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Structure of Ethylene Oxide Oligomer Complexes. III. A 1:2 Complex of Hexaethylene Glycol Diethyl Ether with Mercuric Chloride

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Molecular and crystal structure of a 1 : 2 complex of hexaethylene glycol diethyl ether $CH_3CH_2O(CH_2CH_2O)_6$-CH_2CH_3 (HGE) with $HgCl_2$ has been determined by means of X-ray diffraction. The unit cell is monoclinic with $a=23.34$, $b=7.84$, $c=16.69$ Å, and $\beta=115.0°$. The space group is C2/c. The unit cell contains four HGE and eight $HgCl_2$ molecules. The HGE molecule in the complex has the conformation

$$CH_3-CH_2\underset{T}{-}O\underset{T}{-}CH_2\underset{G}{-}CH_2\underset{T}{-}O\underset{T}{-}CH_2\underset{\overline{G}}{-}CH_2\underset{T}{-}O\underset{T}{-}CH_2\underset{G}{-}CH_2\underset{G}{-}O\underset{G}{-}CH_2\underset{G}{-}CH_2\underset{T}{-}O\underset{T}{-}CH_2\underset{\overline{G}}{-}CH_2\underset{T}{-}O\underset{T}{-}CH_2\underset{G}{-}CH_2\underset{T}{-}O\underset{T}{-}CH_2-CH_3,$$

where T, G, and $\overline{G}$ denote *trans*, *gauche*, and minus *gauche*, respectively, two $HgCl_2$ molecules being coordinated with one HGE molecule. The asymmetric unit consists of a half of HGE and one $HgCl_2$ molecule. The four oxygen atoms of either half of HGE, which are coplanar, are coordinated with one Hg atom with close interatomic distances (2.66—2.91 Å) between the O and Hg atoms, the central oxygen atom of HGE being coordinated with two Hg atoms. The $HgCl_2$ molecule is distorted from the linear form by 4°.

Structures of the molecular complexes of tetraethylene glycol dimethyl ether $CH_3O(CH_2CH_2O)_4CH_3$ (TGM) and tetraethylene glycol diethyl ether CH_3CH_2O-$(CH_2CH_2O)_4CH_2CH_3$ (TGE) with $HgCl_2$ were reported in previous papers.[1,2] It has been found that TGE is the limiting case in which one TGE molecule encloses one $HgCl_2$ without drastic change of the molecular conformation consisting of a succession of $\underset{T}{-}CH_2\underset{G}{-}CH_2\underset{T}{-}O\underset{T}{-}CH_2\underset{\overline{G}}{-}CH_2\underset{T}{-}O-$. The present paper deals with the complex of hexaethylene glycol diethyl ether CH_3CH_2O-$(CH_2CH_2O)_6CH_2CH_3$ (HGE) with $HgCl_2$.

Experimental

Samples. HGE was synthesized according to the method of Fordyce *et al.*[3] The synthesized HGE was purified by distillation and the purity was checked by gas chromatography.

The crystalline complex with $HgCl_2$ was prepared in quite the same way as the TGM–$HgCl_2$ complex.[1] The crystal is transparent and long along the *b* axis. The melting point was found to be 103°C by microscopy. The density of the crystal was measured by the flotation method with the use of a liquid mixture of $CHBr_3$ and CCl_4 as flotation medium.

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[1] R. Iwamoto, This Bulletin, **46**, 1114 (1973).

[2] R. Iwamoto, *ibid.*, **46**, 1118 (1973).

[3] R. Fordyce, E. L. Lovell, and H. Hibbert, *J. Amer. Chem. Soc.*, **61**, 1905 (1939).

The observed value was 2.13 g/cc. From elemental analysis with respect to Hg, the composition was found to be HGE: $HgCl_2$=1:2 (Found: Hg, 46.4%. Calcd for the 1:2 complex: Hg, 45.6%).

