& Youngs, 1979), 1·807 (6) Å in $[W(\equiv CH\cdot AlMe_{1\cdot 82}Cl_{1\cdot 18})(Cl)(PMe_3)_3]$ (Churchill, Rheingold & Wasserman, 1981), 1·82 (2) Å in $[W\{\equiv C(p\text{-tolyl})\}(\eta^5\text{-}C_5H_5)(CO)_2]$ (Huttner, Frank & Fischer, 1976) and 1·89 (3) Å in $[W(\equiv CMe)(Me)(PMe_3)_4]$ (IV) (Chiu, Jones, Wilkinson, Galas, Hursthouse & Malik, 1981). Reported values for W—C double bonds are 1·88 (1) Å in $[W(O)(=CHCMe_3)(PEt_3)Cl_2]$ (Churchill, Missert & Youngs, 1981) and 1·942 (9) Å in (III).

The W—I distance of 2·881 (2) Å is slightly longer than the value of 2·845 (5) Å in $[W(=CC_6H_5)(CO)_4I]$ (Huttner, Lorenz & Gartzke, 1974). Also, the W—P distances of 2·519 (4) and 2·507 (4) Å are slightly longer than the average W—P distances of 2·450 (2) Å in (IV) and 2·467 (2) Å in (II). Other distances and angles in the cation and anion appear to be normal.

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# The Structures of 1,4,7,14,23-Pentaoxa[7]orthobenzeno[2](2,6)pyridino[2]orthobenzenophane* ('Dibenzopyridino-18-crown-6') in its Hydrated Ethanol Inclusion Compound (1), $C_{23}H_{23}NO_5.CH_3CH_2OH.0\cdot 12H_2O$, and its Sodium Isothiocyanate Complex (2), $C_{23}H_{23}NO_5.NaNCS$

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**Abstract.** (1): $M_r = 441\cdot 67$, tetragonal, $I4/m$, $a = 15\cdot 342$ (5), $c = 19\cdot 397$ (6) Å, $U = 4565\cdot 6$ Å$^3$, $Z = 8$, $D_x = 1\cdot 285$ Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71069 Å, $\mu = 0\cdot 08$ mm$^{-1}$, $F(000) = 1882$ (calculated for one water molecule per unit cell), $T = 291$ K, $R = 0\cdot 058$ for 1403 diffractometer data. (2): $M_r = 474\cdot 51$, triclinic, $P\bar{1}$, $a = 11\cdot 529$ (4), $b = 14\cdot 667$ (6), $c = 14\cdot 724$ (6) Å, $\alpha = 87\cdot 12$ (5), $\beta = 81\cdot 11$ (6), $\gamma = 68\cdot 58$ (6)°, $U = 2289\cdot 9$ Å$^3$, $Z = 4$, $D_x = 1\cdot 376$ Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71069 Å, $\mu = 0\cdot 19$ mm$^{-1}$, $F(000) = 988$, $T = 291$ K, $R = 0\cdot 054$ for 4900 reflections. In its ethanol inclusion compound, the title crown ether possesses nearly the same molecular geometry and conformation as its xylylene analogue, but a different packing; on sodium uptake, the slight conformational changes imply weak cation–dipole interactions involving the six heteroatoms.

**Introduction.** The current macrocycle $L$ was reported to coordinate alkali, alkaline-earth and transition-metal ions (Weber & Vögtle, 1976) and also to form a variety of stoicheiometric and non-stoicheiometric crystalline compounds with small neutral molecules (Vögtle & Müller, 1980; Vögtle, Müller & Weber, 1980). In

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* Nomenclature from Weber & Vögtle (1976).

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Table 1. *Atomic coordinates* (× $10^4$) *and isotropic thermal parameters* (Å$^2$ × $10^3$) *for* (1)

| | $x$ | $y$ | $z$ | $U$ |
|---|---|---|---|---|
| O(1) | 6025 (2) | 3238 (2) | 5000 | 53 (1)* |
| C(2) | 6541 (2) | 3144 (2) | 4400 (1) | 55 (1)* |
| C(3) | 5993 (2) | 3273 (2) | 3771 (1) | 56 (1)* |
| O(4) | 5392 (1) | 2568 (1) | 3708 (1) | 51 (1)* |
| C(5) | 4861 (2) | 2569 (2) | 3144 (1) | 42 (1)* |
| C(6) | 4203 (2) | 1932 (2) | 3145 (1) | 42 (1)* |
| O(7) | 4185 (1) | 1407 (1) | 3709 (1) | 53 (1)* |
| C(8) | 3496 (2) | 776 (2) | 3759 (2) | 54 (1)* |
| C(9) | 3660 (2) | 275 (2) | 4409 (1) | 45 (1)* |
| N(10) | 3461 (2) | 689 (2) | 5000 | 46 (1)* |
| C(11) | 4030 (2) | −546 (2) | 4392 (2) | 50 (1)* |
| C(12) | 4224 (3) | −963 (3) | 5000 | 55 (1)* |
| C(13) | 3632 (2) | 1886 (2) | 2595 (1) | 53 (1)* |
| C(14) | 3706 (2) | 2463 (2) | 2046 (2) | 58 (1)* |
| C(15) | 4347 (2) | 3080 (2) | 2044 (1) | 55 (1)* |
| C(16) | 4928 (2) | 3139 (2) | 2594 (1) | 49 (1)* |
| O($E$1)† | 3672 (5) | 3298 (5) | 0 | 134 (3)* |
| O($E$2)† | 3805 (7) | 4892 (9) | 312 (6) | 50 (4) |
| C($E$1) | 3940 (7) | 4130 (6) | 0 | 198 (6)* |
| C($E$2) | 3847 (7) | 4499 (7) | 709 (6) | 124 (3) |
| O($W$)† | 0 | 0 | 0 | 270 (23)* |

* Equivalent isotropic $U$ defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

† Occupancy factors: $f = 0{\cdot}343$ (5) for O($E$1), $0{\cdot}5 - f$ for O($E$2); for O($W$): 0·060 (5).

contrast, some of its homologues [particularly its xylylene analogue (3)] demonstrate little or no such tendencies (Vögtle, Müller & Weber, 1980; *cf.* Cram & Cram, 1978; de Boer, Reinhoudt, Harkema, van Hummel & de Jong, 1982). The structure of (3) has recently been reported (Weber & Jones, 1983*a*). The present X-ray analyses may help to elucidate the correlation between the chemical and/or crystal structures and the coordination (or inclusion) abilities of this class of crown ethers.

