23)	C(15)	3.358	II	III
O(27)	C(14)	3.267	IV	IV
O(27)	C(21)	3.497	V	VI
O(29)	C(5)	3.289	VII	VII
O(31)	C(3)	3.275	VIII	IX
O(31)	C(2)	3.351	VIII	IX
O(33)	C(11)	3.132	VI	V
C(18)	C(22)	3.595	X	X
C(17)	C(21)	3.510	X	X
C(17)	C(20)	3.600	X	X

Roman numerals refer to the following relations to the coordinates x, y, z in Table I

I	$\frac{1}{2} - x, \frac{1}{2} + y, -z$
II	$-\frac{1}{2} + x, \frac{1}{2} - y, z$
III	$\frac{1}{2} + x, \frac{1}{2} - y, z$
IV	$1 - x, -y, -z$
V	$x, y, z - 1$
VI	$x, y, z + 1$
VII	$-x, -y, -z$
VIII	$\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$
IX	$\frac{1}{2} - x, -\frac{1}{2} + y, 1 - z$
X	$1 - x, -y, 1 - z$

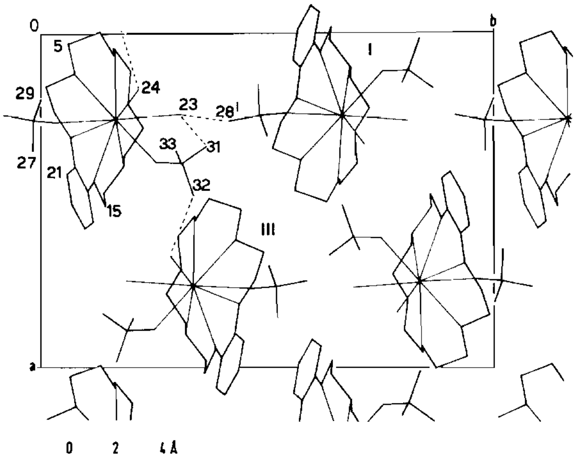

Figure 4. Projection of the structure of the barium complex on the (001) plane. Broken lines indicate hydrogen bonds. Some atoms have been designated by numbers only. The Roman numeral superscripts are defined in Table VII.

TABLE VIII. Intermolecular Distances, in the Strontium Compound.

(a) From Water Molecules (with angles subtended at the water molecules)

O(23)···O(28$^{\mathrm{I}}$)	2.900	O(28$^{\mathrm{I}}$)···O(23)···O(33)	89.7°
O(23)···O(33)	2.843		
O(24)···O(29$^{\mathrm{II}}$)	2.850	O(29$^{\mathrm{II}}$)···O(24)···O(30$^{\mathrm{III}}$)	101.9°
O(24)···O(30$^{\mathrm{III}}$)	3.005		
O(25)···O(26$^{\mathrm{II}}$)	3.141	O(26$^{\mathrm{II}}$)···O(25)···O(31$^{\mathrm{II}}$)	108.7°
O(25)···O(31$^{\mathrm{II}}$)	2.914		

(b) Other Short Contacts (C···C less than 3.6 Å, O···C less than 3.5 Å), including contacts between ionic groups of the same asymmetric unit

Atom a	Atom b	a → b	b → a	Distance
O(26)	C(11)	IV	VII	3.384
O(30)	C(8)	IV	VII	3.454
O(27)	C(6)	V	VIII	3.472
O(32)	C(5)	I	III	3.115
O(32)	C(6)	I	III	3.400
O(33)	C(2)	I	III	3.478
O(32)	C(12)	VI	II	3.251
O(33)	C(15)	VI	II	3.356
O(29)	C(15)	IX	X	3.469
O(30)	C(17)			3.482
O(30)	C(15)			3.317
O(28)	C(21)			3.443
O(29)	C(2)			3.397
O(30)	C(15)			3.317
O(30)	C(17)			3.482
O(31)	C(2)			3.400
O(31)	C(22)			3.195
C(12)	C(20)	I	III	3.580
C(6)	C(6)	XI	XI	3.576

Roman numerals refer to the following relations to the coordinates x, y, z in Table II

I	$-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$
II	$\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$
III	$\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$
IV	$\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$
V	$\frac{1}{2}-x, \frac{1}{2}+y, -\frac{1}{2}-z$
VI	$-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$
VII	$\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$
VIII	$\frac{1}{2}-x, -\frac{1}{2}+y, -\frac{1}{2}-z$
IX	$x, y, z-1$
X	$x, y, z+1$
XI	$1-x, -y, -z$

pound the two σ values were 0.025 and 0.019 Å indicating that the apparent values are optimistic by at least a factor of 2. When allowance is made for this Table V shows no significant difference in bond lengths and angles, while only about C(8)–C(9) and O(10)–C(11) are differences in torsion angles possibly significant.

