The Crystal Structure of a Complex between Barium Perchlorate and Dibenzo-24-crown-8: Bisperchlorato(6,7,9,10,12,13,20,21,23,24,26,27-dodecahydrodibenz[b,n]-[1,4,7,10,13,16,19,22]octaoxacyclotetracosin)barium

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$Ba(ClO_4)_2C_{24}H_{32}O_8$ forms orthorhombic crystals with $a = 21.247$ (4), $b = 8.583$ (1), $c = 34.081$ (3) Å and eight formula units in the unit cell. Systematic absences correspond to the space groups $Pna2_1$ or $Pnam$. Intensities were collected twice, on a Picker four-circle diffractometer and on an Enraf–Nonius CAD-4 diffractometer. The structure was solved by the heavy-atom method with considerable difficulty; there are two molecules pseudocentrosymmetrically related in the asymmetric unit in space group $Pna2_1$. In the final refinement H atoms were omitted, C atoms were isotropic and other atoms anisotropic, parameters of the two molecules being refined in alternate cycles until $R = 0.0598$ for 5554 observations. Each Ba ion is 10-coordinated, by the eight O atoms of the ligand (Ba–O 2.76–3.04 Å) which cradles, but does not enclose, the cation, and by two perchlorate ions, one unidentate (Ba–O 2.72 Å) and the other possibly bidentate (Ba–O 2.79 and 3.3 Å).

Introduction

The macrocyclic polyether dibenzo-24-crown-8 (see Fig. 1) forms complexes with alkali metal and alkaline earth metal salts. With the M^+ cations the stoichiometry may be 2(cations): 1(molecule) or 1 : 1 (Poonia & Truter, 1973). Crystal structure analyses have been carried out on the di(potassium thiocyanate)–dibenzo-24-crown-8 complex (Mercer & Truter, 1973) and on the di(sodium *o*-nitrophenolate)–dibenzo-24-crown-8 complex (Hughes, 1975). Different conformations were found for the molecule in the two complexes. In one of the crystalline forms of the uncomplexed molecule,

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Hanson, Hughes & Truter (1976) found a third conformation.

Investigations of complex formation by alkaline earth metal salts have so far yielded only 1 : 1 complexes (Parsons & Wingfield, 1976*a*; Tušek, Meider-Goričan & Danesi, 1976). One of these, barium perchlorate with dibenzo-24-crown-8, was shown by Parsons & Wingfield (1976*b*), to give an IR spectrum consistent with coordination by one or both perchlorate ions. Suitable unsolvated crystals were obtained from ethanol and we set out to determine the crystal structure, particularly to discover the shape of the molecule when coordinating one cation. The analysis proved unexpectedly difficult because of ambiguity in the space group, pseudosymmetry, and slight disorder.

Experimental

Preliminary investigation by photographic methods established that there were eight formula units in an orthorhombic unit cell; systematic absences $h0l$ with h odd and $0kl$ with k and l odd indicated that the space group is either $Pna2_1$ (C_{2v}^9) or $Pnam$, a non-standard setting of $Pnma$ (D_{2h}^{16}). Accurate unit-cell dimensions were obtained from the settings of 25 high-angle reflections on a CAD-4 diffractometer.
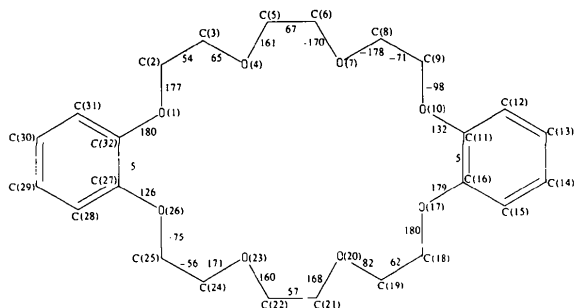

Fig. 1. Designation of atoms in dibenzo-24-crown-8, molecule A; molecule B has the same atom numbers with primes. Torsion angles are shown for molecule A; those of molecule B are in Table 3; standard deviations are in the range 1–2°. H atoms were not located, each C atom in the macrocyclic ring bears two H atoms.

Crystal data

$C_{24}H_{32}BaCl_2O_{16}$, $M_r = 784.73$, orthorhombic, $a = 21.247$ (4), $b = 8.583$ (1), $c = 34.081$ (3) Å, $U =$

6214·8 Å^3, $D_m = 1·67$, $Z = 8$, $D_c = 1·677$ g cm^{-3}; space group $Pna2_1$ by structure analysis, two formula units per asymmetric unit; $F(000) = 3152$, $\lambda(\text{Mo } K\alpha_1) = 0·70926$ Å, $\mu(\text{Mo } K\alpha_1) = 15·1$ cm^{-1}.

Intensity measurements were collected twice. First a crystal 0·2 × 0·3 × 0·15 mm was mounted with the b axis approximately coincident with φ on a Picker four-circle diffractometer. Only for a sphere with $2\theta < 30°$ were the observations sufficiently reliable to be used; 6278 reflections, i.e. hkl, Friedel equivalents and the Bijvoet pairs $hk\bar{l}$, were measured with Zr-filtered radiation and the 2240 unique ones used for initial structure determination. In the following account (P) will be used to distinguish the R values and other numerical results determined from these observations. Lorentz and polarization corrections were applied by the program $PRED$ (X-RAY ARC, 1973).

