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Structure of a Complex between Sodium Perchlorate and 6,7,9,10,12,13,15,16,23,24,26,27-Dodecahydrodibenzo[*b*,*k*][1,4,7,10,13,16,19,22]octaoxacyclotetracosin* (Asymmetric Dibenzo-24-crown-8), $C_{24}H_{32}O_8.NaClO_4$

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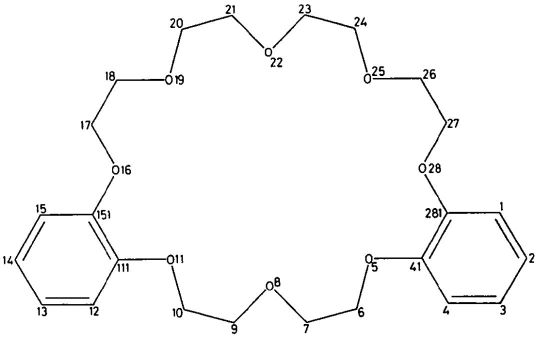
Abstract. $M_r = 571{\cdot}0$, triclinic, $P\bar{1}$, $a = 8{\cdot}782\,(2)$, $b = 11{\cdot}683\,(2)$, $c = 13{\cdot}271\,(2)$ Å, $\alpha = 94{\cdot}92\,(1)$, $\beta = 82{\cdot}52\,(2)$, $\gamma = 96{\cdot}56\,(2)°$, $U = 1338$ Å^3, $Z = 2$, $D_m = 1{\cdot}41$, $D_x = 1{\cdot}42$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 2{\cdot}15$ cm^{-1}, $F(000) = 600$, room temperature, $R = 0{\cdot}095$ for 1488 observations. The structure was solved by direct methods from data collected on a four-circle diffractometer. The polyether 'wraps around' the cation so that eight O atoms are within 2·75 Å of Na^+. The disordered anion is not coordinated to the cation, in agreement with the infrared spectrum.

Introduction. The macrocyclic crown ether (I) shown in Fig. 1 and named in the title is one of three dibenzo-24-crown-8 ligands synthesized in these laboratories (Wingfield, 1980), with benzene rings in different positions on the macrocycle. IR evidence suggests that in their unsolvated 1:1 sodium perchlorate complexes, all three forms contain isolated anions. This indicates that the ligand may be able to 'wrap around' the cations in a similar manner to that in which dibenzo-30-crown-10 can surround K (Bush & Truter, 1972) and Rb (Hašek, Huml & Hlavatá, 1979). Previously reported structures of dibenzo-24-crown-8 (Hughes, Mortimer & Truter, 1978, and references therein) have all shown the cation coordinated to solvent, or the anion(s) or both. This work is the first example of a complex of dibenzo-24-crown-8 where the cation is completely enclosed by the ligand.



(I)

Fig. 1. Molecule of (I) showing the crystallographic numbering scheme.

Experimental. Enraf–Nonius CAD-4 diffractometer; crystal 0·51 × 0·38 × 0·11 mm; 23 reflections (15° < θ < 18°) used to refine the unit-cell parameters; 2500 reflections collected to a maximum θ of 20°, using ω–2θ scans; a control reflection, measured every 120 normal reflections, showed no significant reduction in intensity over the data collection; data processed to give 1489 observed planes with $I > 2\sigma(I)$ (index range h 0–8, k ±11, l ±12); no absorption correction. The statistics of the intensity distribution indicated the structure to be centrosymmetric; this was confirmed by the successful refinement in space group $P\bar{1}$. Structure solved using multisolution direct methods (Main, Woolfson & Germain, 1978); H atoms (numbered according to the atom to which they are bonded, Fig. 1) included in calculated positions (C—H 0·98 Å); benzene H atoms assigned a common $U_{\rm iso}$ which refined to 0·090 (18) Å^2; the remaining H atoms were treated similarly, and their $U_{\rm iso}$ refined to 0·072 (9) Å. *SHELX* (Sheldrick, 1976) was used to refine the structure, and locally written programs for geometry were run on a Prime computer; $\sum w\Delta F^2$ minimized. The perchlorate O atoms appeared to be disordered, but no discrete alternative positions could be found, so they were assigned anisotropic temperature factors, and restrained to be tetrahedrally arranged about Cl. The other O atoms and the C atoms were refined isotropically. The refined value of 1·307 (10) Å for the common Cl—O distance is very short and the thermal parameters took on unrealistic values. The maximum shift/e.s.d. on the final cycle was 0·25 and the final $wR = 0{\cdot}106$. The 211 plane was omitted due to extinction, so 1488 planes were used in the final refinement. The final ΔF map showed a maximum peak height of 1·0 e Å^{-3} close to the perchlorate O atoms,