**Experimental.** Samples kindly provided by Professor F. Vögtle and Dr E. Weber, University of Bonn (FRG). (1) recrystallized from ethyl acetate/hexane (Weber & Vögtle, 1976), (2) from ethyl acetate/methanol. Data for (2), when differing from those for (1), are given in square brackets in the following. Crystal *ca* 0·3 × 0·4 × 0·5 [0·2 × 0·4 × 0·65] mm, Stoe–Siemens AED diffractometer, cell dimensions from $2\theta$ angles for 33 [34] reflections with $20 \leq 2\theta \leq 25°$; 2243 [8829] profile-fitted (Clegg, 1981*a*) data up to $2\theta = 50°$, $0[-13] \leq h \leq 18[1]$, $-1[-17] \leq k \leq 18[17]$, $0[-17] < l < 23[17]$, 2074 [8049] unique ($R_{\rm int} = 0{\cdot}027$ [0·029]), 1403 [4900] with $F > 4\sigma(F)$; no significant decline in intensity for three standard reflections, no absorption correction. Structures solved by multi-solution direct methods and subsequent difference Fourier syntheses, blocked-cascade refinement on $F$, $w^{-1} = \sigma^2(F) + gF^2$ with $g = 6{\cdot}3[1{\cdot}3] \times 10^{-4}$, ligand H atoms in calculated positions (C—H = 0·96 Å) treated as 'riding atoms', all isotropic $U(\mathrm{H}_i)$ fixed at $1{\cdot}2 \times U_{\rm eq}(\mathrm{C}_i)$, anisotropic temperature factors for non-H atoms except O($E$2) and C($E$2) in (1); 161 [596] LS parameters, $wR = 0{\cdot}059$ [0·048], slope of probability plot 1·43 [1·52], max. $\Delta/\sigma$ 0·026 [0·069], mean 0·004 [0·022], max. $\Delta\rho$ excursions 0·28 [0·40, close to C(58)] e Å$^{-3}$, minimum 0·30 [0·28] e Å$^{-3}$; scattering factors from *International Tables for X-ray Crystallography* (1974); program for structure solution, refinement, graphical display and geometrical calculations (*SHELXTL*) written by Professor G. M. Sheldrick (1978), for diffractometer control by Dr W. Clegg, both at Göttingen.

Table 2. *Atomic coordinates* (× $10^4$) *and equivalent isotropic thermal parameters* (Å$^2$ × $10^3$), *defined as one third of the trace of the orthogonalized* $U_{ij}$ *tensor, for* (2)