For the second collection of intensity measurements a needle 0·25 × 0·63 × 0·13 mm was set on an Enraf–Nonius CAD-4 diffractometer with monochromated Mo $K\alpha$ radiation. From analyses of diffracted beam peaks, an $\omega/2\theta$ scan motion and an ω-scan range r of $(0·6 + 0·35 \tan \theta)°$ were found suitable for the peak measurement; the ω-scan range was extended by $r/4$ at each end for background calculations, and was centred at the mean of the α_1 and α_2 peak positions.

Reflections with θ in the range 1–20° were measured. Scanning was in the bisecting mode, i.e. with $\psi = 0°$. Indices were generated in a zigzag mode, with l changing most rapidly, k least rapidly. Friedel pairs of all reflections were measured, each pair consecutively.

All scans (both prescan and final runs) were tested for consistency by comparison of counts in a forward and return run; poor agreement in any section (each background and peak measurement) required a third or even fourth scan. Prescan runs were made at 4° min^{-1}. Reflections with a net intensity $I < \sigma_I/2$ were flagged as weak and not remeasured; those remaining with $I < \sim10\,000$ counts were remeasured at slower speeds (maximum time of 120 s allowed for the two scans) to try to bring I up to this common level.

An intensity-control reflection (212) was recorded every 60 min of X-ray exposure time; no significant change in intensity was observed. Orientation checks were made with respect to θ on each strong reflection, and critical peak centring was performed every 50 reflections; owing to a diffractometer fault, reorientation by centring on 23 high-θ reflections was effected frequently during the data collection.

The peaks for each reflection were split several times over a very small angle of θ, but no better crystals could be found; the poor crystal quality may result from the slight disorder found. No significant differences were found between the Friedel pairs so that the 5555 unique reflections were used for final refinement; eventually 20,4,9 was rejected as being possibly mis-measured.

Structure determination

A Patterson synthesis was computed with $FODAP$ (X-RAY ARC, 1973) and this clearly distinguished between the possibilities that (1) the space group is $Pnam$ with one formula unit per asymmetric unit, or (2) the space group is $Pna2_1$ with two formula units per asymmetric unit. There was no accumulation of peaks along $(0,0,w)$ corresponding to the mirror plane of $Pnam$, nor in Harker planes at $u = \frac{1}{2}$ or $v = \frac{1}{2}$. The Patterson synthesis could be interpreted on assumption (2) with two independent barium ions: Ba at $(0·17,0·25,0·00)$ and Ba' at $(0·42,0·25,0·24)$. With these atoms only, refinement of the scale, coordinates and isotropic vibration parameters led to $R(P) = 0·45$, but no further atoms could be located in Fourier syntheses because of uncertainty in the phases of planes with h odd [$R(P)$ for h even was 0·37 and for h odd 0·67]. There were two molecules of dibenzo-24-crown-8 to be located; the numbering scheme for one (A) is shown in Fig. 1, and the other (B) was allocated the same numbers with primes. There were four perchlorate ions, designated Cl(1) with O(33)–(36) and Cl(2) with O(37)–(40) and two with corresponding primed designations. Re-examination of the Patterson maps revealed a peak at $(0·5,0·6,0·31)$ attributable to Cl(1'); inclusion of this gave phases for a Fourier synthesis, with the program $SHELX$ (Sheldrick, 1976) in which the O atoms attached to Cl(1') appeared. Successive Fourier and difference Fourier syntheses revealed all the non-hydrogen atoms. Full-matrix least-squares refinement with $SHELX$ was carried out, anisotropic vibration parameters being allowed for the Ba and for the perchlorate ions and individual isotropic vibration parameters for the atoms in the crown ether molecules. $R(P)$ was reduced to 0·057. Comparison of the bond lengths in the two independent crown molecules showed that there were several corresponding pairs unexpectedly short in one molecule and long in the other, typical of centrosymmetric entities being refined in a noncentrosymmetric space group.

The two independent molecules were very similar (each Ba ion being coordinated by two perchlorate ions and the eight O atoms of the ligand) and were approximately related by a non-crystallographic centre of symmetry at $(\sim\frac{3}{8},\sim\frac{1}{2},\sim\frac{3}{8})$. The possibility that the true space group was $P2_1/a$ with twinning producing a pseudo n glide was considered but led to unacceptable intermolecular distances.

For further refinement the CAD-4 observations were used. Structure factor calculation with the previous parameters gave $R = 0·11$ and no indication of gross error in the Picker observations. A truly centrosymmetric arrangement was assumed as the next model; in one cycle of refinement, the symmetry cards for $Pna2_1$ were supplemented by cards X to generate molecules B from molecule A by centres of symmetry,

and the refinement parameters were those of the atoms of molecule A. In the second cycle, cards X were removed, and the positions of A and B as rigid groups were refined, *i.e.* a new site was found for the pseudo centre of symmetry, and thus new cards X, were generated. These two cycles of refinement were alternated and led to reasonable bond lengths, a centre of symmetry at $(0.372, 0.500, 0.370)$ and $R = 0.0946$, a value too high to establish a true centrosymmetric relationship.

