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The structure of the title compound has been redetermined. Hydrogenation of dibenzo-18-crown-6 yields two conformational isomers which were proposed to be the *cis-syn-cis* and the *cis-trans-cis* isomers of dicyclohexyl-18-crown-6. The previous study had established that the title complex contains the ligand which has the *cis-syn-cis* conformation but had resulted in some inaccurate bond lengths and also in an uncertainty regarding the presence of a water of hydration in the crystal. This study confirmed the report of the general conformation of the complex, resulted in more precise bond lengths and clearly established that a water of hydration was present at the crystal.

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Introduction.

During the past several years interest in cyclic polyether molecules has grown because of their ability to selectively complex various cations. The selectivity is a function of several factors including the size of the opening of the ring often referred to as the cavity, the type of the donor atoms and the flexibility of the ring. Several crystallographic studies of cyclic polyethers and their complexes have been made in order to identify structural parameters which are related to the observed selectivities [2]. One of the first cyclic polyethers investigated was dibenzo-18-crown-6 [3]. Hydrogenation of that compound yields two isomers of dicyclohexyl-18-crown-6, one having a *cis-syn-cis* conformation and the other a *cis-trans-cis* conformation. The isomers can readily be distinguished by their melting points as one melts at 61-62° and the other at 69-70° [4]. This study was initiated in order to determine the conformation of the lower melting isomer and to study the complexation of the Ba²⁺. A preliminary report of the structure [1] showed the isomer to be the *cis-syn-cis* isomer but because of the poor quality of the crystal and the data, the bond lengths were rather inaccurate and there was an uncertainty with regard to the presence of a water of hydration in the coordination sphere of Ba²⁺. For these reasons a new set of data has been collected and the structure redetermined.

Data Collection and Structure Refinement.

Crystals for both studies were prepared in a straight-forward manner by adding the polyether ligand to an aqueous solution containing excess Ba(SCN)₂ and allowing the solution to evaporate [5]. A small nearly spherical crystal with average diameter of 0.15 mm was used for the determination of lattice parameters and data collection. The crystal was mounted on a Nicolet P3 autodiffractometer. Data was collected utilizing graphite-monochromated Mo K α radiation, $\lambda = 0.71069 \text{ \AA}$. The lattice parameters were

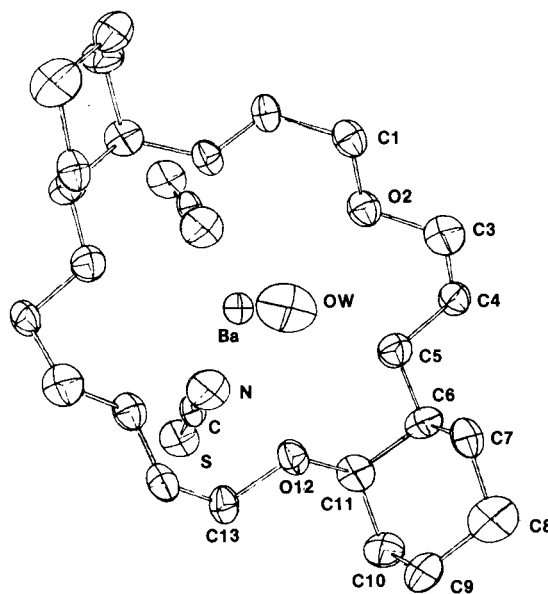


Figure 1. ORTEP [8] drawing of the title compound.

obtained using a least-square refinement of 15 centered 2θ values ($13^\circ < 2\theta < 25^\circ$). These parameters along with the rest of the crystal data are listed in Table 1. Single crystal data were collected using a θ - 2θ scan technique to a $\sin \theta/\lambda$ limit of 0.54. A total of 872 reflections were collected of which 725 were considered observed as $I > 2\sigma(I)$. Positional parameters of non-hydrogen atoms from the previous study with the exception of the oxygen of the questioned water of hydration were used for the trial structure. All heavy atoms were refined anisotropically [6]. A difference map calculated at this stage of refinement clearly indicated the presence of the water of hydration. The water oxygen is located on the two-fold axis with z parameter approximately the same as that of the suspected oxygen in the initial study. Hydrogen positions of the macrocyclic ligand