| | $x$ | $y$ | $z$ | $U$ |
|---|---|---|---|---|
| Na | 2151 (1) | −181 (1) | 1774 (1) | 61 (1) |
| S | −2331 (1) | 665 (1) | 3351 (1) | 81 (1) |
| C | −955 (4) | 478 (2) | 2742 (2) | 61 (2) |
| N | −10 (3) | 337 (3) | 2288 (2) | 105 (2) |
| Na(1) | 2297 (1) | −5699 (1) | 6705 (1) | 63 (1) |
| S(1) | −2203 (1) | −4782 (1) | 8461 (1) | 79 (1) |
| C(1) | −814 (3) | −5031 (2) | 7844 (2) | 54 (1) |
| N(1) | 152 (3) | −5187 (2) | 7404 (2) | 82 (2) |
| O(1) | 2314 (2) | −1498 (1) | 3077 (1) | 59 (1) |
| C(2) | 1704 (3) | −2139 (2) | 2914 (2) | 62 (2) |
| C(3) | 2399 (3) | −2713 (2) | 2065 (2) | 62 (2) |
| O(4) | 2296 (2) | −2035 (1) | 1321 (1) | 54 (1) |
| C(5) | 2913 (3) | −2419 (2) | 481 (2) | 47 (1) |
| C(6) | 2874 (3) | −1736 (2) | −220 (2) | 50 (1) |
| O(7) | 2255 (2) | −777 (1) | 59 (1) | 62 (1) |
| C(8) | 1808 (3) | −90 (2) | −608 (2) | 78 (2) |
| C(9) | 1391 (3) | 934 (2) | −252 (2) | 51 (1) |
| N(10) | 1901 (2) | 1084 (2) | 447 (2) | 52 (1) |
| C(11) | 1623 (3) | 2014 (2) | 693 (2) | 51 (1) |
| C(12) | 2301 (3) | 2201 (2) | 1410 (2) | 70 (2) |
| O(13) | 2461 (2) | 1476 (1) | 2096 (1) | 56 (1) |
| C(14) | 3119 (3) | 1547 (2) | 2778 (2) | 48 (1) |
| C(15) | 3202 (3) | 857 (2) | 3479 (2) | 51 (1) |
| O(16) | 2601 (2) | 224 (2) | 3391 (1) | 63 (1) |
| C(17) | 2645 (3) | −480 (2) | 4107 (2) | 70 (2) |
| C(18) | 1813 (3) | −1002 (2) | 3929 (2) | 67 (2) |
| C(19) | 3854 (3) | 858 (2) | 4184 (2) | 65 (2) |
| C(20) | 4410 (3) | 1557 (3) | 4196 (2) | 74 (2) |
| C(21) | 4307 (3) | 2231 (3) | 3520 (3) | 75 (2) |
| C(22) | 3664 (3) | 2227 (2) | 2806 (2) | 62 (2) |
| C(23) | 833 (3) | 2801 (2) | 263 (2) | 63 (1) |
| C(24) | 300 (3) | 2628 (2) | −447 (2) | 73 (2) |
| C(25) | 575 (3) | 1683 (2) | −709 (2) | 66 (2) |
| C(26) | 3478 (3) | −2044 (2) | −1090 (2) | 61 (2) |
| C(27) | 4134 (3) | −3033 (2) | −1271 (2) | 66 (2) |
| C(28) | 4173 (3) | −3704 (2) | −588 (2) | 64 (2) |
| C(29) | 3552 (3) | −3404 (2) | 289 (2) | 59 (1) |
| O(51) | 2546 (2) | −4564 (1) | 7918 (1) | 57 (1) |
| C(52) | 2120 (3) | −4875 (2) | 8795 (2) | 59 (1) |
| C(53) | 3035 (3) | −5863 (2) | 8974 (2) | 59 (1) |
| O(54) | 3082 (2) | −6505 (1) | 8256 (1) | 57 (1) |
| C(55) | 3682 (3) | −7487 (2) | 8372 (2) | 47 (1) |
| C(56) | 3558 (3) | −8091 (2) | 7729 (2) | 51 (1) |
| O(57) | 2920 (2) | −7616 (1) | 7019 (1) | 66 (1) |
| C(58) | 2136 (4) | −7977 (4) | 6728 (3) | 132 (3) |
| C(59) | 1601 (3) | −7488 (2) | 5885 (2) | 59 (2) |
| N(60) | 1877 (2) | −6712 (2) | 5570 (2) | 57 (1) |
| C(61) | 1465 (3) | −6315 (2) | 4791 (2) | 53 (1) |
| C(62) | 1888 (3) | −5510 (2) | 4391 (2) | 69 (2) |
| O(63) | 2537 (2) | −5235 (2) | 4979 (1) | 72 (1) |
| C(64) | 3168 (3) | −4622 (2) | 4663 (2) | 56 (1) |
| C(65) | 3136 (3) | −3944 (2) | 5296 (2) | 55 (1) |
| O(66) | 2450 (2) | −3966 (1) | 6135 (1) | 60 (1) |
| C(67) | 2464 (3) | −3327 (2) | 6834 (2) | 70 (2) |
| C(68) | 1814 (3) | −3584 (2) | 7710 (2) | 64 (2) |
| C(69) | 3783 (3) | −3315 (2) | 5053 (2) | 70 (2) |
| C(70) | 4486 (3) | −3390 (2) | 4190 (2) | 76 (2) |
| C(71) | 4533 (3) | −4064 (2) | 3568 (2) | 75 (2) |
| C(72) | 3855 (3) | −4680 (2) | 3790 (2) | 71 (2) |
| C(73) | 739 (3) | 6646 (2) | 4341 (2) | 65 (2) |
| C(74) | 452 (3) | −7437 (2) | 4679 (2) | 67 (2) |
| C(75) | 912 (3) | 7879 (2) | 5456 (2) | 60 (2) |
| C(76) | 4093 (3) | −9087 (2) | 7794 (2) | 65 (2) |
| C(77) | 4765 (3) | −9495 (2) | 8515 (2) | 66 (1) |
| C(78) | 4912 (3) | −8908 (2) | 9142 (2) | 62 (1) |
| C(79) | 4372 (3) | −7898 (2) | 9080 (2) | 56 (1) |

Table 3. *Bond lengths* (Å) *and angles* (°) *for* (1) *and* (2)

