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Structure of Ethylene Oxide Oligomer Complexes. II. A 1:1 Complex of Tetraethylene Glycol Diethyl Ether with Mercuric Chloride

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Structure of a 1:1 complex of tetraethylene glycol diethyl ether $CH_3CH_2O(CH_2CH_2O)_4CH_2CH_3$ (TGE) with mercuric chloride has been investigated by means of X-ray diffraction. The complex has a cubic unit cell with $a=12.54$ Å and four molecules of both TGE and $HgCl_2$ are contained in the unit cell. The space group is Pa3-T_h^6. Four Hg atoms are located at the positions corresponding to the face centered arrangement. The TGE molecule is statistically arranged around the Hg atom located at the position having site symmetry $\bar{3}$. The following molecular conformation of TGE was suggested:

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

where T, G, and $\bar{G}$ indicate *trans*, *gauche*, and minus *gauche* forms, respectively. The TGE molecule encloses the $HgCl_2$ molecule around the Hg atom with close interatomic distances between the Hg and O atoms.

Structure of the molecular complex of tetraethylene glycol dimethyl ether $CH_3O(CH_2CH_2O)_4CH_3$ (TGM) with $HgCl_2$ has been reported in a previous paper.[1] Tetraethylene glycol diethyl ether $CH_3CH_2O(CH_2CH_2O)_4CH_2CH_3$ (TGE) also forms a 1:1 molecular complex with $HgCl_2$. Replacement of CH_3 by CH_2CH_3 for the terminal groups causes a remarkable change in the symmetry of the unit cell: that is, the TGM–$HgCl_2$ complex has a monoclinic unit cell, while the TGE–$HgCl_2$ complex has a cubic unit cell. The occurrence of the cubic unit cell for the complex may be noticeable because, generally speaking, only simple or highly symmetric molecules form a cubic unit cell. In the present paper the structure of the TGE–$HgCl_2$ complex is described.

Experimental

Samples. TGE was synthesized according to the method of Fordyce, Lovell, and Hibbert.[2] The synthesized TGE was purified by distillation, the purity being checked by means of gas chromatography.

Crystals of TGE–$HgCl_2$ were prepared in the same way as for TGM–$HgCl_2$.[1] The crystal is transparent; the melting point is 88°C as determined microscopically. The density of the crystal was measured by the flotation method with the use of a liquid mixture of CCl_4 and $CHBr_3$ as the flotation medium. The observed density was 1.76 g/cc. The composition was found to be TGE: $HgCl_2$=1:1 by elemental analysis (Found: Hg, 38.3%. Calcd for the 1:1 complex: Hg, 38.2%).

Unit Cell and Space Group. At first the unit cell was mistaken as monoclinic but more detailed investigation revealed that the crystal has a three-fold symmetry axis along the direction perpendicular to the axis around which X-ray photographs were taken at an early stage. Finally, it was found that the unit cell is cubic. The unit cell para-

Table 1. Crystallographic and physical data of the TGE–$HgCl_2$ complex

Formula	$CH_3CH_2O(CH_2CH_2O)_4CH_2CH_3 \cdot HgCl_2$
MW	521.7
Mp	88 °C
Crystal system	cubic
Space group	Pa3-T_h^6
a	12.54 Å
Z	4
Vol.	1971.9 Å^3
D_c	1.76 g/cc
D_m	1.76 g/cc
μ (Cu$K\alpha$)	177.8 cm^{-1}
F(000)	1008

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

2) R. Fordyce, E. L. Lövell, and H. Hibbert, *J. Amer. Chem. Soc.*, **61**, 1095 (1939).

meter was measured by a powder camera with diameter of 11.46 cm and calibrated with silicon powder. The crystallographic data are given in Table 1, together with some physical constants. The assumption that the unit cell contains four molecules of both TGE and $HgCl_2$ gives the calculated density of 1.76 g/cc, which is reasonable as regards the observed density of 1.76 g/cc. The systematic absences observed are $h0l$ with l odd, $hk0$ with h odd, and $0kl$ with k odd. The space group is, therefore, $Pa3\text{-}T_h^6$.