Unit Cell and Space Group. The unit cell parameters were determined with a Weissenberg camera and calibrated by silicon powder. Systematic absences were observed for hkl with $h+k$ odd and $h0l$ with l odd. From the observed absences the possible space groups were C2/c and Cc, C2/c being finally chosen. The crystallographic data are given in Table 1, together with some physical constants.

TABLE 1. CRYSTALLOGRAPHIC AND PHYSICAL DATA OF THE HGE–$HgCl_2$ COMPLEX

Formula	$CH_3CH_2O(CH_2CH_2O)_6CH_2CH_3 \cdot 2HgCl_2$
MW	881.3
Mp	103 °C
Crystal system	monoclinic
Space group	C2/c-C_{2h}^6
a	23.34 Å
b	7.84 Å
c	16.69 Å
β	115.0°
Z	4
Vol.	2767.9 Å
D_c	2.18 g/cc
D_m	2.13 g/cc
μ (Cu$K\alpha$)	256.9 cm^{-1}
F(000)	1656

Intensity Measurement. The X-ray diffraction photographs were taken by use of Cu$K\alpha$ radiation. The crystals used were about 0.2 mm × 0.3 mm × 0.2 mm in size. Intensity data were collected around the b axis from $k=0$ to 4 layer lines by equi-inclination Weissenberg multiple film method, the number of the observed reflections being 1491. The intensities were measured by visual comparison with standard scales. Intensity data were corrected only for Lorentz and polarization factors, although the absorption coefficient is very large ($\mu=257$ cm^{-1} for Cu$K\alpha$ radiation). The smallest possible crystal was used for collecting the intensity data and was renewed for each layer line because of its decomposition under irradiation of X-rays.

Structure Determination

The atomic positions of the Hg and Cl atoms were easily determined by the Patterson method. The Patterson map showed strong peaks due to Hg at $v=0.0$. This suggested that the crystal lattice should have a two-fold symmetry axis along the b axis and the space group should be C2/c. Based upon the atomic positions of the Hg and Cl atoms, the atomic positions for all the C and O atoms of HGE, the asymmetric unit of which is a half, were determined by the difference Fourier method. Calculation of structure factors and the Fourier synthesis were made according to the space group C2/c. The results were quite reasonable. The space group was, thus, taken as C2/c. Atomic scattering factors were taken from the *International Table for X-Ray Crystallogrphy* (1962).

The atomic coordinates and temperature factors for all the atoms except hydrogen were refined by the least squares method of isotropic and diagonal approximation. The least squares method improved the R factor ($\sum||F_o|-|F_c||/\sum|F_o|$) to 14.0%. The resulting atomic coordinates and temperature factors are given in Table 2, and the molecular dimensions in Table 3.

TABLE 2. ATOMIC COORDINATES AND TEMPERATURE FACTORS IN THE HGE–$HgCl_2$ COMPLEX

Atom	x	y	z	B
Hg	0.0844	0.0693	0.2487	3.76Å^2
Cl_1	0.0008	0.2156	0.1419	4.40
Cl_2	0.1653	−0.0761	0.3635	4.55
O_1	0.0	−0.2002	0.2500	3.96
C_1	−0.0224	−0.3062	0.1678	4.64
C_2	0.0376	−0.3466	0.1461	3.86
O_2	0.0537	−0.1720	0.1221	4.09
C_3	0.1090	−0.1989	0.0936	5.02
C_4	0.1155	−0.0220	0.0591	4.27
O_3	0.1368	0.0736	0.1380	4.58
C_5	0.1540	0.2676	0.1163	5.88
C_6	0.1975	0.3324	0.2048	5.62
O_4	0.1689	0.3559	0.2693	4.56
C_7	0.2143	0.3954	0.3570	6.60
C_8	0.1747	0.4021	0.4177	6.20