| | | | |
|---|---|---|---|
| Compound (1) | | | |
| O(1)—C(2) | 1·415 (3) | C(2)—C(3) | 1·494 (4) |
| C(3)—O(4) | 1·427 (3) | O(4)—C(5) | 1·364 (3) |
| C(5)—C(6) | 1·406 (3) | C(5)—C(16) | 1·382 (4) |
| C(6)—O(7) | 1·359 (3) | C(6)—C(13) | 1·382 (4) |
| O(7)—C(8) | 1·436 (3) | C(8)—C(9) | 1·499 (4) |
| C(9)—N(10) | 1·345 (3) | C(9)—C(11) | 1·381 (4) |
| C(11)—C(12) | 1·375 (3) | C(13)—C(14) | 1·389 (4) |
| C(14)—C(15) | 1·365 (4) | C(15)—C(16) | 1·394 (4) |
| O(*E*2)—C(*E*1) | 1·333 (15) | C(*E*1)—C(*E*2) | 1·495 (12) |
| O(*E*1)—C(*E*1) | 1·341 (12) | | |
| Compound (2) | | | |
| S—C | 1·631 (4) | C—N | 1·140 (5) |
| S(1)—C(1) | 1·637 (3) | C(1)—N(1) | 1·148 (4) |
| O(1)—C(2) | 1·412 (5) | O(1)—C(18) | 1·413 (3) |
| C(2)—C(3) | 1·489 (4) | C(3)—O(4) | 1·431 (3) |
| O(4)—C(5) | 1·362 (3) | C(5)—C(6) | 1·396 (4) |
| C(5)—C(29) | 1·381 (4) | C(6)—O(7) | 1·375 (3) |
| C(6)—C(26) | 1·373 (4) | O(7)—C(8) | 1·386 (4) |
| C(8)—C(9) | 1·494 (4) | C(9)—N(10) | 1·327 (4) |
| C(9)—C(25) | 1·382 (4) | N(10)—C(11) | 1·337 (4) |
| C(11)—C(12) | 1·498 (5) | C(11)—C(23) | 1·378 (4) |
| C(12)—O(13) | 1·410 (4) | O(13)—C(14) | 1·378 (4) |
| C(14)—C(15) | 1·398 (4) | C(14)—C(22) | 1·364 (5) |
| C(15)—O(16) | 1·367 (5) | C(15)—C(19) | 1·373 (5) |
| O(16)—C(17) | 1·431 (4) | C(17)—C(18) | 1·486 (6) |
| C(19)—C(20) | 1·396 (6) | C(20)—C(21) | 1·354 (5) |
| C(21)—C(22) | 1·378 (5) | C(23)—C(24) | 1·369 (5) |
| C(24)—C(25) | 1·366 (5) | C(26)—C(27) | 1·386 (4) |
| C(27)—C(28) | 1·366 (4) | C(28)—C(29) | 1·384 (4) |
| O(51)—C(52) | 1·423 (3) | O(51)—C(68) | 1·422 (3) |
| C(52)—C(53) | 1·488 (4) | C(53)—O(54) | 1·433 (4) |
| O(54)—C(55) | 1·366 (3) | C(55)—C(56) | 1·386 (4) |
| C(55)—C(79) | 1·387 (4) | C(56)—O(57) | 1·382 (3) |
| C(56)—C(76) | 1·367 (4) | O(57)—C(58) | 1·332 (6) |
| C(58)—C(59) | 1·504 (5) | C(59)—N(60) | 1·332 (5) |
| C(59)—C(75) | 1·373 (5) | N(60)—C(61) | 1·333 (4) |
| C(61)—C(62) | 1·498 (5) | C(61)—C(73) | 1·371 (5) |
| C(62)—O(63) | 1·388 (5) | O(63)—C(64) | 1·373 (5) |
| C(64)—C(65) | 1·384 (5) | C(64)—C(72) | 1·391 (4) |
| C(65)—O(66) | 1·366 (3) | C(65)—C(69) | 1·385 (5) |
| O(66)—C(67) | 1·431 (4) | C(67)—C(68) | 1·491 (4) |
| C(69)—C(70) | 1·384 (4) | C(70)—C(71) | 1·361 (5) |
| C(71)—C(72) | 1·393 (6) | C(73)—C(74) | 1·370 (5) |
| C(74)—C(75) | 1·368 (4) | C(76)—C(77) | 1·392 (4) |
| C(77)—C(78) | 1·363 (5) | C(78)—C(79) | 1·386 (4) |
| Compound (1)* | | | |
| C(2)—O(1)—C(2*a*) | 110·7 (3) | O(1)—C(2)—C(3) | 110·1 (2) |
| C(2)—C(3)—O(4) | 109·5 (2) | C(3)—O(4)—C(5) | 117·0 (2) |
| O(4)—C(5)—C(6) | 115·3 (2) | O(4)—C(5)—C(16) | 125·1 (2) |
| C(6)—C(5)—C(16) | 119·6 (2) | C(5)—C(6)—O(7) | 115·3 (2) |
| C(5)—C(6)—C(13) | 119·3 (2) | O(7)—C(6)—C(13) | 125·4 (2) |
| C(6)—O(7)—C(8) | 117·9 (2) | O(7)—C(8)—C(9) | 106·2 (2) |
| C(8)—C(9)—N(10) | 115·9 (2) | C(8)—C(9)—C(11) | 121·1 (2) |
| N(10)—C(9)—C(11) | 123·0 (3) | C(9)—N(10)—C(9*a*) | 116·8 (3) |
| C(9)—C(11)—C(12) | 119·5 (3) | C(11)—C(12)—C(11*a*) | 118·2 (4) |
| C(6)—C(13)—C(14) | 120·5 (3) | C(13)—C(14)—C(15) | 120·1 (3) |
| C(14)—C(15)—C(16) | 120·3 (3) | C(5)—C(16)—C(15) | 120·2 (2) |
| O(*E*1)—C(*E*1)—C(*E*2) | 109·4 (6) | O(*E*2)—C(*E*1)—C(*E*2*b*) | 94·1 (8) |
| Compound (2) | | | |
| S—C—N | 177·3 (4) | S(1)—C(1)—N(1) | 178·6 (3) |
| C(2)—O(1)—C(18) | 112·1 (2) | O(1)—C(2)—C(3) | 107·9 (3) |
| C(2)—C(3)—O(4) | 107·4 (2) | C(3)—O(4)—C(5) | 116·3 (2) |
| O(4)—C(5)—C(6) | 115·2 (2) | O(4)—C(5)—C(29) | 125·2 (3) |
| C(6)—C(5)—C(29) | 119·5 (2) | C(5)—C(6)—O(7) | 114·4 (2) |
| C(5)—C(6)—C(26) | 120·0 (3) | O(7)—C(6)—C(26) | 125·5 (3) |
| C(6)—O(7)—C(8) | 117·6 (2) | O(7)—C(8)—C(9) | 111·8 (3) |
| C(8)—C(9)—N(10) | 117·8 (2) | C(8)—C(9)—C(25) | 118·7 (3) |
| N(10)—C(9)—C(25) | 123·2 (3) | C(9)—N(10)—C(11) | 117·1 (2) |
| N(10)—C(11)—C(12) | 117·7 (2) | N(10)—C(11)—C(23) | 123·1 (3) |
| C(12)—C(11)—C(23) | 119·0 (3) | C(11)—C(12)—O(13) | 110·6 (3) |
| C(12)—O(13)—C(14) | 116·0 (3) | O(13)—C(14)—C(15) | 115·1 (3) |
| O(13)—C(14)—C(22) | 124·9 (3) | C(15)—C(14)—C(22) | 120·0 (3) |
| C(14)—C(15)—O(16) | 115·1 (3) | C(14)—C(15)—C(19) | 119·6 (3) |
| O(16)—C(15)—C(19) | 125·3 (3) | C(15)—O(16)—C(17) | 116·6 (3) |
| O(16)—C(17)—C(18) | 107·2 (3) | O(1)—C(18)—C(17) | 107·9 (3) |
| C(15)—C(19)—C(20) | 119·4 (3) | C(19)—C(20)—C(21) | 120·5 (4) |
| C(20)—C(21)—C(22) | 120·4 (4) | C(14)—C(22)—C(21) | 120·1 (3) |
| C(11)—C(23)—C(24) | 118·8 (3) | C(23)—C(24)—C(25) | 118·9 (3) |
| C(9)—C(25)—C(24) | 118·8 (3) | C(6)—C(26)—C(27) | 120·0 (3) |
| C(26)—C(27)—C(28) | 120·2 (3) | C(27)—C(28)—C(29) | 120·3 (3) |
| C(5)—C(29)—C(28) | 120·0 (3) | C(52)—O(51)—C(68) | 113·3 (2) |
| O(51)—C(52)—C(53) | 108·1 (2) | C(52)—C(53)—O(54) | 107·7 (2) |
| C(53)—O(54)—C(55) | 117·5 (2) | O(54)—C(55)—C(56) | 115·8 (2) |
| O(54)—C(55)—C(79) | 124·6 (3) | C(56)—C(55)—C(79) | 119·6 (3) |
| C(55)—C(56)—O(57) | 115·5 (2) | C(55)—C(56)—C(76) | 120·6 (3) |
| O(57)—C(56)—C(76) | 123·8 (3) | C(56)—O(57)—C(58) | 118·0 (3) |
| O(57)—C(58)—C(59) | 114·2 (4) | C(58)—C(59)—N(60) | 117·3 (4) |
| C(58)—C(59)—C(75) | 119·2 (4) | N(60)—C(59)—C(75) | 123·4 (3) |
| C(59)—N(60)—C(61) | 117·2 (3) | N(60)—C(61)—C(62) | 116·9 (3) |
| N(60)—C(61)—C(73) | 122·7 (3) | C(62)—C(61)—C(73) | 120·3 (3) |
| C(61)—C(62)—O(63) | 111·4 (2) | C(62)—O(63)—C(64) | 119·2 (2) |
| O(63)—C(64)—C(65) | 115·3 (2) | O(63)—C(64)—C(72) | 124·4 (3) |
| C(65)—C(64)—C(72) | 120·2 (3) | C(64)—C(65)—O(66) | 115·1 (3) |
| C(64)—C(65)—C(69) | 119·7 (3) | O(66)—C(65)—C(69) | 125·2 (3) |
| C(65)—O(66)—C(67) | 117·2 (3) | O(66)—C(67)—C(68) | 107·1 (3) |
| O(51)—C(68)—C(67) | 106·9 (2) | C(65)—C(69)—C(70) | 119·8 (3) |
| C(69)—C(70)—C(71) | 120·8 (4) | C(70)—C(71)—C(72) | 120·2 (3) |
| C(64)—C(72)—C(71) | 119·3 (3) | C(61)—C(73)—C(74) | 119·3 (3) |
| C(73)—C(74)—C(75) | 118·8 (4) | C(59)—C(75)—C(74) | 118·5 (3) |
| C(56)—C(76)—C(77) | 119·5 (3) | C(76)—C(77)—C(78) | 120·4 (3) |
| C(77)—C(78)—C(79) | 120·4 (3) | C(55)—C(79)—C(78) | 119·5 (3) |