Intensity Measurement. X-Ray diffraction photographs of the complex crystal were taken by using Cu$K\alpha$ radiation. The crystal used were about 0.2 mm × 0.2 mm × 0.2 mm. Intensity data of the complex were recorded on photographs, using equi-inclination Weissenberg multiple film method, around the [110] direction from the equator to the fifth layer line. The number of recorded reflections having non-zero intensities was 200. The intensities were measured by visual comparison with standard scales. Although the absorption coefficient ($\mu = 178\ cm^{-1}$ for Cu$K\alpha$ radiation) is large, the intensity data were not corrected for absorption. They were corrected only for Lorentz and polarization factors. The smallest possible crystals were used for collecting diffraction intensities. The crystal used for collection of intensity data was renewed for each layer line.

Infrared Measurement. Infrared spectra of the TGE–$HgCl_2$ and related complexes were measured by the Nujol mull method with a Japan Spectroscopic Co., Ltd. model IR-G and 402G infrared spectrometers.[3]

Structure Determination

Reflections having indices hkl with $h+k$ even, $k+l$ even, and $h+l$ even are selectively very strong and reflections of other indices are, in general, quite weak. These strong reflections decrease in intensity apparently only with increasing $\sin\theta/\lambda$. Since the general feature of the diffraction pattern was supposed to be regulated by the atomic position of Hg, the characteristic feature led to the conclusion that the four Hg atoms are located at such special positions as 0,0,0; 0,1/2,1/2; 1/2,0,1/2; 1/2,1/2,0. Thus, the contribution of the Hg atoms to a reflection having an index, hkl, is as follows.

$$F(hkl)_{Hg} = 4f_{Hg}(hkl)$$

for hkl with h even, k even, and l even, and

$$F(hkl)_{Hg} = -4f_{Hg}(hkl)$$

for hkl with h odd, k odd, and l odd. Thus, the Hg atoms do not interfere with each other among themselves for these reflections but contribute to them to their full scattering power, making the contribution of the Hg atoms to intensities of these reflections overwhelming as compared with that of the C and O atoms of TGE. The atomic position of Cl was easily determined by the Fourier method. However, due to the dominant contribution of the Hg atom, it was not possible to determine the atomic positions of the C and O atoms by the heavy atom method. Therefore, the conformation of the TGE molecule and the arrangement of the molecules in the crystal lattice was assumed by referring to the TGM–$HgCl_2$ complex[1] as described below.

In the first place, it seems reasonable to assume the following conformation of TGE which is similar to that of TGM[1];

$$CH_3\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_3$$
$$T\ T\quad G\quad T\ T\quad \bar{G}\quad T\ T\quad G\quad T\ T\quad \bar{G}\quad T\ T$$

However, this model gives the very short interatomic distance of 2.2 Å between the two C atoms of the terminal CH_3 groups. To overcome the difficulty, one of the internal rotation angles about the terminal CH_2–O bonds was changed to a gauche form (−80°) by referring to the angles of the *gauche* CH_2–O bond in the $CH_3CH_2O(CH_2CH_2O)_6CH_2CH_3$ (HGE)[4] and PEO of type II[5] in the complexes with $HgCl_2$ so that the molecular model gave reasonable distances between the terminal groups. The assumed model is shown in Fig. 1 for which the conformation of the bonds along the chain can be given approximately by