A series of difference Fourier syntheses were calculated. These were phased by parts of the molecule with pseudocentrosymmetrically related portions omitted, *e.g.* a benzene ring, a perchlorate ion, *etc.* This led

to relocation of all the non-hydrogen atoms in the two independent molecules. Large-block-matrix refinement of molecule A and molecule B in alternate cycles (with the scale factor in all cycles) allowing isotropic vibration parameters for C atoms and anisotropic vibration parameters for the others led to $R = 0.0598$ when the most significant shift was 0.4 of the corresponding standard deviation. The weighted R factor was 0.0701 with the weighting scheme, automatically refined by *SHELX*, $w = 0.0068/(\sigma_F^2 + 0.259706F^2)$. H atoms were omitted because evidence from difference syntheses indicated that the other atoms had markedly anisotropic vibrations; with a limitation of 800 in the total number of parameters, the refinement of 38 atoms

Table 1. *Fractional atomic coordinates* ($\times 10^4$)

Here and throughout this paper standard deviations in the least significant digits are in parentheses.

	x	y	z		x	y	z
Ba	3245·8 (2)	7346·6 (6)	4997·7 (2)	Ba'	4210·2 (2)	2665·7 (6)	2397·4 (2)
O(1)	4071 (4)	10001 (9)	4757 (3)	O(1')	3387 (4)	22 (9)	2658 (3)
C(2)	3963 (5)	11519 (13)	4927 (3)	C(2')	3480 (5)	−1522 (14)	2491 (3)
C(3)	3329 (5)	11528 (15)	5108 (4)	C(3')	4132 (5)	−1533 (14)	2318 (3)
O(4)	3255 (3)	10289 (9)	5376 (2)	O(4)	4236 (4)	−238 (10)	2053 (3)
C(5)	3646 (8)	10335 (20)	5721 (5)	C(5')	3870 (7)	−416 (19)	1684 (4)
C(6)	3333 (11)	9283 (32)	6004 (8)	C(6')	4194 (6)	676 (18)	1394 (5)
O(7)	3385 (8)	7751 (12)	5851 (3)	O(7')	4189 (5)	2198 (12)	1562 (3)
C(8)	2963 (11)	6603 (29)	6097 (7)	C(8')	4493 (7)	3263 (20)	1301 (5)
C(9)	3031 (9)	5113 (25)	5961 (6)	C(9')	4455 (7)	4880 (17)	1476 (4)
O(10)	2717 (4)	5190 (12)	5592 (3)	O(10')	4735 (4)	4914 (10)	1857 (2)
C(11)	2109 (6)	4686 (15)	5574 (4)	C(11')	5378 (5)	5387 (14)	1864 (4)
C(12)	1960 (10)	3140 (26)	5719 (6)	C(12')	5537 (7)	6807 (18)	1735 (4)
C(13)	1323 (8)	2678 (18)	5652 (5)	C(13')	6200 (8)	7231 (19)	1795 (5)
C(14)	901 (7)	3558 (20)	5475 (5)	C(14')	6602 (7)	6363 (20)	1933 (5)
C(15)	1058 (7)	5040 (17)	5348 (4)	C(15')	6443 (7)	4756 (17)	2067 (4)
C(16)	1684 (5)	5601 (15)	5396 (4)	C(16')	5802 (5)	4328 (13)	2025 (3)
O(17)	1894 (3)	7010 (10)	5278 (3)	O(17')	5578 (4)	2914 (10)	2141 (3)
C(18)	1449 (7)	8006 (18)	5079 (4)	C(18')	6027 (7)	1952 (18)	2332 (4)
C(19)	1752 (6)	9459 (16)	4974 (4)	C(19')	5692 (6)	450 (18)	2453 (4)
O(20)	2259 (3)	9192 (9)	4714 (2)	O(20')	5173 (3)	811 (9)	2708 (2)
C(21)	2076 (5)	9010 (14)	4306 (4)	C(21')	5346 (6)	935 (16)	3123 (4)
C(22)	2672 (6)	9082 (16)	4065 (4)	C(22')	4748 (6)	865 (15)	3347 (4)
O(23)	3088 (4)	7906 (9)	4200 (2)	O(23')	4363 (4)	2063 (10)	3215 (3)
C(24)	3559 (6)	7528 (14)	3920 (4)	C(24')	3856 (7)	2442 (17)	3491 (5)
C(25)	4022 (6)	6473 (16)	4127 (4)	C(25')	3426 (6)	3534 (16)	3299 (4)
O(26)	4273 (3)	7193 (9)	4473 (3)	O(26')	3169 (4)	2816 (10)	2958 (3)
C(27)	4712 (5)	8339 (13)	4395 (3)	C(27')	2720 (5)	1692 (14)	3014 (3)
C(28)	5273 (6)	8039 (15)	4184 (4)	C(28')	2179 (7)	2072 (18)	3230 (4)
C(29)	5712 (7)	9163 (19)	4143 (5)	C(29')	1715 (6)	820 (18)	3269 (4)
C(30)	5631 (7)	10651 (17)	4297 (4)	C(30')	1812 (6)	−640 (17)	3105 (4)
C(31)	5071 (6)	10926 (16)	4516 (4)	C(31')	2374 (6)	−976 (15)	2894 (4)
C(32)	4631 (5)	9776 (13)	4552 (3)	C(32')	2818 (5)	233 (14)	2853 (3)
Cl(1)	2476 (1)	3972 (3)	4359 (1)	Cl(1')	4975 (1)	6005 (3)	3056 (1)
O(33)	2600 (8)	4961 (15)	4663 (3)	O(33')	4874 (10)	4990 (20)	2754 (3)
O(34)	3058 (5)	3155 (15)	4238 (3)	O(34')	4385 (5)	6772 (19)	3181 (5)
O(35)	2251 (5)	4795 (12)	4032 (3)	O(35')	5187 (5)	5244 (14)	3395 (3)
O(36)	2046 (5)	2804 (11)	4496 (4)	O(36')	5389 (5)	7165 (11)	2940 (4)
Cl(2)	4679 (1)	5310 (4)	5295 (1)	Cl(2')	2797 (2)	4594 (5)	2040 (1)
O(37)	4062 (4)	4894 (10)	5159 (3)	O(37')	3386 (3)	5080 (10)	2195 (3)
O(38)	4701 (6)	6960 (12)	5347 (4)	O(38')	2825 (8)	2906 (17)	2028 (6)
O(39)	5133 (5)	4812 (17)	5008 (4)	O(39')	2311 (5)	5118 (18)	2305 (6)
O(40)	4803 (7)	4535 (19)	5646 (5)	O(40')	2753 (8)	5331 (23)	1674 (5)