* Atoms indicated by *a* are generated by *x*, *y*,1−*z*, that indicated by *b* is generated by *x*, *y*, −*z*.

For (1) only: four peaks of about 1 to 2 e Å$^{-3}$ on and near the mirror were taken as fourfold-disordered ethanol O(*E*1)—C(*E*1)—C(*E*2*b*), O(*E*1)—C(*E*1)—C(*E*2), O(*E*2)—C(*E*1)—C(*E*2*b*), and O(*E*2*b*)—C(*E*1)—C(*E*2) (*b* = *x*, *y*, −*z*); occupancy factors of C(*E*1) (special position) and C(*E*2) (disorder) were kept fixed at 0·5, that of O(*E*1) (special position) was allowed to vary according to $f[\mathrm{O}(E2)] = 0{\cdot}5 - f[\mathrm{O}(E1)]$; distances O(*E*1)—C(*E*1) and O(*E*2)—C(*E*1) restrained to be identical with weights derived from $\sigma = 0{\cdot}005$ Å; one more peak on the origin taken as water (*ca* 50% occupied).

For (2) only: empirical isotropic extinction correction coefficient $x = 7{\cdot}7\,(8) \times 10^{-7}$, where $F' = F/(1{\cdot}0 + 2xF^2/\sin 2\theta)^{0{\cdot}25}$; $Z = 4$ in $P\bar{1}$ confirmed by a cell-reduction program (Clegg, 1981*b*): neither unusual extinctions (indicative of a possible twinning) nor higher symmetry could be detected.

**Discussion.** Final atom parameters are given in Tables 1 and 2,* derived bond lengths and angles in Table 3; the numbering scheme may be taken from Fig. 1.