TABLE 3. BOND LENGTHS AND BOND ANGLES IN THE HGE–$HgCl_2$ COMPLEX

Hg–Cl_1	2.298Å	Cl_1–Hg–Cl_2	175.9°
Hg–Cl_2	2.319	C_1'–O_1–C_1	111.2
O_1–C_1	1.47	O_1–C_1–C_2	107.6
C_1–C_2	1.61	C_1–C_2–O_2	102.2
C_2–O_2	1.51	C_2–O_2–C_3	106.4
O_2–C_3	1.56	O_2–C_3–C_4	102.1
C_3–C_4	1.53	C_3–C_4–O_3	104.1
C_4–O_3	1.40	C_4–O_3–C_5	111.9
O_3–C_5	1.59	O_3–C_5–C_6	102.0
C_5–C_6	1.46	C_5–C_6–O_4	114.3
C_6–O_4	1.48	C_6–O_4–C_7	112.2
O_4–C_7	1.41	O_4–C_7–C_8	104.4
C_7–C_8	1.62		

Results and Discussion

Figure 1 shows the crystal structure of the HGE–$HgCl_2$ complex. Table 4 gives the internal rotation angles for each bond of the asymmetric unit of the molecule. The CH_2–CH_2 bonds are approximately *gauche* (67—77°) and the CH_2–O bonds are nearly *trans* (169—176°) with the exception of the *gauche* CH_2–O bonds located at the center of the molecule, the angle of which is 88° and considerably deviated from the ordinary *gauche* angle. The conformation of the whole molecule is then denoted by

$$CH_3-CH_2\underset{T}{-}O\underset{T}{-}CH_2\underset{G}{-}CH_2\underset{T}{-}O\underset{T}{-}CH_2\underset{\bar{G}}{-}CH_2\underset{T}{-}O\underset{T}{-}CH_2\underset{G}{-}CH_2\underset{G}{-}O\underset{G}{-}$$

$$CH_2\underset{G}{-}CH_2\underset{T}{-}O\underset{T}{-}CH_2\underset{\bar{G}}{-}CH_2\underset{T}{-}O\underset{T}{-}CH_2\underset{G}{-}CH_2\underset{T}{-}O\underset{T}{-}CH_2-CH_3.$$

The HGE molecule encloses two $HgCl_2$ molecules in the way shown in Figs. 2 and 3, having the two-fold symmetry axis passing through the central O_1 atom. It should be noted that each half of HGE enclosing

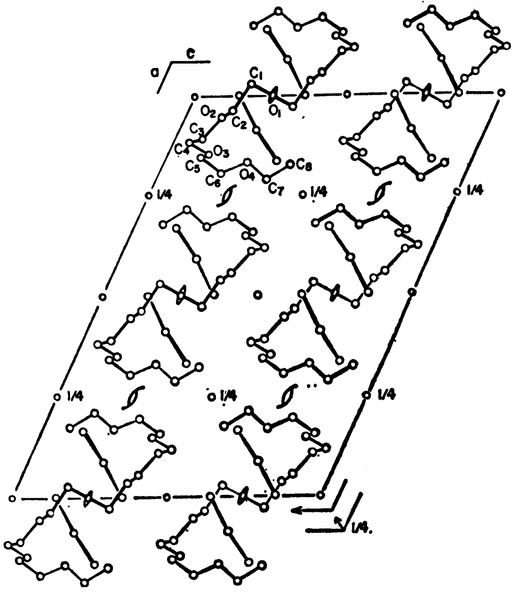

Fig. 1. Crystal structure of the HGE-$HgCl_2$ complex.