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* IUPAC name: 6,7,9,10,12,13,15,16,23,24,26,27-dodecahydro-5,8,11,14,17,22,25,28-octaoxadibenzo[*a*,*j*]cyclotetracosene.

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and this unexplained disorder accounts for the rather high R factors. Weights proportional to $1/\sigma^2(F_o)$ were used, and scattering factors were calculated using an analytical approximation (*International Tables for X-ray Crystallography*, 1974).

Discussion. The final atomic parameters are given in Table 1,* and a stereopair (Johnson, 1971) of the complex cation is shown in Fig. 2.

Table 1. *Fractional coordinates* (×10⁴), *and isotropic temperature factors* (×10³) *for the non-hydrogen atoms*

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{iso}/U_{eq}*(Å²)
Na	3156 (5)	7139 (4)	1991 (4)	44 (2)*
C(1)	−600 (18)	7450 (13)	4580 (12)	66 (4)
C(2)	−1305 (21)	8462 (15)	4934 (15)	87 (5)
C(3)	−1413 (20)	9266 (15)	4339 (13)	76 (5)
C(4)	−854 (18)	9183 (13)	3318 (12)	68 (4)
C(41)	−162 (15)	8198 (12)	2931 (10)	50 (4)
O(5)	494 (10)	8093 (7)	1918 (7)	50 (2)
C(6)	−429 (18)	7338 (13)	1269 (11)	63 (4)
C(7)	590 (19)	6945 (14)	344 (12)	68 (4)
O(8)	1591 (10)	6201 (7)	650 (7)	56 (3)
C(9)	2529 (21)	5646 (15)	−145 (14)	83 (5)
C(10)	3854 (19)	6355 (15)	−545 (13)	75 (5)
O(11)	4724 (10)	6870 (7)	268 (7)	51 (2)
C(111)	5906 (15)	7699 (11)	−58 (10)	42 (3)
C(12)	6968 (16)	7483 (12)	−877 (10)	53 (4)
C(13)	8167 (16)	8343 (11)	−1142 (11)	54 (4)
C(14)	8219 (17)	9364 (13)	−579 (11)	60 (4)
C(15)	7148 (15)	9606 (12)	253 (10)	49 (4)
C(151)	5970 (14)	8750 (10)	518 (9)	39 (3)
O(16)	4797 (9)	8873 (7)	1293 (6)	40 (2)
C(17)	4939 (15)	9900 (11)	1955 (10)	44 (3)
C(18)	3593 (16)	9806 (12)	2792 (11)	53 (4)
O(19)	3461 (10)	8758 (7)	3272 (6)	45 (2)
C(20)	4597 (17)	8685 (12)	3923 (12)	60 (4)
C(21)	4747 (19)	7478 (12)	4043 (12)	65 (4)
O(22)	5239 (11)	6933 (8)	3061 (7)	60 (3)
C(23)	5573 (20)	5766 (14)	3064 (14)	79 (5)
C(24)	4182 (17)	4954 (13)	3285 (12)	65 (4)
O(25)	3112 (10)	5067 (7)	2586 (7)	49 (2)
C(26)	1569 (15)	4624 (11)	2894 (10)	49 (4)
C(27)	738 (16)	5454 (11)	3656 (10)	50 (4)
O(28)	748 (10)	6467 (7)	3100 (6)	48 (2)
C(281)	−26 (15)	7360 (11)	3549 (10)	48 (4)
Cl	2474 (5)	7354 (4)	−3090 (3)	67 (2)*
O(1)	3946 (12)	7677 (12)	−3202 (13)	178 (10)*
O(2)	2234 (20)	6347 (12)	−2652 (17)	238 (18)*
O(3)	1754 (19)	8092 (15)	−2452 (18)	300 (21)*
O(4)	1884 (23)	7190 (22)	−3933 (11)	403 (30)*

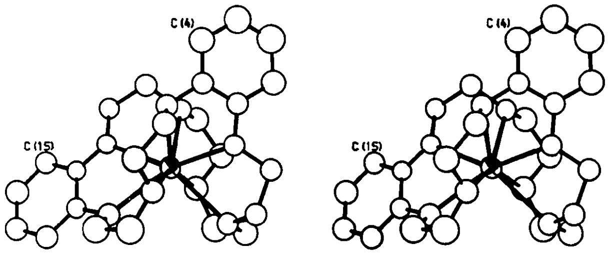

Fig. 2. The molecule of the complex with atoms represented by their 50% thermal ellipsoids.