anisotropically took precedence. The final parameters are in Table 1* and show that this was necessary.

For all atoms the analytical scattering factors (Cromer & Mann, 1968) were used and anomalous-dispersion factors (Cromer & Liberman, 1970) included. Although the space group is polar the pseudo-centrosymmetric relationship of the molecules explains the lack of difference between the Friedel or Bijvoet pairs of reflections.

A final difference map was not featureless; there were small peaks in positions indicating alternative sites for C(12), C(13), C(12')···C(15'), the O atoms of the Cl(1) and Cl(1') perchlorate ions, and C(6) and C(8). This disorder seems quite reasonable for a flexible molecule and is consistent with the poor crystal quality. No attempt was made to increase the number of parameters still further by introduction of alternative sites and refinement of occupation factors.

Discussion

Molecule A is shown as a stereopair in Fig. 2; molecule B is not detectably different, as can be seen qualitatively in the packing diagram (Fig. 3). Quantitatively the deviations can be judged by calculating the position of the 'centre of symmetry' from each pair of atoms and the standard deviation from the spread about the mean; the result is 0·3733 (18), 0·4984 (32), 0·3710 (7). Only for the z of Cl(2') and its associated O atoms was a significantly different value obtained, 0·3670 (13). This does not result in a significant difference in the Ba—O(37)—Cl(2) angles, as shown in Table 2. It is only in the intermolecular distances, discussed later, that the local nature of the centre of symmetry becomes apparent.

The mean value of the Cl—O bond lengths is 1·42 Å with a standard deviation calculated from the spread about the mean of 0·03 Å which indicates that the

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0·01–0·02 Å of Table 2 is an underestimate, as might be expected because the refinement procedure did not give correlation coefficients between parameters of molecules A and B. Appropriate caution will be observed in the subsequent discussion of dimensions.

Each Ba ion is coordinated by 10 or 11 O atoms depending upon the definition of a meaningful distance. Perchlorate ions (1) and (1') are clearly monodentate with Ba—O(33)—Cl(1) at 152°; however, with an angle of 116° at O(37), perchlorate ions (2) and (2') provide a second contact at 3·33 or 3·21 Å to O(38). In the empirical treatment of Brown & Wu (1976), based on electrostatic bond valence, $s = (R/2\cdot297)^7$, the average valences are Ba—O(33) 0·305, Ba—O(37) 0·256 and Ba—O(38) 0·084. The eight contacts from the O atoms of the crown ligand cradle, but do not enclose, the Ba and the two perchlorate ions; the average Ba—O(crown) distances are 2·96 Å to the O atoms attached to benzene rings (with a bond valence of 0·170) and 2·83 Å to the aliphatic ether O atoms (with a higher bond valence of 0·232).

In the perchlorate ions there is no significant or systematic difference in the Cl—O bond distances. The different environments of the Cl(1) and Cl(2) perchlorate ions are consistent with the multiple splitting observed in the IR spectrum (Parsons & Wingfield, 1976a).
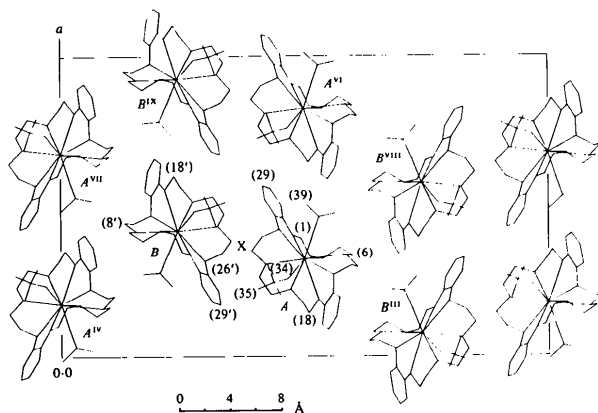

Fig. 3. View of the structure projected down the b axis. The pseudo centre of symmetry is marked with a cross. Molecules of types A and B are indicated; Roman-numeral superscripts are defined in Table 5.
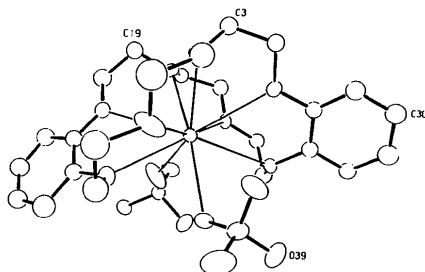

Fig. 2. Stereodiagram of molecule A, drawn by the program ORTEP (Johnson, 1965).