Table 4. Internal rotation angles for the HGE molecule in the complex

$C_1'-O_1-C_1-C_2$	−88°
$O_1-C_1-C_2-O_2$	−67
$C_1-C_2-O_2-C_3$	−176
$C_2-O_2-C_3-C_4$	173
$O_2-C_3-C_4-O_3$	77
$C_3-C_4-O_3-C_5$	−176
$C_4-O_3-C_5-C_6$	−169
$O_3-C_5-C_6-O_4$	−74
$C_5-C_6-O_4-C_7$	172
$C_6-O_4-C_7-C_8$	−176

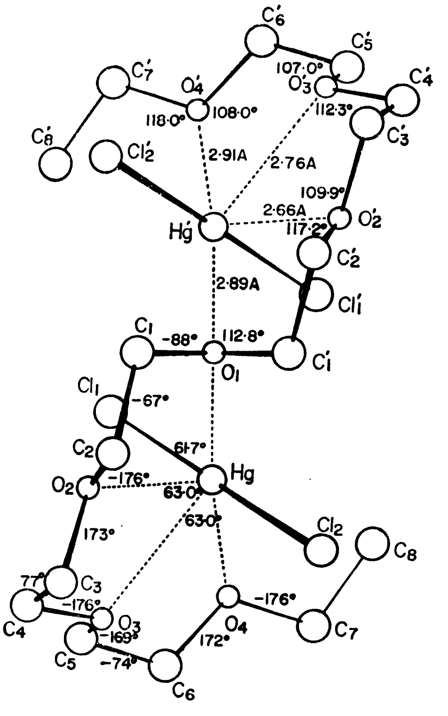

Fig. 2. Structure of one pair of the HGE-$HgCl_2$ complex projected on the *ac* plane.

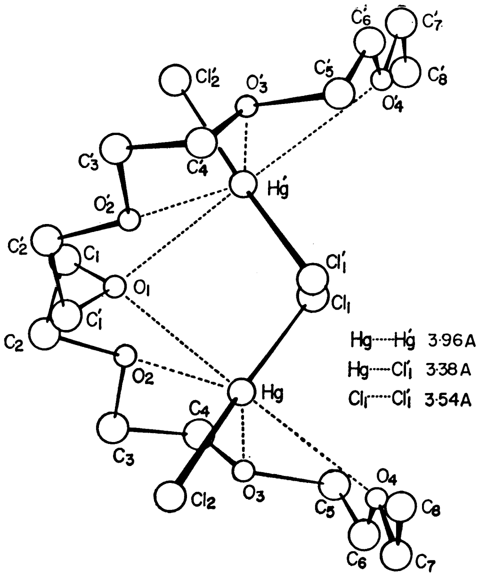

Fig. 3. Structure of one pair of the HGE-$HgCl_2$ complex projected along the *c* axis.

one $HgCl_2$ consists of a sequence of the conformation $\underset{T}{-}CH_2\underset{G}{-}CH_2\underset{T}{-}O\underset{T}{-}CH_2\underset{\bar{G}}{-}CH_2\underset{T}{-}O-$ as found in the TGM-$HgCl_2$[1] but the central part of HGE combining the two halves has the conformation $\underset{T}{-}CH_2\underset{G}{-}CH_2\underset{G}{-}O\underset{G}{-}CH_2\underset{G}{-}CH_2\underset{T}{-}O-$.

Table 5. Interatomic distances and angles for non-bonded atoms in the HGE–HgCl complex

$O_1\cdot\cdot Hg\cdot\cdot O_2$	61.7°	$Hg\cdot\cdot O_1$	2.89Å
$O_2\cdot\cdot Hg\cdot\cdot O_3$	63.0	$Hg\cdot\cdot O_2$	2.66
$O_2\cdot\cdot Hg\cdot\cdot O_4$	63.0	$Hg\cdot\cdot O_3$	2.76
		$Hg\cdot\cdot O_4$	2.91
$Cl_1-Hg\cdot\cdot O_1$	90.4		
$Cl_2-Hg\cdot\cdot O_1$	87.7	$C_1-O_1\cdot\cdot Hg$	112.8°
$Cl_1-Hg\cdot\cdot O_2$	84.5	$C_2-O_2\cdot\cdot Hg$	117.2
$Cl_2-Hg\cdot\cdot O_2$	97.8	$C_3-O_2\cdot\cdot Hg$	109.9
$Cl_1-Hg\cdot\cdot O_3$	90.7	$C_4-O_3\cdot\cdot Hg$	112.3
$Cl_2-Hg\cdot\cdot O_3$	93.3	$C_5-O_3\cdot\cdot Hg$	107.0
$Cl_1-Hg\cdot\cdot O_4$	91.1	$C_6-O_4\cdot\cdot Hg$	108.0
$Cl_2-Hg\cdot\cdot O_4$	90.3	$C_7-O_4\cdot\cdot Hg$	118.0
		$Hg\cdot\cdot O_1\cdot\cdot Hg$	86.3
		$Hg\cdot\cdot Hg$	3.96Å