Table 2. *Bond lengths* (Å) *and torsion angles* (°); *mean e.s.d. for torsion angles* 2°

Na–O(5)	2·718 (10)	C(111)–C(151)	1·389 (17)
Na–O(8)	2·493 (10)	C(12)–C(13)	1·402 (19)
Na–O(11)	2·525 (10)	C(13)–C(14)	1·352 (19)
Na–O(16)	2·519 (9)	C(14)–C(15)	1·386 (19)
Na–O(19)	2·447 (9)	C(15)–C(151)	1·387 (17)
Na–O(22)	2·502 (11)	C(151)–O(16)	1·369 (14)
Na–O(25)	2·605 (10)	O(16)–C(17)	1·428 (15)
Na–O(28)	2·502 (10)	C(17)–C(18)	1·514 (18)
C(1)–C(2)	1·413 (23)	C(18)–O(19)	1·415 (15)
C(1)–C(281)	1·394 (20)	O(19)–C(20)	1·416 (16)
C(2)–C(3)	1·297 (22)	C(20)–C(21)	1·455 (20)
C(3)–C(4)	1·379 (22)	C(21)–O(22)	1·436 (17)
C(4)–C(41)	1·390 (19)	O(22)–C(23)	1·428 (18)
C(41)–O(5)	1·393 (16)	C(23)–C(24)	1·472 (22)
C(41)–C(281)	1·355 (18)	C(24)–O(25)	1·427 (17)
O(5)–C(6)	1·438 (17)	O(25)–C(26)	1·415 (15)
C(6)–C(7)	1·493 (21)	C(26)–C(27)	1·515 (18)
C(7)–O(8)	1·422 (17)	C(27)–O(28)	1·446 (15)
O(8)–C(9)	1·410 (19)	O(28)–C(281)	1·362 (15)
C(9)–C(10)	1·421 (23)	Cl–O(1)	1·298 (9)
C(10)–O(11)	1·452 (18)	Cl–O(2)	1·340 (10)
O(11)–C(111)	1·389 (15)	Cl–O(3)	1·311 (11)
C(111)–C(12)	1·363 (18)	Cl–O(4)	1·285 (10)

C(281)–C(41)–O(5)–C(6)	81	O(16)–C(17)–C(18)–O(19)	52
O(28)–C(281)–C(41)–O(5)	−1	C(17)–C(18)–O(19)–C(20)	73
C(41)–O(5)–C(6)–C(7)	−159	C(18)–O(19)–C(20)–C(21)	−157
O(5)–C(6)–C(7)–O(8)	69	O(19)–C(20)–C(21)–O(22)	62
C(6)–C(7)–O(8)–C(9)	173	C(20)–C(21)–O(22)–C(23)	175
C(7)–O(8)–C(9)–C(10)	79	C(21)–O(22)–C(23)–C(24)	71
O(8)–C(9)–C(10)–O(11)	52	O(22)–C(23)–C(24)–O(25)	55
C(9)–C(10)–O(11)–C(111)	−171	C(23)–C(24)–O(25)–C(26)	−161
C(10)–O(11)–C(111)–C(151)	130	C(24)–O(25)–C(26)–C(27)	80
O(11)–C(111)–C(151)–O(16)	−5	O(25)–C(26)–C(27)–O(28)	62
C(111)–C(151)–O(16)–C(17)	174	C(26)–C(27)–O(28)–C(281)	175
C(151)–O(16)–C(17)–C(18)	−176	C(27)–O(28)–C(281)–C(41)	−170

The Na^+ cation is surrounded by eight O atoms from the ligand, forming a distorted square antiprism. Seven O—Na distances fall in the range 2·45–2·61 (1) Å (Table 2), but one, Na—O(5), at 2·72 (1) Å is much longer than the rest. Bond lengths and angles* in (I) fall in the range expected for crown ethers and their complexes.