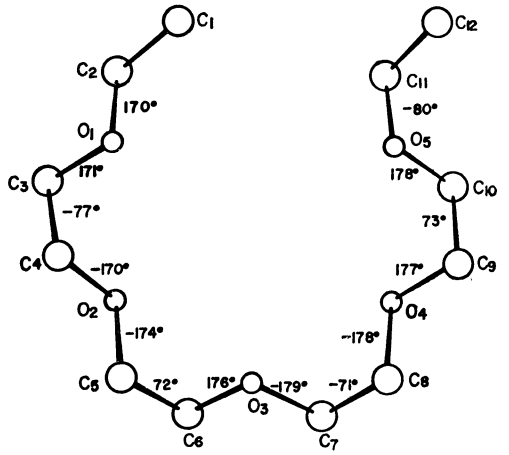

Fig. 1. The adopted molecular model for TGE in the complex.

$$CH_3\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_3$$
$$T\ T\quad G\quad T\ T\quad \bar{G}\quad T\ T\quad G\quad T\ T\quad \bar{G}\quad T\ G$$

For this model, the nearest distance between C_1 and

Table 2. Molecular constants for the adopted molecular model of the TGE molecule

C_1–C_2	1.54Å	C_1–C_2–O_1	109.5°	C_1–C_2–O_1–C_3	170°
C_2–O_1	1.47	C_2–O_1–C_3	108.3	C_2–O_1–C_3–C_4	171
O_1–C_3	1.40	O_1–C_3–C_4	101.7	O_1–C_3–C_4–O_2	−77
C_3–C_4	1.58	C_3–C_4–O_2	108.3	C_3–C_4–O_2–C_5	−170
C_4–O_2	1.44	C_4–O_2–C_5	113.9	C_4–O_2–C_5–C_6	−174
O_2–C_5	1.45	O_2–C_5–C_6	109.6	O_2–C_5–C_6–O_3	72
C_5–C_6	1.50	C_5–C_6–O_3	106.7	C_5–C_6–O_3–C_7	176
C_6–O_3	1.37	C_6–O_3–C_7	113.2	C_6–O_3–C_7–C_8	−179
O_3–C_7	1.44	O_3–C_7–C_8	109.7	O_3–C_7–C_8–O_4	−71
C_7–C_8	1.52	C_7–C_8–O_4	104.4	C_7–C_8–O_4–C_9	−178
C_8–O_4	1.51	C_8–O_4–C_9	106.8	C_8–O_4–C_9–C_{10}	177
O_4–C_9	1.50	O_4–C_9–C_{10}	97.4	O_4–C_9–C_{10}–O_5	73
C_9–C_{10}	1.62	C_9–C_{10}–O_5	108.4	C_9–C_{10}–O_5–C_{11}	178
C_{10}–O_5	1.38	C_{10}–O_5–C_{11}	113.2	C_{10}–O_5–C_{11}–C_{12}	−80
O_5–C_{11}	1.44	O_5–C_{11}–C_{12}	109.5		
C_{11}–C_{12}	1.54				

3) Infrared spectra at low temperature were measured by the courtesy of Professor H. Tadokoro and Mr. S. Ishikawa, Osaka University.

4) R. Iwamoto, This Bulletin, **46**, 1123 (1973).

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

C_{11} is 3.84 Å (for the numbering of atoms, see Fig. 1). This value may be allowable in comparison with the van der Waals distance, 4.0 Å. The assumed molecular dimensions are listed in Table 2 and were taken from those of TGM–$HgCl_2$[1] except for the terminal C–C bonds.

Next, we have to consider the arrangement of the TGE molecules in the crystal lattice. By analogy with the case of TGM–$HgCl_2$,[1] it was assumed that the TGE molecule encloses one $HgCl_2$ molecule with nearly equal interatomic distances between Hg and five O atoms. The atomic parameters of the atoms were determined in the following way.

First, a Cartesian right-handed coordinate system fixed to the molecule was assumed and is denoted by X^m. In this coordinate system the x axis is along the first bond and the y axis is in the plane of the first and second bonds and perpendicular to the x axis. The z axis was chosen so as to be perpendicular to the x and y axes and to make the right-handed system. Here, a dummy oxygen atom was assumed to be bonded to the first C atom with the bond length of 1.43 Å, bond angle of 109°28′ and internal rotation angle of 70°. This was chosen to facilitate the setting of the origin of the following X_0^m coordinate system at the position equidistant from the five oxygen atoms. The dummy atom is denoted by O_0.