Table 2. *Bond distances* (Å), *angles* (°) *and torsion angles* (°)

(a) Distances for Ba—O and Cl—O bonds

	A	B		A	B
Ba—O(1)	2·990 (8)	3·000 (8)	Cl(1)—O(33)	1·37 (1)	1·37 (2)
Ba—O(4)	2·835 (8)	2·755 (9)	Cl(1)—O(34)	1·48 (1)	1·48 (1)
Ba—O(7)	2·943 (11)	2·875 (10)	Cl(1)—O(35)	1·41 (1)	1·40 (1)
Ba—O(10)	2·965 (10)	2·892 (8)	Cl(1)—O(36)	1·43 (1)	1·38 (1)
Ba—O(17)	3·041 (7)	3·041 (8)	Cl(2)—O(37)	1·44 (1)	1·42 (1)
Ba—O(20)	2·800 (7)	2·799 (7)	Cl(2)—O(38)	1·43 (1)	1·45 (2)
Ba—O(23)	2·780 (7)	2·853 (9)	Cl(2)—O(39)	1·44 (1)	1·44 (2)
Ba—O(26)	2·824 (8)	2·924 (8)	Cl(2)—O(40)	1·39 (2)	1·40 (2)
Ba—O(33)	2·715 (14)	2·728 (18)			
Ba—O(37)	2·782 (8)	2·799 (8)			
Ba—O(38)	3·330 (13)	3·208 (17)			

(b) Angles subtended at the Ba atoms in the form O(a)—Ba—O(b) and O(b')—Ba'—O(a') such that the angles about Ba are in the top-right and those about Ba' in the bottom-left halves of the table. Standard deviations are in the range 0·2–0·4°.

b,a' a,b'	O(1)	O(4)	O(7)	O(10)	O(17)	O(20)	O(23)	O(26)	O(33)	O(37)	O(38)
O(1)	–	56·1	97·0	152·3	135·4	85·0	70·8	53·8	139·1	105·4	68·3
O(4)	56·9	–	56·3	104·4	87·0	70·0	106·9	108·9	150·0	125·4	85·4
O(7)	100·3	56·8	–	55·7	78·2	110·5	163·2	123·6	123·7	80·3	64·2
O(10)	156·7	108·9	57·9	–	50·8	107·8	136·9	134·1	67·9	68·2	92·6
O(17)	134·0	85·5	75·0	53·3	–	57·0	102·1	157·5	65·4	117·1	139·1
O(20)	83·3	68·4	107·8	109·8	56·7	–	58·3	112·7	84·5	164·4	151·1
O(23)	68·9	104·5	160·7	134·4	100·6	56·3	–	58·8	70·1	113·5	118·6
O(26)	53·0	109·5	129·8	132·7	155·1	109·3	57·0	–	95·1	67·0	60·3
O(33)	136·3	147·2	123·4	66·2	65·3	82·5	68·9	93·9	–	80·1	122·9
O(37)	105·6	125·2	81·3	65·8	118·4	166·2	116·5	69·8	83·8	–	43·5
O(38)	68·3	84·8	66·8	93·5	139·4	148·8	119·9	63·9	127·0	44·1	–

Table 2 (*cont.*)

(c) Angles subtended at the Cl atoms in the form O(a)—Cl(1)—O(b), O(b')—Cl(1')—O(a'), O(c)—Cl(2)—O(d), O(d')—Cl(2')—O(c'); standard deviations are in the range 0·6–1·1°.

b,a' a,b'	O(33)	O(34)	O(35)	O(36)
O(33)	–	110·2	110·9	108·1
O(34)	111·6	–	107·5	107·0
O(35)	112·0	104·0	–	113·2
O(36)	110·1	107·5	111·4	–

d,c' c,d'	O(37)	O(38)	O(39)	O(40)
O(37)	–	108·5	108·7	109·3
O(38)	105·5	–	110·9	111·1
O(39)	107·8	110·9	–	108·3
O(40)	105·0	115·4	111·6	–

(d) Angles Ba—O—Cl

	A	B
Ba—O(33)—Cl(1)	152·3 (9)	152·0 (11)
Ba—O(37)—Cl(2)	116·4 (5)	115·2 (5)
Ba—O(38)—Cl(2)	91·4 (6)	95·2 (7)

The dimensions in Table 3 show no significant differences between the independent molecules, and the bond lengths and bond angles are the same as in the other forms. The torsion angles of the polyether ring differ from those of previous analyses and correspond approximately to a twofold axis relating the benzene rings. These angles are displayed in Fig. 1 for molecule A and in Table 3 for both molecules. Standard deviations in the torsion angles are in the range 1–2° for the macrocyclic ring and 1·7–2·7° for the benzene rings; the maximum deviation from 0° in the benzene rings, other than O—C—C—O, is 3·5°. The differences in conformation between molecules A and B are not chemically significant; this form is the fourth found for this molecule and the first in which no symmetry is imposed crystallographically. Comparative values for the other three are in Hanson, Hughes & Truter (1976) and further discussion will appear when results for compounds now in hand can be included. Table 4 gives the mean planes through various groups of atoms; the benzene rings are satisfactorily planar; the appearance in Fig. 3 that the Ba atoms are out of the planes of C(11)—C(16) and approximately coplanar with C(27)—C(32) is confirmed. The O atoms of the macrocyclic ether are not sufficiently nearly coplanar for the least-squares treatment (Schomaker, Waser, Marsh & Bergman, 1959; Blow, 1960) to be valid but Table 4 shows the equations for deviations from planes normal to the approximate twofold axis revealed by the torsion angles.