Table 5 gives the interatomic distances and angles for non-bonded atoms in HGE–$HgCl_2$. The four oxygen atoms contained in the half of HGE enclosing one Hg atom are nearly coplanar and the interatomic distances between the O and Hg atoms range from 2.66 to 2.91 Å. The angles $O_i\cdots Hg\cdots O_{i+1}$ are nearly 60° (61.7—63.0°) and the angles $C_j-O_i\cdots Hg$ are nearly a tetrahedral angle. The spatial arrangement of the Hg and O atoms in the part enclosing one $HgCl_2$ is very similar to the case of TGM-$HgCl_2$.[1] In the HGE–$HgCl_2$, genearlly, one oxygen atom is coordinated to one Hg but the O_1 atom only is coordinated with two Hg atoms. It may be considered that the interatomic interactions between the Hg and O atoms

Table 6. Molecular constants of $HgCl_2$, interatomic distances Hg··O, the angles for O··Hg··O and Hg··O··Hg, the number of coordinating oxygen atoms per Hg(N), and the average number of coordination per oxygen atom (M) in the TGM–$HgCl_2$, TGE–$HgCl_2$, HGE–$HgCl_2$, and PEO–$HgCl_2$ complexes

	Hg–Cl (Å)	ClHgCl (°)	Hg··O (Å)	OHgO (°)	HgOHg (°)	N	M
TGM–$HgCl_2$[a]	2.29 2.31	174.2	2.78—2.96	59.9—62.0	—	5	1
TGE–$HgCl_2$[b]	2.35	180 (?)	(2.81—2.91)	(58.7—60.6)	—	5	1
HGE–$HgCl_2$	2.30 2.32	175.9	2.66—2.91	61.7—63.0	86.3	4	8/7
PEO–$HgCl_2$(I)[c]	2.30	176.6	2.62	62.9	—	2	1/2
PEO–$HgCl_2$(II)[d]	2.23 2.25	171.7	2.79	64.0	85.5	2	2
$HgCl_2$[e]	2.23 2.27	180					

a) See Ref. 1. b) See Ref. 2. c) See Ref. 4. d) See Ref. 5. e) See Ref. 6.

must have greater influence on the O_1 atom causing the two CH_2–O bonds involving the O_1 atom to take a *gauche* form.

Table 6 summarizes the molecular constants of $HgCl_2$,Hg···O interatomic distances, the angles for O···Hg···O and Hg···O···Hg, the number of coordination per Hg (N) and the average number of coordination per O (M) in the TGM–$HgCl_2$,[1] TGE–$HgCl_2$,[2] HGE–$HgCl_2$, and polyethylene oxide (PEO)–$HgCl_2$.[4,5] The molecular constants of $HgCl_2$ reveal some differences among these complexes. The longest bond length of Hg–Cl is 2.35 Å in the TGE–$HgCl_2$ and the shortest is 2.23 Å in the PEO–$HgCl_2$ of type II. The two Hg–Cl bonds of $HgCl_2$ are non-equivalent in the TGM–$HgCl_2$, HGE–$HgCl_2$, and PEO–$HgCl_2$ (type II), and they are significantly different in the bond length. The $HgCl_2$ molecule is, in general, deviated from the linear form in the complexes. The angle of the deviation ranges from 3.4 (PEO–$HgCl_2$ of type I) to 8.3° (PEO–$HgCl_2$ of type II). The interatomic distances between the O and Hg atoms are in the 2.66—2.96 Å range and the O···Hg···O angle is in the 59.9—64.0° range for all these complexes. The Hg···O···Hg angle is 86.3 and 85.5° in HGE–$HgCl_2$ and PEO–$HgCl_2$ (type II), respectively. The number of the coordinating oxygen atoms around a Hg atom (N) ranges from 2 to 5 among these complexes.