Secondly, the coordinate system X^m was transformed into the other Cartesian coordinate system X_0^m fixed to the molecule. In this system, the z axis was set along the direction of the following vector.

$$\overrightarrow{O_0O_1} \times \overrightarrow{O_1O_2} + \overrightarrow{O_1O_2} \times \overrightarrow{O_2O_3} + \overrightarrow{O_2O_3} \times \overrightarrow{O_3O_4} + \overrightarrow{O_3O_4} \times \overrightarrow{O_4O_5} + \overrightarrow{O_4O_5} \times \overrightarrow{O_5O_0} + \overrightarrow{O_5O_0} \times \overrightarrow{O_0O_1},$$

where O_i is the ith oxygen atom and each vector product $O_{i-1}O_i \times O_iO_{i+1}$ was normalized to a unit vector. The origin of the coordinate system was set at the center of gravity of the five oxygen atoms and the dummy atom. The x axis is perpendicular to the plane including the z axis and O_0; that is, it is parallel to the $\overrightarrow{O_gO_0} \times \vec{z}$ direction, where O_g is the center of gravity. The y axis is taken along the $\vec{z} \times \vec{x}$ direction as shown in Fig. 2.

Finally the X_0^m was transformed into the coordinate system fixed to the crystal lattice so that the molecular axis (z axis) is along [111] as shown in Fig. 3, where the TGE molecule was simply drawn around the $HgCl_2$ molecule located at the origin. This transformation was made according to the transformation matrix expressed by the Eulerian angles. The rotation angle around [111] is denoted by χ.

Figure 4 shows some of the symmetry elements existing in the space group Pa3-T_h^6. The Hg atoms are located at the positions having site symmetry $\bar{3}$. Since the TGE molecule enclosing the Hg atom has no symmetry, it should be assumed that the TGE molecules are rotated statistically around the Cl–Hg–Cl direction in order to satisfy the site symmetry. Figure

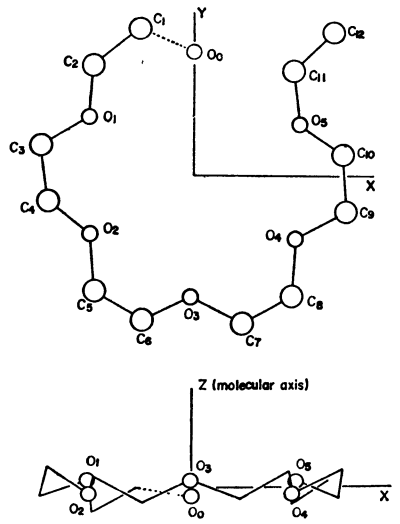

Fig. 2. Molecular coordinate system for the TGE molecule. The dummy atom O_0 was assumed to be bonded to C_1 in order to set the origin at the equi-distant position from the five oxygen atoms.

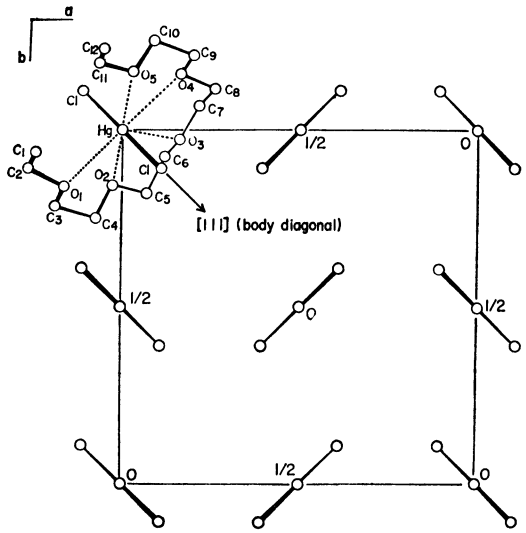

Fig. 3. Molecular arrangement of the TGE molecule in the complex crystal. Only one molecule around $HgCl_2$ at the origin is shown for simplicity.