Table 1

Crystal and Physical Data

Space Group		Aba2(C ₂ v, No. 41)
a	=	21.239(9) Å
b	=	13.551(3) Å
c	=	9.635(2) Å
Z	=	4
Dm	=	1.53 g cm ⁻³
Dc	=	1.54 g cm ⁻³
F(000)	=	1424
μ	=	16.5 cm ⁻¹

Table 2

Atomic Coordinates and Thermal Parameters (with estimated standard deviations) for non-hydrogen atoms. Positional Parameters are $\times 10^4$ and Thermal Parameters (U_{eq}) are $\times 10^3$

Atom	x	y	z	U_{eq}
C1	616(6)	-2364(8)	1335(16)	46
O2	863(4)	-1491(6)	671(8)	39
C3	1447(5)	-1182(9)	1221(17)	44
C4	1694(6)	-299(7)	449(13)	42
O5	1285(4)	512(6)	802(9)	40
C6	1470(5)	1449(8)	207(20)	36
C7	2142(5)	1733(9)	525(13)	45
C8	2234(6)	1832(9)	2110(13)	44
C9	1778(5)	2559(12)	2657(26)	56
C10	1104(6)	2337(10)	2337(20)	40
C11	1020(6)	2212(9)	783(14)	38
O12	387(4)	1935(5)	432(9)	48
C13	-66(8)	2709(7)	540(14)	47
OW	0(0)	0(0)	2941(11)	67
S	1307(1)	68(4)	-5056(9)	55
C	985(5)	4(14)	-3496(13)	41
N	763(4)	29(12)	-2405(11)	60
Ba	0(0)	0(0)	0(0)	30

were then calculated based on geometrical considerations but hydrogen parameters were not refined. When refinement was terminated the conventional R was 0.033 and the weighted R was 0.028. The resulting difference map did not show the presence of any other atoms.

The positional and thermal parameters for the non-hydrogen atoms of the compound are listed in Table 2 [7]. Consideration was made for the anomalous dispersion of barium but no absorption correction was made ($\mu_r = 0.12$).

Discussion.

The barium atom is located on the 2-fold axis and lies in the cavity of the macrocycle (Figure 1). The symmetry of the space group requires that the macrocycle have a two-fold axis of symmetry which established that this isomer must have the *cis-syn-cis* conformation. The bond lengths and angles are listed in Table 3. Both bond lengths and angles are similar to those found in other cyclic polyethers

Table 3

Interatomic Distances (Å) and Angles (°) for Non-hydrogen Atoms with e.s.d.'s in Parenthesis

1	2	3	1-2 (Å)	1-2-3 (°)
C13'	C1	O2	1.473(13)	108.3(1.1)
C1	O2	C3	1.443(13)	113.3(1.0)
O2	C3	C4	1.412(13)	110.9(1.1)
C3	C4	O5	1.503(15)	106.3(1.0)
C4	O5	C6	1.441(11)	114.4(0.8)
O5	C6	C11	1.448(13)	106.4(1.0)
O5	C6	C7	a*	113.6(1.1)
C6	C11	O12	1.514(17)	109.0(1.0)
C11	O12	C13	1.437(14)	114.9(1.0)
O12	C13	C1'	1.427(14)	107.5(1.1)
C6	C7	C8	1.510(15)	110.0(1.1)
C7	C6	C11	a	110.4(1.1)
C7	C8	C9	1.546(15)	109.1(1.4)
C8	C9	C10	1.479(19)	114.8(1.5)
C9	C10	C11	1.496(17)	109.8(1.7)
C10	C11	O12	1.517(20)	111.8(1.2)
C10	C11	C6	a	111.4(1.2)
N	C	S	1.152(14)	175.3(2.1)
C	S		1.654(15)	
Ba	O2		2.804(8)	
Ba	O5		2.920(9)	
Ba	O12		2.779(7)	
Ba	OW		2.833(11)	
Ba	N		2.828(10)	

*a indicates that the bond length appears earlier in the listing.