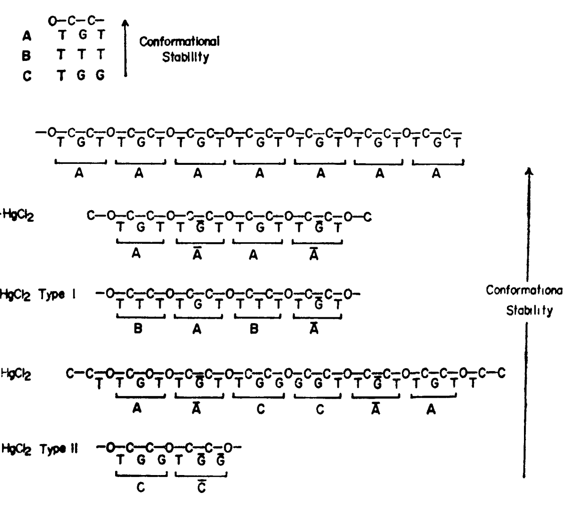

Fig. 4. Molecular conformations of TGM and HGE in the crystalline complex with $HgCl_2$, and of PEO in the ordinary polymer and the complexes with $HgCl_2$.

General Discussion

In the molecular conformations of $RO(CH_2CH_2O)_mR$ and PEO in the complexes with $HgCl_2$,[1,2,4,5] the *gauche* form of the CH_2–CH_2 bond is essentially favorable for coordination between the O and Hg atoms, while the CH_2–O bond takes either a *trans* or a *gauche* form depending on the situation, although the *gauche* form

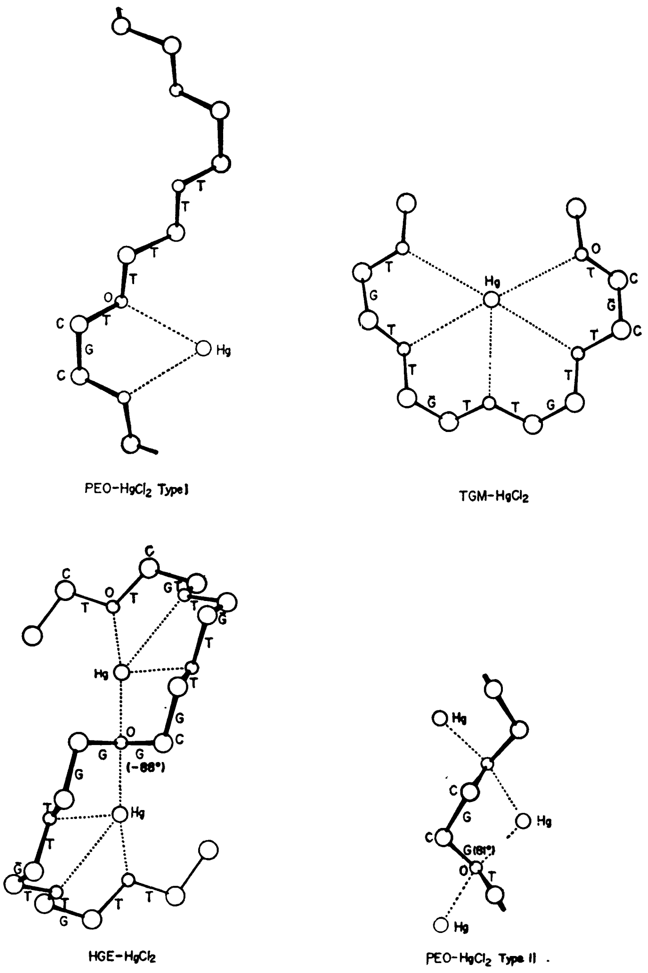

Fig. 5. Way of the interactions between the O and Hg atoms in the TGM–$HgCl_2$, HGE–$HgCl_2$, and PEO–$HgCl_2$ complexes.