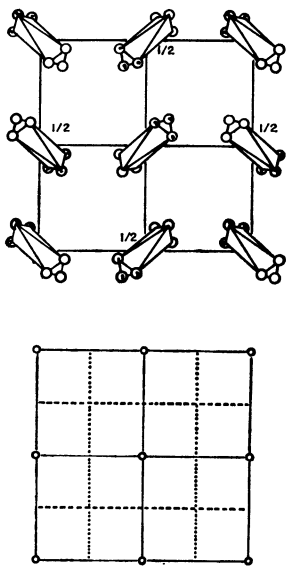

Fig. 4. Some of the symmetry elements in the space group Pa3–T_h^6.

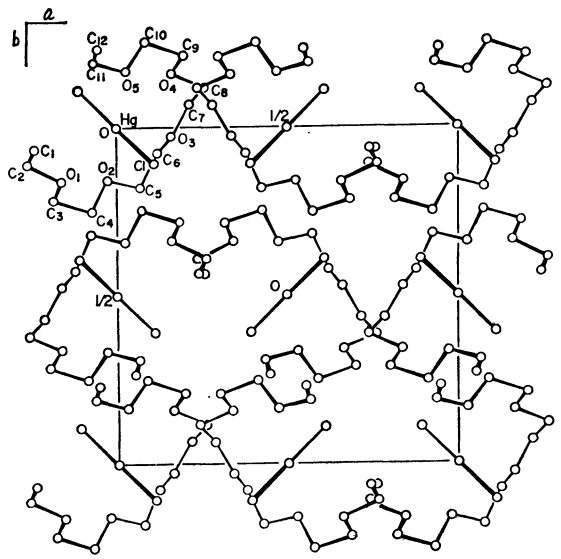

Fig. 5. Crystal structure of the TGE-$HgCl_2$ complex. The statistical arrangement of TGE molecules in the crystal lattice is not drawn for simplicity.

5 shows the crystal structure of the complex. However, the statistical arrangement of the TGE molecule is not shown in order to avoid complication of the figure. Structure factors of the TGE–$HgCl_2$ complex were calculated on the basis of the atomic coordinates deduced above assuming the statistical structure. It was found that the R factor ($\sum||F_o|-|F_c||/\sum|F_o|$) varies with χ. From this dependence the χ angle of 115° was found most reasonable.

Least squares refinement of isotropic approximation was applied to all the atoms except hydrogen and the resulting R factor was 11.0%. However, the resulting molecular dimensions for the TGE molecule were so distorted that they were not allowable in comparison with the ordinary bond lengths and angles. The atomic coordinates for TGE were, then, fixed and the least squared method was applied to the Hg and Cl atoms only, the resulting R factor being 12.3%. The $HgCl_2$ molecule was assumed to be linear. The atomic coordinates are given in Table 3.

Table 3. Atomic coordinates and temperature factors in the TGE–$HgCl_2$ complex

Atom	x	y	z	B
Hg	0.0	0.0	0.0	5.44 Å^2
Cl	0.1081	0.1081	0.1081	6.30
C_1	0.0627	−0.2414	0.1778	6.0
C_2	0.1101	−0.2611	0.0662	6.0
O_1	0.1609	−0.1625	0.0272	6.0
C_3	0.2185	−0.1869	−0.0647	6.0
C_4	0.2503	−0.0725	−0.1059	6.0
O_2	0.1582	−0.0255	−0.1561	6.0
C_5	0.1811	0.0723	−0.2136	6.0
C_6	0.0786	0.1212	−0.2519	6.0
O_3	0.0283	0.1619	−0.1637	6.0
C_7	−0.0686	0.2178	−0.1888	6.0
C_8	−0.1177	0.2619	−0.0872	6.0
O_4	−0.1575	0.1644	−0.0286	6.0
C_9	−0.2107	0.2034	0.0708	6.0
C_{10}	−0.2502	0.0888	0.1144	6.0
O_5	−0.1626	0.0339	0.1521	6.0
C_{11}	−0.1891	−0.0686	0.1971	6.0
C_{12}	−0.2317	−0.0534	0.3113	6.0