The structure as a whole is seen in Fig. 3 with the intermolecular distances less than 3·5 Å in Table 5.

Table 3. *Bond lengths* (Å), *bond angles* (°) *and torsion angles* (°) *in the dibenzo-24-crown-8 molecules*

(a) Bond lengths

	A	B		A	B
C(32)—O(1)	1·39 (1)	1·39 (1)	C(16)—O(17)	1·35 (2)	1·36 (1)
O(1)—C(2)	1·44 (1)	1·46 (1)	O(17)—C(18)	1·44 (2)	1·42 (2)
C(2)—C(3)	1·48 (2)	1·51 (2)	C(18)—C(19)	1·45 (2)	1·53 (2)
C(3)—O(4)	1·41 (2)	1·45 (1)	C(19)—O(20)	1·41 (2)	1·44 (2)
O(4)—C(5)	1·44 (2)	1·49 (2)	O(20)—C(21)	1·45 (1)	1·47 (2)
C(5)—C(6)	1·48 (3)	1·52 (2)	C(21)—C(22)	1·51 (2)	1·49 (2)
C(6)—O(7)	1·42 (3)	1·43 (2)	C(22)—O(23)	1·42 (2)	1·39 (2)
O(7)—C(8)	1·58 (3)	1·43 (2)	O(23)—C(24)	1·42 (2)	1·47 (2)
C(8)—C(9)	1·37 (3)	1·51 (2)	C(24)—C(25)	1·51 (2)	1·46 (2)
C(9)—O(10)	1·43 (2)	1·43 (2)	C(25)—O(26)	1·43 (2)	1·43 (2)
O(10)—C(11)	1·37 (2)	1·43 (1)	O(26)—C(27)	1·38 (1)	1·37 (1)
C(11)—C(12)	1·45 (3)	1·34 (2)	C(27)—C(28)	1·42 (2)	1·40 (2)
C(11)—C(16)	1·34 (2)	1·39 (2)	C(27)—C(32)	1·36 (2)	1·38 (2)
C(12)—C(13)	1·43 (3)	1·47 (2)	C(28)—C(29)	1·35 (2)	1·46 (2)
C(13)—C(14)	1·32 (2)	1·23 (2)	C(29)—C(30)	1·39 (2)	1·39 (2)
C(14)—C(15)	1·38 (2)	1·49 (2)	C(30)—C(31)	1·42 (2)	1·42 (2)
C(15)—C(16)	1·43 (2)	1·42 (2)	C(31)—C(32)	1·37 (2)	1·41 (2)

(b) Bond angles at the carbon atoms are in the ranges 117–123° (aromatic) or 106–113° (aliphatic) except for those listed below

	A	B		A	B
C(6)—C(5)—O(4)	104·8 (1·5)	104·4 (1·1)	C(16)—C(15)—C(14)		115·2 (1·2)
C(13)—C(12)—C(11)	113·9 (1·6)	115·0 (1·3)	C(27)—C(28)—C(29)		115·4 (1·3)
C(12)—C(13)—C(14)	124·0 (1·6)	124·7 (1·6)			
O(17)—C(16)—C(11)	115·9 (1·0)		C(8)—C(9)—O(10)	101·9 (1·7)	
O(17)—C(16)—C(15)	125·2 (1·1)		O(10)—C(11)—C(16)		116·1 (1·0)
O(1)—C(32)—C(27)	115·6 (0·9)	115·9 (1·0)	C(12)—C(11)—C(16)		124·0 (1·1)

(c) Bond angles at the oxygen atoms within the macrocycles

	A	B		A	B
C(32)—O(1)—C(2)	117·5 (8)	115·1 (8)	C(16)—O(17)—C(18)	117·0 (9)	114·6 (9)
C(3)—O(4)—C(5)	116·3 (10)	111·7 (9)	C(19)—O(20)—C(21)	114·4 (9)	114·0 (9)
C(6)—O(7)—C(8)	109·8 (16)	109·4 (11)	C(22)—O(23)—C(24)	112·5 (9)	112·9 (10)
C(9)—O(10)—C(11)	117·9 (12)	114·9 (9)	C(25)—O(26)—C(27)	113·6 (9)	117·2 (9)

(d) Torsion angles in the macrocycles; standard deviations are in the range 1–2°.

	A	B		A	B
C(32)—O(1)—C(2)—C(3)	177	-177	C(16)—O(17)—C(18)—C(19)	180	178
O(1)—C(2)—C(3)—O(4)	54	-52	O(17)—C(18)—C(19)--O(20)	62	-59
C(2)—C(3)—O(4)—C(5)	65	-70	C(18)—C(19)—O(20)—C(21)	82	-86
C(3)—O(4)—C(5)—C(6)	161	-161	C(19)—O(20)—C(21)—C(22)	168	-165
O(4)—C(5)—C(6)—O(7)	67	-57	O(20)—C(21)—C(22)—O(23)	57	-57
C(5)—C(6)—O(7)—C(8)	-170	180	C(21)—C(22)—O(23)—C(24)	160	-161
C(6)—O(7)—C(8)—C(9)	-178	177	C(22)—O(23)—C(24)—C(25)	171	-171
O(7)—C(8)—C(9)—O(10)	-71	58	O(23)—C(24)—C(25)—O(26)	-56	61
C(8)—C(9)—O(10)—C(11)	-98	95	C(24)—C(25)—O(26)—C(27)	-75	74
C(9)—O(10)—C(11)—C(16)	132	-122	C(25)—O(26)—C(27)—C(32)	126	-124
O(10)—C(11)—C(16)—O(17)	-5	3	O(26)—C(27)—C(32)—O(1)	-5	3
C(11)—C(16)—O(17)—C(18)	179	-175	C(27)—C(32)—O(1)—C(2)	180	180