The bond lengths and angles in the crown ligands agree with those reported previously, typical features include short aliphatic C–C bond lengths, C–O–C bond angles greater than 109.5° and C–C–O angles for the catechol oxygen atoms, *i.e.* C(17)–C(22)–O(1) and C(22)–C(17)–O(16) of less than 120°. With no benzene rings in the molecule, as in 18-crown-6, a conformation can be adopted with the six oxygen atoms equidistant (~2.8 Å) from a point and more or less coplanar; this is found in complexes with cations, potassium [10], rubidium [11] and caesium [12], in the adduct with hydrated uranyl nitrate [13], and the hydrogen-bonded complex with dimethyl acetylene dicarboxylate [14]. This conformation has approximately D_{3d} symmetry and the torsion angles are *gauche* (~ ± 60°) about the C–C bonds and *trans* (~180°) about the C–O bonds. If there are two benzene rings substituted in the molecule to allow approximate *mm* symmetry, torsion angles are constrained to be *ca.* zero at the benzene rings but the oxygen atoms may still be nearly coplanar, ±0.1

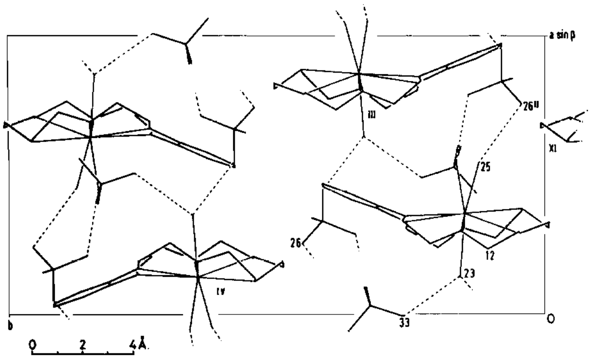

Figure 5. Projection of the structure of the strontium compound down the *c* axis. Broken lines indicate hydrogen bonds. Some of the atoms have been designated by numbers only. Roman numeral superscripts are defined in Table VIII. In this view O(30) and O(31) are nearly coincident, ions with relation X and IX are respectively nearer to and further from the reader than those with the coordinates of Table II. Similarly, ions of relation II are nearer than those of relation III. The hydrogen bond from water molecules O(24) and O(25) to the perchlorate oxygen atoms $O(30^{III})$ and $O(31^{II})$ respectively are not shown by broken lines, they hold the cations and anions alternately along the *c* axis.

Å, as in the sodium or rubidium complexes of dibenzo-18-crown-6 [15, 16]; substitution in the macrocyclic ring leads to greater deviations from the plane, ±0.24 and ±0.34 Å in the caesium complexes with two different isomers of tetramethyl dibenzo-18-crown-6 [17]. For benzo-18-crown-6, two-fold symmetry might be expected; in fact, the torsion angles show mirror symmetry from the benzene ring to C(5)–C(6) and C(11)–C(12) but very different values about C(6)–O(7) and O(10)–C(11) with the result that, as shown in Table VI plane C, the ring can be considered as having 5 oxygen atoms in one plane with the sixth, O(7), being out of this plane on the same side as the barium ion and its three additional ligating atoms.

The asymmetry is more pronounced in the strontium complex, the torsion angle at C(6)–O(7) being 95° and that at O(10)–C(11) –174°; and O(7) is 1.0 Å out of the plane F of the other five oxygen atoms. This is comparable with, but less marked than, the behaviour of 18-crown-6 with sodium thiocyanate [18] in which one oxygen atom is 1.95 Å out of the plane of the other five thus allowing all six oxygen atoms to be within 2.6 Å of the cation.

Values for 45 Ba–O distances and for 31 Sr–O distances have been summarised by Brown and Wu [19] in the form of parameters R_1 and N in the empirical relation $S = (R/R_1)^{-N}$ where S is the 'bond valence' and R the cation to oxygen distance. In the present compound the barium oxygen distances are similar whether they are from the macrocyclic ether, the perchlorate ions or water molecules, with 'bond valences' of between 0.18 and 0.26 for the longest and shortest respectively; the total bond valence, as so often for barium compounds, adds up to 2.3 instead of the ideal value of 2.0. In the strontium compound, on the other hand, the water molecules, with less steric restriction, are closer to the strontium, their average 'bond valence' being 0.28 while for the oxygen atoms of the macrocyclic ether, the average bond valence is 0.21; the total from the nine contacts is 2.09.