The molecular geometry of the title ligand in (1) is nearly identical to that of its xylylene analogue (3) (Weber & Jones, 1983*a*), including a crystallographic mirror generating the second half of the molecule. Hetero-atoms are coplanar to within ±0·03 Å (plane IV) [*cf.* ±0·09 Å in (3), including C instead of N] and form a fairly regular hexagon with O(1)···O(4) = 2·878 (2) [2·873 (1) in (3)], O(4)···O(7) = 2·570 (2) [2·580 (1)], O(7)···N(10) = 2·952 (2) [O(7)···C(10) = 2·897 (1) in (3)], O(1)···N(10) = 5·547 (2) [O(1)···C(10) = 5·454 (1)], and O(4)···O(7a),

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38965 (44 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

O(4a)···O(7) = 5·631 (2) Å [5·624 (1) Å]. The sequence $ag^+aasaag^-aag^+aasaag^-a$ (Fig. 1) of endocyclic torsion angles* in (1) [and (3)] associated with the 'round' conformation of the macrocyclic chain was also found in dibenzo-18-crown-6 *complexes* (*e.g.* Bright & Truter, 1970; Bush & Truter, 1971), and a related 'round', *i.e.* '$D_{3d}$', conformation is observed in most *complexes* of 18-crown-6 itself (*e.g.* Dunitz, Dobler, Seiler & Phizackerley, 1974; Bandy, Truter & Vögtle, 1981; Weber, 1983). However, in the *uncomplexed* state [as $L$ is in (1)], the former ligands each display a different, more elongated (Bright & Truter, 1970; Maverick, Seiler, Schweizer & Dunitz, 1980) and (attributed to reduced O···O interactions) energetically more favourable (Bovill, Chadwick, Sutherland & Watkin, 1980) conformation. [More recent calculations (Wipff, Weiner & Kollman, 1982) show the difference in energies of the various conformations of 18-crown-6 to be strongly dependent on the dielectric constant, *i.e.* the polarity, of the environment.]

The pyridine nucleus (II) is bent towards the opposite side of the plane of the hetero-atoms, as are both the benzene nuclei (I) and (III) [dihedral angle (I)/(III) = 55·2 (6)°], probably to avoid steric overcrowding; the 'dentist's chair' thus formed by the present macrocycle seems a common feature in pyridino/xylyleno-benzo-crowns since it is not only found in (1) and (3) but also, in a slightly modified form, in tribenzo-pyridino-21-crown-7 (Weber & Jones, 1983*b*).

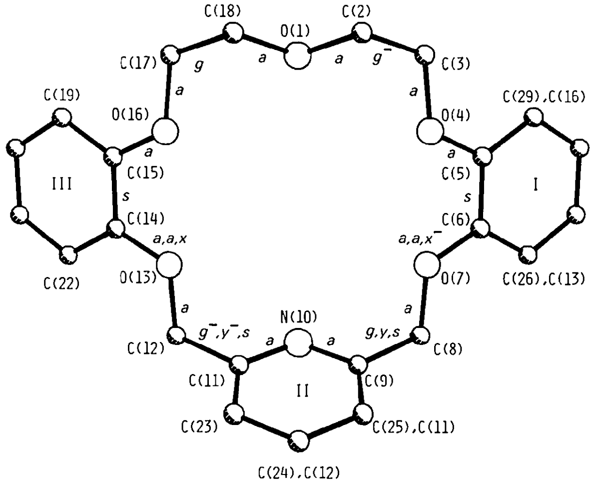

Fig. 1. The chemical structure of the title ligand $L$ [illustrated in a view down the normal to the best plane through all atoms of $L$ in (1)], showing the designation of aromatic nuclei and the numbering scheme adopted in this study. The alternative atom numbering in (I) and (II) applies to $L$ in (1), since in that structure a mirror running through O(1), N(10) [and C(12)] generates the second half of the macrocycle. In (2) there are two independent complex ion pairs, (2)*A* and (2)*B*, in the asymmetric unit; atoms in (2)*B* were numbered by adding 50. Endocyclic torsion angles [*a* = *anti*, $g^{(-)} = (-)$*gauche*, *s* = *syn*, $x^{(-)} \simeq (-)140°$, $y^{(-)} \simeq (-)30°$] are also indicated; the second and third symbols, where present, represent torsion angles in (2)*A* and (2)*B*, respectively, when differing from those in (1).