Contacts across the pseudo centre of symmetry are between the ring atoms C(24) and C(25) and perchlorate O(34'), and vice versa. Contacts between molecules in the next cell in the b direction (relations I and II) are not visible in the figure. Like molecules also contact parallel to a (relations V, VI, IX and X); note that here $y \sim 0.75$ for Ba and ~ 0.25 for Ba'. Molecules of types A and B alternate along c and contact each other by n-glide and screw-axis relations. The limit of the pseudo centre of symmetry is illustrated by the difference in contacts between molecules A and B across the planes at $z = 0.12$ and at $z = 0.62$.

The parameters, in the empirical equation of Brown & Wu (1976), summarize the Ba—O distances found in 45 inorganic and organic oxy-compounds, including hydrates. Complexes of Ba most comparable with this one are the cryptates in which the cation is nearly, but not completely, enclosed in the cavity of the ligand and

Table 4. *Mean planes through the carbon atoms of the benzene rings*

Deviations are in Å and those for other atoms are shown in italics. Standard deviations are 0·011–0·020 Å for C, 0·007–0·009 Å for O and 0·0006 Å for Ba. In the equations of planes, X, Y, and Z are in Å.

(i) $0·2587X - 0·3847Y - 0·8859Z + 17·2213 = 0$
(ii) $0·2006X - 0·3596Y - 0·9112Z + 5·1499 = 0$
(iii) $-0·4465X + 0·3038Y - 0·8415Z + 14·9044 = 0$
(iv) $-0·4465X + 0·2981Y - 0·8436Z + 10·8168 = 0$

	A (i)	B (ii)		A (iii)	B (iv)
C(11)	0·001	−0·009	C(27)	0·003	0·003
C(12)	−0·007	0·020	C(28)	−0·003	−0·006
C(13)	−0·001	−0·015	C(24)	−0·007	0·000
C(14)	0·010	−0·004	C(30)	0·015	0·007
C(15)	−0·009	0·010	C(31)	−0·012	−0·007
C(16)	0·003	−0·001	C(32)	0·003	0·001
O(10)	*0·115*	*−0·115*	O(1)	*0·007*	*−0·034*
O(17)	*0·010*	*−0·022*	O(26)	*−0·103*	*0·026*
Ba	*1·489*	*1·322*	Ba	*−0·593*	*0·613*

Angles (°) between normals to planes

(i)–(iii)	59·1	(i)–(v)	125	(iii)–(v)	71
(ii)–(iv)	55·1	(ii)–(vi)	120	(iv)–(vi)	69
(i)–(ii)	4·1	(v)–(vi)	2		
(iii)–(iv)	1·1				

The oxygen atoms of the macrocyclic ligand are not nearly coplanar (see text); the direction cosines in equations (v) and (vi) are those of approximate twofold axes through the macrocycles.

(v) $-0·375X + 0·917Y + 0·135Z - 6·187 = 0$
(vi) $-0·389X + 0·916Y + 0·100Z + 1·267 = 0$

	A	B		A	B		A	B
O(1)	0·6	−0·6	O(17)	0·3	−0·3	Ba	−0·7	0·7
O(4)	1·8	−1·7	O(20)	1·4	−1·5	O(33)	−2·2	2·1
O(7)	−0·1	0·1	O(23)	−0·5	0·4	O(37)	−3·2	3·2
O(10)	−1·7	1·8	O(26)	−1·9	1·9	O(38)	−2·0	1·9

Table 5. *Intermolecular distances less than 3·50 Å*

Atom a Atom b	$a \to b$	$b \to a$	
Molecules of A			
C(2)···O(37)	I	II	3·01
O(2)···O(34)	I	II	3·34
C(3)···O(34)	I	II	3·33
C(3)···O(37)	I	II	3·29
C(18)···O(39)	V	VI	3·37
O(20)···O(36)	I	II	3·22
C(21)···O(36)	I	II	3·32
C(29)···O(35)	VI	V	3·41
C(30)···O(36)	VI	V	3·36
Molecules of B			
C(2')···O(37')	II	I	3·09
C(2')···O(34')	II	I	3·37
C(3')···O(34')	II	I	3·33
C(3')···O(37')	II	I	3·34
C(18')···O(39')	IX	X	3·26
C(19')···O(36')	II	I	3·34
C(20')···O(36')	II	I	3·26
C(21')···O(36')	II	I	3·30
C(29')···O(35')	X	IX	3·40
C(30')···O(36')	X	IX	3·34
Molecules A and B			
C(6)···O(40')	III	IV	3·37
C(8')···O(40)	VII	VIII	3·28
C(9')···O(40)	VII	VIII	3·28
C(24')···O(34)			3·12
C(24)···O(34')			3·14
C(25')···O(34)			3·31
C(25)···O(34')			3·33

Symmetry code

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

two further contacts are made, viz $|Ba(222)(NCS)-H_2O]^+NCS^-$ (Metz, Moras & Weiss, 1973a) and $[Ba(223)(H_2O)_2]^{2+}(NCS^-)_2$ (Metz, Moras & Weiss, 1973b). In the former the Ba is 10-coordinated with the average Ba–H_2O 2·86 Å and Ba–O(aliphatic) 2·79 Å, and in the latter 11-coordinated with the Ba–H_2O 2·84 Å and Ba–O(aliphatic) 2·93 Å. The average Ba–O(aliphatic) in molecules A and B is 2·83 Å, intermediate between those in the 10- and 11-coordinated cryptates.