Table 4

Torsion Angles (°) Involving the Atoms of the Cavity

1	2	3	4	1-2-3-4 (°)
C13'	C1	O2	C3	171.0
C1	O2	C3	C4	-178.5
O2	C3	C4	O5	-69.5
C3	C4	O5	C6	176.9
C4	O5	C6	C11	175.4
O5	C6	C11	O12	57.9
C6	C11	O12	C13	162.4
C11	O12	C13	C1'	131.0
O12	C13	C1'	O2'	56.1

[2]. The torsion angles involving atoms in the ether cavity are also normal as the average absolute values of the torsion angles about C-C and C-O bonds are 61(7)° and 166(18)° respectively. Individual torsion angle values are listed in Table 4.

The quality of the single crystal data in this study was much better than that of the previous study. This is reflected in the precise bond length values. The data clearly indicates that there is a water of hydration in the crystal. The coordination about the barium is 9-fold as it interacts with six oxygen atoms of the macrocycle, two nitrogen atoms of the two SCN⁻ groups and the water oxygen. The

barium atom has the ability to organize the opening of the ligand into a nearly symmetrical cavity with the non-bonding electron pairs of the oxygen atoms directed towards the cation. An indication of the nearly circular cavity is the Ba-O distances which range from 2.78 to 2.92 Å. This is in contrast to the conformation of the uncomplexed macrocycle in which the opening of the ring is highly elliptical [9]. The radius of the cavity of the complex is nearly equal to the sum of the ionic radius of Ba²⁺ (1.36 Å) [10] the van der Waal radius of oxygen (1.40 Å) [11]. The stability of the Ba complex must be in part related to the good fit of the barium in the cavity of the macrocycle.

There are no unusually short intermolecular interactions in the crystal structure. However, there is a possibility of hydrogen bonding between the water of one molecule and the sulfur atoms of the two of a SCN⁻ of a molecule translated a unit cell in the z direction. Unfortunately, because the single crystal data is dominated by the heavy barium atom, it is not possible to locate the hydrogen atoms of the water molecule. Therefore hydrogen bonding is only speculation. Even if this interaction is present it links molecules in only the z direction. This indicates that packing forces are of great importance in the structure.

REFERENCES AND NOTES

- [1] N. K. Dalley, D. E. Smith, R. M. Izatt and J. J. Christensen, *J. Chem. Soc. Chem. Commun.*, 90 (1972).
- [2] For example, see N. K. Dalley, "Structural Studies" Chapter in "Synthetic Multidentate Macrocyclic Compounds", R. M. Izatt and J. J. Christensen, eds, Academic Press, New York, NY, 1978, pp 207-243.
- [3] D. Bright and M. R. Truter, *J. Chem. Soc. (B)*, 1544 (1970).
- [4] R. M. Izatt, D. P. Nelson, J. H. Rytting, B. L. Haymore, and J. J. Christensen, *J. Am. Chem. Soc.*, **93**, 1619 (1971).
- [5] B. L. Haymore, Ph.D. Dissertation, Brigham Young University, (1972).
- [6] Computer programs used in the solution of this structure are contained in the computer package SHELX-76, G. M. Sheldrick, "A Program for X-Ray Crystal Structure Determinations", Cambridge University, England, 1976.
- [7] A table of structure factors and tables of anisotropic thermal parameters for non-hydrogen atoms and calculated positions for hydrogen atoms can be obtained by writing N. K. Dalley, Department of Chemistry, Brigham Young University, Provo, Utah 84602.
- [8] C. K. Johnson, ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1965.
- [9] N. K. Dalley, J. S. Smith, S. B. Larson, J. J. Christensen and R. M. Izatt, *J. Chem. Soc., Chem. Commun.*, 43 (1975).
- [10] R. D. Shannon and C. T. Prewitt, *Acta Crystallogr.*, **B25**, 925 (1969).
- [11] L. Pauling, "The Nature of the Chemical Bond", 3rd Ed, Cornell University Press, Ithaca, New York, 1960, p 260.