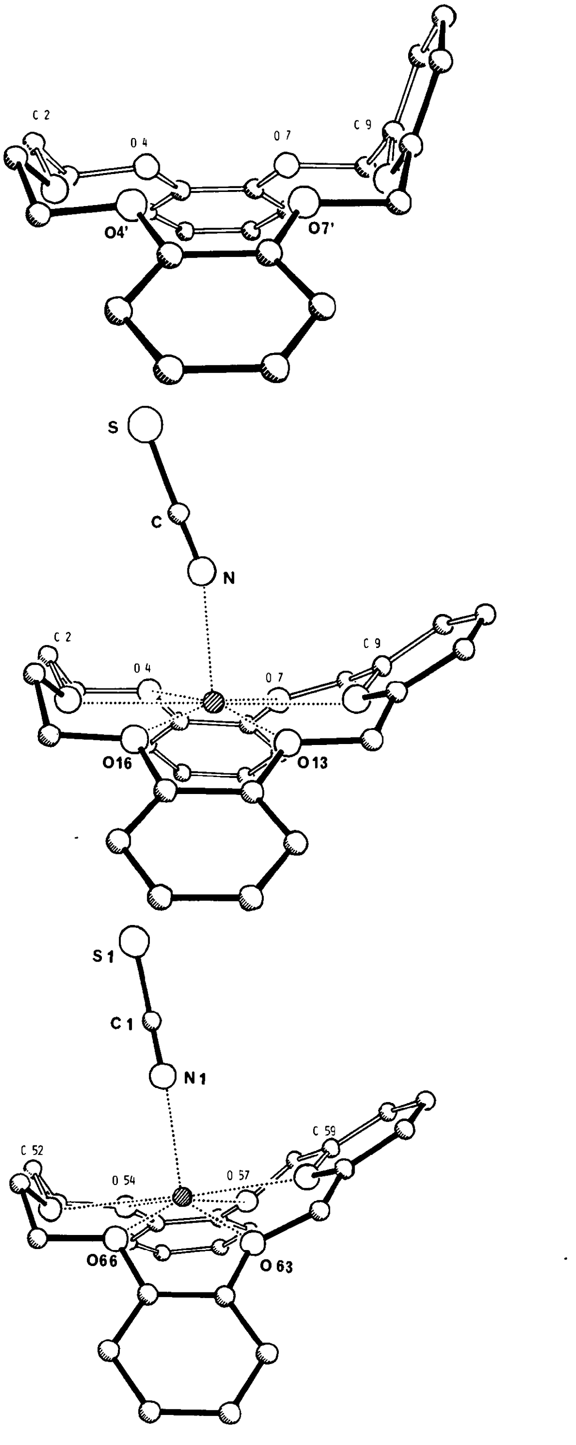

Fig. 2. Perspective views of the macrocycle $L$ in (1) (top) and of its complexes (2)*A* and (2)*B*. Radii are arbitrary, H atoms omitted for clarity. Possible interactions of Na$^+$ and Na(1)$^+$, respectively, are indicated by dotted lines.

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* See deposition footnote.

Table 4. *Coordination distances* (Å) *in* (2)

| *A* | | *B* | |
|---|---|---|---|
| Na···O(1) | 2·631 (2) | Na(1)···O(51) | 2·618 (2) |
| Na···O(4) | 2·772 (2) | Na(1)···O(54) | 2·650 (2) |
| Na···O(7) | 2·685 (2) | Na(1)···O(57) | 2·670 (2) |
| Na···N(10) | 2·601 (3) | Na(1)···N(60) | 2·501 (2) |
| Na···O(13) | 2·658 (2) | Na(1)···O(63) | 2·596 (2) |
| Na···O(16) | 2·654 (2) | Na(1)···O(66) | 2·696 (2) |
| Na···N | 2·335 (3) | Na(1)···N(1) | 2·382 (3) |

The latter forms a methanol adduct (Weber & Vögtle, 1980) *via* one strong N···H—O bond by rotation of one of the neighbouring phenylene entities, thus facilitating the attack of the lone pair of the basic pyridine N (the crown O atoms are not involved in obvious interactions) and adopting an irregular and non-symmetric conformation (Weber & Jones, 1983*b*). Conformational changes in the present ligand when binding Na are much less drastic (Figs. 1 and 2): The widening of the angle between the plane of the O atoms and the pyridine plane from 109·9 (4)° in (1) to 142·0 (5)° in (2)*A* and 144·9 (5)° in (2)*B*, respectively, [accompanied by changes in endocyclic torsion angles close to (II), see Fig. 1] enables the lone pair of the pyridine N to point towards the centre of the macrocycle and hence to participate in coordination together with the O atoms. N(10) then deviates by 0·50 (3) Å [in (2)*A*] and N(60) by as much as 0·96 (3) Å [in (2)*B*] from the plane of the O atoms [coplanar to within ±0·09 and ±0·12 Å, respectively, plane (IV)] but the 'dentist's chair' form is nevertheless retained (Fig. 2) [dihedral angle (I)/(III) = 66·5 (6) in (2)*A* and 70·4 (6)° in (2)*B*].

The cation is located approximately at the centre of the crown in both the crystallographically independent complexes (2)*A* and (2)*B* (Fig. 2); the unfavourable geometry of the (equatorial) hexagon of hetero-atoms implies only weak $Na^+\cdots O$(ether) interactions [mean distance 2·68 (5) in (2)*A* and 2·65 (5) Å in (2)*B*; for details see Table 4], since from steric considerations $Na^+$ ($r = 0{\cdot}97$ Å) (*Handbook of Chemistry and Physics*, 1970) might be regarded as a suitable guest ion for 15-membered ($d_{\text{inner}} = 1{\cdot}7$–$2{\cdot}2$ Å) rather than for 18-membered crown ethers ($d_{\text{inner}} = 2{\cdot}6$–$3{\cdot}2$ Å) (Frensdorff, 1971). Accordingly, Na usually prefers fivefold equatorial coordination with linear (*e.g.* Suh, Weber & Saenger, 1978) or annular oligoethers: in benzo-15-crown-5.NaI (Bush & Truter, 1972) the mean $Na^+\cdots O$(ether) distance of 2·39 Å nearly corresponds to the sum of respective radii (2·37 Å) (*Handbook of Chemistry and Physics*, 1970); diphenylmethano-18-crown-5 contracts its cavity on ligating Na such that the five O atoms form an approximately regular pentagon [mean $Na^+\cdots O$(ether) = 2·46 Å] (von Itter, Vögtle, Weber & Sheldrick, 1983); in 18-crown-6.NaNCS (Dobler, Dunitz & Seiler, 1974) one O atom is rotated out of the plane of the other five giving rise to a (distorted) pentagonal-(bi)pyramidal cation environment [mean $Na^+\cdots O$(ether) = 2·55 Å]. Only dibenzo-18-crown-6/$Na^+$ complexes (Bright & Truter, 1970; Bush & Truter, 1971) show a sixfold equatorial coordination [mean $Na^+\cdots O$(ether) *ca* 2·80, 2·71 Å] comparable to those in compounds (2)*A* and (2)*B*. This analogy might be attributed to the two rigid catechyl entities, present in both ligands.