Discussion

Since it is not possible to determine the atomic positions of the C and O atoms directly by the heavy atom method, it is necessary to consider whether the adopted molecular model is reasonable.

Since the composition (TGE: $HgCl_2$) of the complex is 1 : 1 and all the four $HgCl_2$ molecules contained in the unit cell are symmetrically equivalent, one TGE molecule should enclose one $HgCl_2$ molecule. In the HGE–$HgCl_2$,[4] each half part of the HGE molecule enclosing one $HgCl_2$ has the conformation

$$CH_3\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}.$$
$$\quad T\ T\quad G\quad T\ T\quad G\quad T\ T\quad G\quad G$$

It should be noted that this conformation and the spatial configuration are very similar to those of TGM in the complex,[1] indicating that the conformation is very stable and favorable to form coordination between the O and Hg atoms. Therefore, it seems reasonable to assume essentially the same conformation of TGE for TGM except for the terminal groups to which a *gauche* CH_2–O bond is assigned in order to avoid too close approach between the terminal groups.

Improvement of the R factor by 4% (from 16.4 to 12.3) by taking into account the TGE molecule having the adopted molecular conformation might indicate that the molecular model and the arrangement are reasonable. Although the 4% improvement for the TGE–$HgCl_2$ is smaller in comparison with 6% for the TGM–$HgCl_2$,[1] this may be accounted for by the fact that in the former complex the Hg atoms are located at special positions and contribute much more greatly to structure factors, while in the latter complex they are located at general positions.

In the present structure, the TGE molecule must be located around the position whose site symmetry is $\bar{3}$. However, the molecule does not have any symmetry and the statistical structure must be assumed, in which the six molecules having the structure shown in Fig. 1

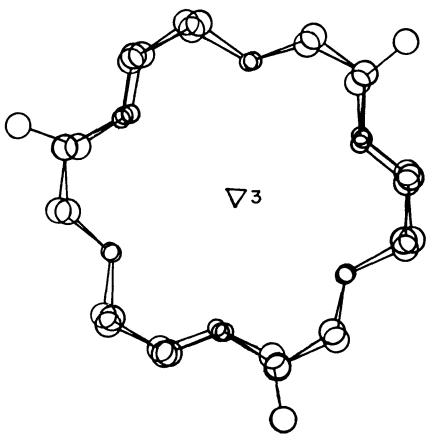

Fig. 6. Statistical sructure having the symmetry 3 produced by the three molecules of TGE.

are arranged around the Hg atom with the weight of 1/6 for each molecule, satisfying symmetry 3. Figure 6 shows the statistical arrangement in which the three TGE molecules are arranged so as to produce symmetry 3. In order to give the statistical arrangement having the $\bar{3}$ symmetry, another of these molecules related by $\bar{1}$ at the position of Hg should be superposed in the figure. It should be noticed that the molecules generated by the symmetry operation 3 coincide approximately with the original molecule if the molecular ends are neglected.

In the adopted molecular model of Fig. 1, a *gauche* form was fixed to the O_5–C_{11} bond in order to avoid the intramolecular steric hindrance, but there is no necessity of assigning the gauche CH_2–O bond to the O_5–C_{11} bond. Any CH_2–O bond of the TGE molecule can be *gauche* and furthermore there is a possibility that the *gauche* CH_2–O bond can move from time to time through the whole molecule; that is, the *gauche* CH_2–O bond may be delocalized over the whole molecule. The delocalization of the *gauche* CH_2–O bond may give rise to vigorous molecular motion of the TGE molecule around the Hg atom. Evidence of some kind of molecular motion is shown by the temperature dependence of the infrared spectra as discussed below. Combination of the molecular model in which the *gauche* CH_2–O bond moves through the whole molecule with time and the molecular motion around the Hg atom may produce the apparent site symmetry, $\bar{3}$, observed for the TGE–$HgCl_2$ complex.