References

Blow, D. M. (1960). *Acta Cryst.* **13**, 168.
Brown, I. D. & Wu, K. K. (1976). *Acta Cryst.* **B32**, 1957–1959.
Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
Hanson, I. R., Hughes, D. L. & Truter, M. R. (1976). *J. Chem. Soc. Perkin Trans.* 2, pp. 972–976.
Hughes, D. L. (1975). *J. Chem. Soc. Dalton Trans.* pp. 2374–2378.
Johnson, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
Mercer, M. & Truter, M. R. (1973). *J. Chem. Soc. Dalton Trans.* pp. 2469–2473.
Metz, B., Moras, D. & Weiss, R. (1973a). *Acta Cryst.* **B29**, 1382–1387.

METZ, B., MORAS, D. & WEISS, R. (1973b). Acta Cryst. B29, 1388–1393.

PARSONS, D. G. & WINGFIELD, J. N. (1976a). Inorg. Chim. Acta, 18, 263–267.

PARSONS, D. G. & WINGFIELD, J. N. (1976b). Inorg. Chim. Acta, 17, L25–L26.

POONIA, N. S. & TRUTER, M. R. (1973). J. Chem. Soc. Dalton Trans. pp. 2062–2065.

SCHOMAKER, V., WASER, J., MARSH, R. E. & BERGMAN, G. (1959). Acta Cryst. 12, 600–604.

SHELDRICK, G. M. (1976). SHELX 76. Program system for crystal structure determination, Univ. of Cambridge, England.

TUŠEK, LJ., MEIDER-GORIČAN, H. & DANESI, P. R. (1976). Z. Naturforsch. Teil B, 31, 330–335.

X-RAY ARC (1973). Library of programs for the IBM 1130 computer. World List of Crystallographic Computer Programs. J. Appl. Cryst. 6, 309–346.

# A Tetranuclear Cobalt Complex*

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$[Co_4(OH)_6(C_2N_2H_8)_6]^{6+} \cdot 4SCN^- \cdot 2NO_3^- \cdot 2H_2O$; monoclinic, space group $P2_1/n$, $a = 13 \cdot 489$ (6), $b = 11 \cdot 713$ (2), $c = 27 \cdot 102$ (5) Å, $\beta = 100 \cdot 02$ (8)°, $Z = 4$. The cation comprises a central Co atom, bridged through pairs of OH groups to three peripheral Co atoms. The configurations of the Co atoms in the two enantiomeric forms of the cation are $\Lambda(\Delta\Delta\Delta)$ and $\Delta(\Lambda\Lambda\Lambda)$.

Introduction

The tetranuclear cobalt cations (I) and (II) were first prepared by Jörgensen (1898) and Werner (1907), and were used by Werner to prove his theories of optical activity. Cation (I) was the first completely inorganic complex to be resolved into its optical isomers (Werner, 1914).

en= ethylenediamine

(I)   (II)
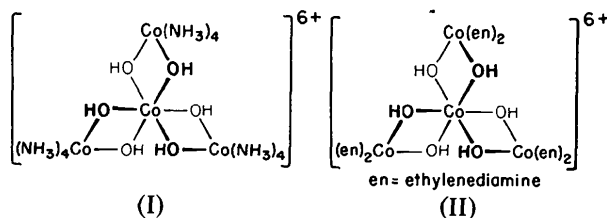
Thewalt (1971) has reported on the structure of the trisdithionate octahydrate salt of (II), which confirmed Werner's description of the cation as a tetranuclear species with six bridging OH groups; later, Thewalt &

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Ernst (1975) also reported on the structure of the monobromide pentathiocyanate trihydrate salt of the same cation. We report here the structure of another mixed salt of cation (II), containing two nitrate groups, four thiocyanate groups, and two water molecules per cation.

The compound was prepared by U. Thewalt in these laboratories as follows: 150 g of cobaltous nitrate were added to 150 g of water, and 300 ml of ethylenediamine were added to the solution. Soft, brown, powderish crystals were filtered out and were recrystallized from KSCN solution and further recrystallized from water; well-formed black crystals resulted. Subsequent attempts to repeat the preparation have resulted, instead, in small, grayish crystals of irregular habit, which we have not characterized.

Preliminary crystal data (Table 1) were obtained from Straumanis-type Weissenberg photographs. Intensities were collected from a cube-shaped crystal approximately 0·15 mm on an edge, with a Datex-automated General Electric diffractometer, Co $K\alpha$ radiation ($\lambda = 1 \cdot 7902$ Å), a θ–2θ scan mode at a scanning rate of 4° min^{-1}, and 15 s background counts at each end of the scans. Observational variances $\sigma^2(I)$ were calculated on the basis of normal counting