The 'chair' conformations in the current complexes allow only one apex to be occupied [contrasting with dibenzo-18-crown-6.NaBr (Bush & Truter, 1971)], with $SC—N\cdots Na^+ = 162{\cdot}2$ (3)° in (2)*A* and 169·8 (2)° in (2)*B*. These different angles might be a consequence of the slightly different dihedral angles (II)/(IV) (see above), which may also give rise to the difference between $Na^+\cdots N(10) = 2{\cdot}601$ (3) and $Na(1)^+\cdots N(60) = 2{\cdot}501$ (2) Å, and the different deviations of $Na^+$ [0·25 (2) Å] and $Na(1)^+$ [0·65 (2) Å] from the respective planes (IV).

There are no unusual features in the packing of the discrete complex ion pairs in (2). In the lattice of (1), the fourfold axis is associated with channels along **c**, which are formed between macrocyclic molecules and occupied by disordered solvent molecules (Fig. 3). (1) was originally meant to be the free ligand (and not an inclusion compound), but it had already been stated (Vögtle, Müller & Weber, 1980) that 'on the contrary it proved difficult to find a solvent *not* retained' by *L*. In this connection it seems noteworthy that an *L*.diglyme compound (Müller, Vögtle & Weber, unpublished) also crystallizes in *I*4/*m* with $a = 15{\cdot}344$ (4), $c = 19{\cdot}123$ (6) Å with atomic positions for *L* deviating by at most 0·08 Å from those in (1) (G. Weber; unpublished because of insuperable difficulties in obtaining a chemically reasonable resolution of the disordered guest molecules).

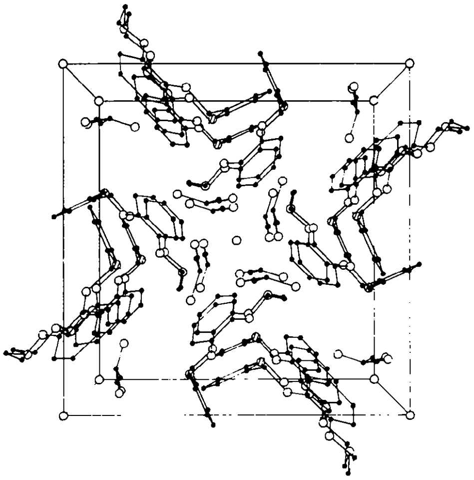

Fig. 3. The packing of macrocycles in (1); channels along **c** are occupied by disordered solvent molecules.

Differences and angles between the electron maxima of a difference map suggested ethanol to be the solvent included in (1) [probably originating from the preparation of $L$ (Weber & Vögtle, 1976)] which seems confirmed by contacts $\mathrm{O}(E2)\cdots\mathrm{O}(E2^{\mathrm{i,ii}}) = 2{\cdot}87\,(2)$ and $\mathrm{O}(E2)\cdots\mathrm{O}(E1^{\mathrm{ii}}) = 2{\cdot}41\,(1)$ Å [(i) $1-y, x, -z$; (ii) $y, 1-x, -z$]. However, $\mathrm{C}(E1)\cdots\mathrm{C}(E1^{\mathrm{ii}}) = 2{\cdot}98\,(1)$, $\mathrm{C}(E2)\cdots\mathrm{C}(E2^{\mathrm{iii}}) = 2{\cdot}73\,(1)$ Å [(iii) $1-y, x, z$], $\mathrm{C}(E2)\cdots\mathrm{O}(E2^{\mathrm{i}}) = 2{\cdot}97\,(2)$ and $\mathrm{C}(E2)\cdots\mathrm{C}(E1^{\mathrm{ii}}) = 2{\cdot}80\,(1)$ Å indicate an even more severe, but irresolvable, disorder – possibly the presence of water instead of ethanol in some sites. (Refinement with one disordered water instead of one ethanol converged at $R = 0{\cdot}076$ and $R_M{}^* = 0{\cdot}106$; *cf.* $R_M = 0{\cdot}064$ with the ethanol model.) The assumption of a (half-occupied) water molecule at the origin may be justified by the distances of 3·127 (2) Å to the O(1) atoms of neighbouring macrocycles, and by the packing (Fig. 3).

The poor ligand properties of (3) can probably be attributed (*a*) to the sterically shielding effect of the non-coordinating xylylene entity (*cf.* de Boer *et al.*, 1982), (*b*) to the lack of one basic hetero-atom, since N seems preferably involved in interactions between pyridino crowns and cationic guest species (*e.g.* Maverick, Grossenbacher & Trueblood, 1979; Weber, 1982), and (*c*) to the attenuated donor abilities of the four catecholic O atoms in (3); a hydrogen-bonded xylylo-18-crown-5/*tert*-butylammonium complex has recently been reported (Reinhoudt, den Hertog & de Jong, 1981).

The high affinity of $L$ for binding cations of different radii may be explained by the presence of a pyridine N instead of an ether O (see above) in the macrocycle, and by the slight conformational changes necessary (or possible) on complex formation. Apart from $\mathrm{Cd}^{2+}$, $\mathrm{Na}^+$ is the smallest cation reported to be ligated by $L$ (Weber & Vögtle, 1976); much larger cations will possibly be located farther from the plane of the hetero-atoms, but will be coordinated in a similar way as in (3) [*cf.* the series of $\mathrm{K}^+$,$\mathrm{Rb}^+$,$\mathrm{Cs}^+$/18-crown-6 complexes (Dunitz *et al.*, 1974)].

These considerations may also hold for the adduct formation *via* H bonds between $L$ and C—H acidic molecules (Vögtle, Müller & Weber, 1980), comparable to the widely known and structurally investigated 18-crown-6 adducts (*e.g.* Bandy *et al.*, 1981; de Boer *et al.*, 1982; Weber, 1983). However, reasons for the different packing of $L$ in (1) and of (3) (Weber & Jones, 1983*a*), *i.e.* for the differing tendencies to form inclusion compounds, are not so obvious.

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* $R_M$ is as defined in *SHELXTL*.