Figure 7 shows infrared spectra of the TGE–$HgCl_2$ at room temperature and at a low temperature (liquid nitrogen). Absorption bands, even if they are weak or have shoulders at room temperature, become strikingly sharp and well-defined at low temperature in the whole region. On the other hand, for TGM–$HgCl_2$, temperature dependence of the infrared spectrum (Fig. 8) is not so marked as in the former. It should be noted that, although the nature of the spectral change in TGE–$HgCl_2$ is not clear, each absorption corresponds well between the two temperatures, even if some bands are very weak or have shoulders at room temperature.

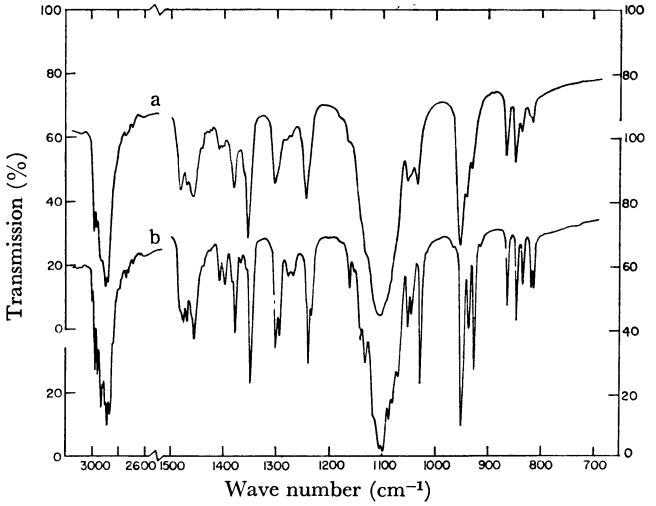

Fig. 7. Infrared spectra of the TGE–$HgCl_2$ complex at (a) room temperature and (b) a low temperature (liquid nitrogen).

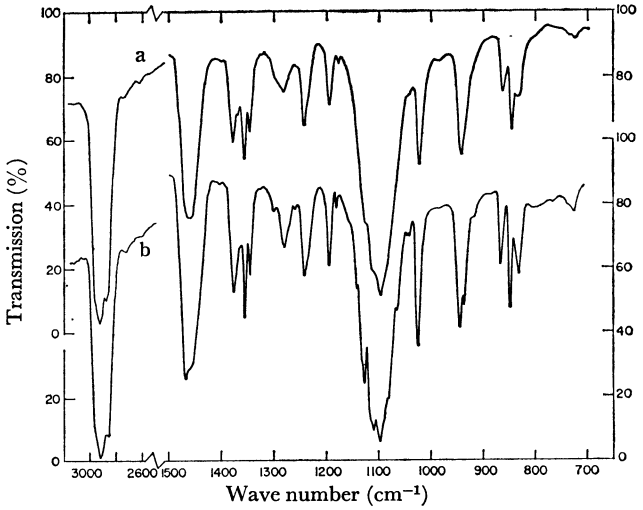

Fig. 8. Infrared spectra of the TGM–$HgCl_2$ complex at (a) room temperature and (b) a low temperature (liquid nitrogen).