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[4] R. Iwamoto, Y. Saito, H. Ishihara, and H. Tadokoro, *J. Polymer Sci., A-2*, **6**, 1509 (1968).

[5] M. Yokoyama, H. Ishihara, R. Iwamoto, and H. Tadokoro, *Macromolecules*, **2**, 184 (1969).

[6] H. Bräkken and L. Harang, *Z. Krist.*, **68**, 123 (1928).

is considerably deviated from the ordinary *gauche* angle. These molecular conformations in the complexes may be considered to be governed by two factors: (i) conformational stability of a single chain and (ii) stabilization by the interactions between the O and Hg atoms.

Figure 4 gives the molecular conformations of TGM,[1] HGE in the $HgCl_2$ complexes and of PEO in the pure polymer[7] and the $HgCl_2$ complexes.[4,5] The three possible forms for the O–CH_2–CH_2– group are TGT, TTT, and TGG in the order of conformational stability,[1] and are denoted as types A, B, and C, respectively, as shown in Fig. 4.

PEO in the pure polymer consists of type A only[7] and the TGM molecule is composed of alternations A and $\bar{A}$ ($\bar{A}$: minus A).[1] PEO in the type I complex is composed of A (or $\bar{A}$) and B,[4] and the HGE molecule has the $A\bar{A}CC\bar{A}A$ form. PEO in the type II complex is composed of type C only.[5] Therefore, from the viewpoint of conformational stability, these molecules can be arranged from top to bottom in the order of conformational stability as shown in Fig. 4. PEO in the pure polymer and TGM are the most stable as a single chain, while the PEO molecule in the type II complex is the least stable among these molecules.

The correlation of the conformational stability with the mode of coordination between the O and Hg atoms in the complexes is considered next. Figure 5 gives the way of coordination between the O and Hg atoms in the complexes. The numbers given under M in Table 6 indicate the average number of coordination per oxygen atom and are, therefore, a measure of the strength of the interactions between $HgCl_2$ and the oligomer or polymer molecules. In the PEO–$HgCl_2$ of type I,[4] only two of the four oxygen atoms in the fiber identity period are coordinated with one Hg atom and M is 1/2. In the case of the TGM–$HgCl_2$[1] all the five oxygen atoms are coordinated with one Hg and M is 1. In the HGE–$HgCl_2$, three oxgyen atoms of either half of HGE are coordinated with one Hg atom as in the TGM–$HgCl_2$[1] and the central oxygen atom between the two gauche CH_2–O bonds is coordinated to two Hg atoms, giving 8/7 for M. In the PEO–$HgCl_2$ of type II,[5] each oxygen atom is coordinated to two Hg atoms just as the central oxygen atom of HGE and M is 2. Thus, the strength of the interactions between ethylene oxide oligomers or polymer and $HgCl_2$ is least effective for the PEO–$HgCl_2$ of type I and most effective for the PEO–$HgCl_2$ of type II, increasing from upper left to down right in Fig. 5.

It is thus found that the less stable conformation has stronger interactions between the O and Hg atoms in the complexes. These interactions might cause the molecule to take a more favorable conformation for coordination between ethylene oxide oligomers or polymer and $HgCl_2$ in the complexes, which is usually less stable as a single chain. Thus, the two factors, conformational stability and stabilization by the interactions between the O and Hg atoms, are very important when we consider the resulting conformation of these molecules.

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[7] H. Tadokoro, Y. Chatani, T. Yoshihara, S. Tahara, and S. Murahashi, *Makromol. Chem.*, **73**, 109 (1964).