Torsion angles about C—C bonds are *gauche* as expected; five torsion angles about C—O bonds are between 71 and 81 (2)°, and the rest are larger (Table 2). The atoms forming the benzene rings form good planes with χ^2 values of 0·25 and 0·09 for three degrees of freedom. The O atoms attached to the benzene rings are all *ca* 0·05 Å from the planes.

Non-bonded contacts between H atoms both within and between molecules are all of the expected length, and there are no close contacts to the anions.

The perchlorate anions are not coordinated to the cations, and there is no solvent present in the crystals. These observations confirm both the infrared-spectrum interpretation, and also that dibenzo-24-crown-8 is capable of forming 1:1 wrap-around complexes, at least with the smaller cations of Groups I*a* and II*a*.

I thank Dr J. N. Wingfield for supplying the crystals and suggesting the work, and the Royal Society for some apparatus.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38476 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* See deposition footnote.

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[*N*,*N*′-Ethylenebis(salicylideneiminato)]nickel(II),* [Ni($C_{16}H_{14}N_2O_2$)]. A Redetermination

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Abstract. $M_r = 325{\cdot}0$, orthorhombic, *Pbca*, $a = 13{\cdot}831\,(3)$, $b = 26{\cdot}155\,(5)$, $c = 7{\cdot}482\,(2)$ Å, $Z = 8$, $D_x = 1{\cdot}595$ Mg m^{-3}, $F(000) = 1344$, $\mu = 2{\cdot}08$ mm^{-1} [λ(Cu $K\alpha$)], $T = 298$ K. The structure has been refined by full-matrix least-squares methods to a final $R = 0{\cdot}042$ for 1975 independent significant reflections. All H atoms have been directly located. The geometry of the molecule, as a whole, is in agreement with that found by Shkol'nikova, Yumal', Shugam & Voblikova [*Zh. Strukt. Khim.* (1970). **5**, 886–890] in a previous determination, but the precision of the analysis is now high enough to allow a detailed description of the molecular conformation.

Introduction. The crystal structure of the title compound was determined to define the details of its conformation which could not be obtained from the analysis by Shkol'nikova, Yumal', Shugam & Voblikova (1970) and which, even if correct, were not accurate enough for this purpose.

Experimental. Cell parameters and intensity data measured on a Siemens AED autodiffractometer, Ni-filtered Cu $K\alpha$ radiation (1·54178 Å); accurate lattice parameters from least-squares refinement of 20 reflections ($35° < 2\theta < 62°$); crystal used was approximately cylindrical, mean radius 0·11 mm; one reflection remeasured after 20 reflections as a check on crystal and instrument stability showed no significant change; 2566 independent reflections ($2\theta_{\max}$ 140°), 585 of which were considered unobserved [$I < 2\sigma(I)$]; structure solved, independently of earlier work, by heavy-atom method; full-matrix least-squares refinement of positional and anisotropic thermal parameters for non-hydrogen atoms converged with $R = 4{\cdot}8\%$; all H atoms located from a difference Fourier synthesis and introduced in further refinement as fixed-atom contributions ($B_{\rm iso} = 6{\cdot}3$ Å^2); final convergence reached with $R = 4{\cdot}2\%$, $R_w = 4{\cdot}8\%$; $\sum w|\Delta F|^2$ minimized with $w = 1/[\sigma^2(F_o) + 0{\cdot}008328\ F_o^2]$; in the final cycle no shift-over-error ratio, Δ/σ, was greater than 0·3; overdetermination ratio was NO:NV = 1975:246 = 8:1; final difference Fourier map revealed no unusual features; atomic scattering factor tables for Ni from *International Tables for X-ray Crystallography* (1974), those for O, N, C from Cromer & Mann (1968) and those for H from Stewart, Davidson & Simpson (1965).

Discussion. Final positional parameters for all atoms and isotropic $B_{\rm eq}$ for non-hydrogen atoms are reported in Table 1.† Bond lengths and bond angles are given in Table 2. The numbering scheme adopted is shown in Fig. 1.

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* The 'salen' ligand is also known as 'salicylideneaminate'.

† Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38383 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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