Some recently published comparable structures include the hydrated glycine complexes of barium and strontium chlorides [20]. In these complexes, (i) the anion is coordinated to barium but not to strontium, (ii) there is no distinction between M^{2+}–O distances from H_2O or glycine (Ba–O in the range 2.745–2.892 Å and Sr–O in the range 2.537–2.746 Å) and (iii) in both the cations are 9 coordinated.

In both our structures, the average value for the perchlorate Cl–O bond lengths are smaller than the value of 1.45 Å as established by low temperature work on small molecules [21]. This is probably due to errors caused by the librational motion of the ions. As shown in Tables I and II and Figure 2 the perchlorate oxygen atoms have large vibrations, the smallest values being for O(26) and O(30) which are attached to the barium atom. Individual Cl–O distances can be affected by the other interactions of the oxygen atom (see below).

Although in both structures it was possible to include the estimated contributions of hydrogen atoms on the carbon atoms, in neither was it possible to locate the hydrogen atoms of the water molecules so that deductions about hydrogen bonding are made from interatomic distances and angles. In the strontium compound, Table VIII and Figure 5, the water molecule O(23) makes two contacts to other oxygen atoms 2.9 and 2.8 Å with an angle of 90°, O(24) has one short contact of 2.85 Å and a rather long one of 3.0 with a very satisfactory angle, and both contacts from O(25) would correspond to long hydrogen bonds but again at a satisfactory angle. These bonds hold the structure in the *ac* plane reinforcing the electrostatic attraction between the complex cations and the anions. Three of the oxygen atoms of each perchlorate ion accept hydrogen bonds, and have Cl–O bond lengths greater than 1.41 Å while the fourth has a shorter bond, Cl(1)–O(27) = 1.386 Å and Cl(2)–O(32) = 1.383 Å. From the O···O distances electrostatic hydrogen bond acceptor values can be calculated as in Brown's treatment [21] of the hydrates of perchloric acid, and from these the bond valence of each O–H in the water molecules can be deduced. It will be seen in Table IX that the sum of the bond valences round the oxygen atoms of the coordinated water molecules is close to the ideal value of 2.

In the barium complex, as shown in Table VII and

TABLE IX. Sum of 'Bond Valences' round Oxygen Atoms of the Water Molecules in the Strontium Compound (a), the Barium Compound (b).

(a)			
O(23)–H···$O(28^{I})$	0.85	O(24)–H···$O(29^{II})$	0.81
O(23)–H···O(33)	0.83	O(24)–H···$O(30^{III})$	0.88
O(23)–Sr	0.29	O(24)–Sr	0.27
	1.97		1.96
O(25)–H···$O(26^{II})$	0.91		
O(25)–H···$O(31^{II})$	0.85		
O(25)–Sr	0.27		
	2.03		
(b)			
O(23)–H···$O(28^{I})$	0.86	O(24)–H···$O(32^{II})$	0.87
O(23)–H···O(31)	0.83	O(24)–H···O(33)	0.93
O(23)–Ba	0.26	O(24)–Ba	0.22
	1.95		2.02

Figure 4, the water molecule O(23) forms two hydrogen bonds while O(24) forms a longer one, to $O(32^{II})$ along the *a* axis, with a further intramolecular contact to O(33) which is probably not a hydrogen bond. This difference in hydrogen bonding donor capacity is consistent with the shorter Ba–O(23) bond. Hydrogen bonding holds the molecules in the *ab* plane. The shortest intermolecular distance, 2.45 Å between hydrogen atoms is also in this plane (H(12A) to H-$(8A^{III})$ or H(8A) to $H(12A^{III})$. The most important packing contact in the *c* axis direction appears to be between the parallel planes of the benzene rings related by centres of symmetry at ½, 0, ½, *etc.*, several carbon···carbon distances, relation X, being between 3.5 and 3.6 Å.

Of the perchlorate oxygen atoms, O(26) and O(30) coordinate the barium ion while O(31), O(28), O(32) and, possibly O(33) are acceptors of hydrogen bonds. There is no correlation between these other contacts and the Cl–O bond lengths.

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