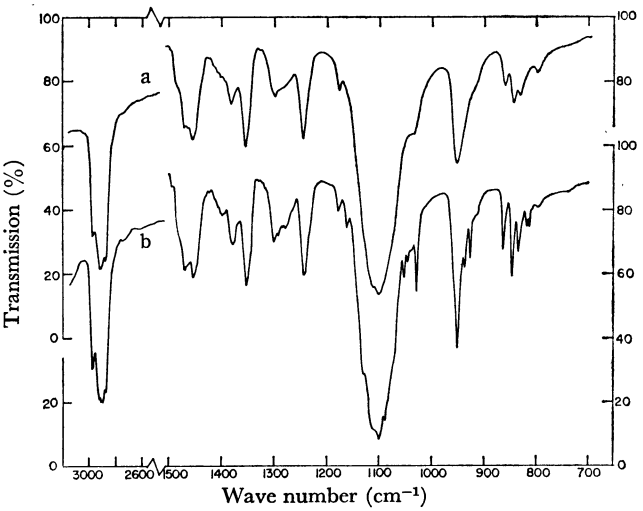

Fig. 9. Infrared spectra of the TGE–$HgBr_2$ complex at (a) room temperature and (b) a low temperature (liquid nitrogen).

Consequently, the observed spectral change is due to a molecular motion but not to a conformational change of the TGE molecule.

A similar spectral change is observed for the $HgBr_2$ complex of TGE as shown in Fig. 9, which has a monoclinic unit cell. The infrared spectrum of the TGE–$HgBr_2$ becomes sharp and well-defined at low temperature as observed in the $HgCl_2$ complex. Since it is considered that a TGE molecule encloses one Hg atom in TGE–$HgBr_2$, the same kind of intramolecular steric hindrance must occur between the terminal groups as was found in TGE–$HgCl_2$. These observations lead to the conclusion that too close approach between the terminal groups causes some kind of molecular motion of the chain in the complex crystal.

Since the $HgCl_2$ molecule is bent by 4—5° from the linear form both in the cases of TGM–$HgCl_2$ and HGE–$HgCl_2$,[1,4] it may be reasonable to consider that the $HgCl_2$ molecule is also deviated from the linear form in TGE–$HgCl_2$. This study gave no conclusive information as to whether the molecule is bent or not,

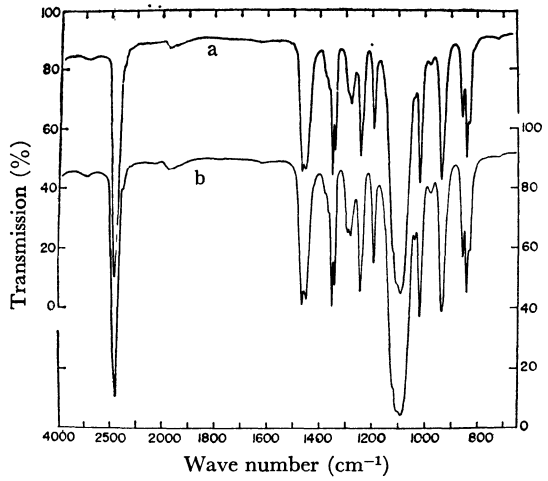

Fig. 10. Infrared spectra of (a) $HgCl_2$ and (b) $HgBr_2$ complexes of TGM at room temperature.

although the R factor was slightly improved for the structure having the bent $HgCl_2$.

It is interesting to note that the complex consisting of such fairly complicated molecules as TGE and $HgCl_2$ forms a cubic unit cell, while the $HgBr_2$ complex which should have the same situation as the $HgCl_2$ complex with respect to the intramolecular steric hindrance of the TGE molecule, has a monoclinic unit cell. The infrared spectrum of the TGE–$HgBr_2$ (Fig. 9) is similar to that of the $HgCl_2$ complex as a whole but they differ to some extent in detail in the whole region. On the other hand, the infrared spectra of the $HgCl_2$ and $HgBr_2$ complexes of TGM are quite the same in detail as shown in Fig. 10 but their unit cells differ. Therefore, the observed spectral difference between the $HgCl_2$ and $HgBr_2$ complexes of TGE must be closely correlated with the occurrence of the cubic unit cell for the $HgCl_2$ complex.

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