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Structure of Ethylene Oxide Oligomer Complexes. 5. A Complex of Tetraethylene Glycol Dimethyl Ether with Cadmium Chloride[1]

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Abstract: The molecular and crystal structure of the 1:2 complex of tetraethylene glycol dimethyl ether (TGM), $CH_3O(CH_2CH_2O)_4CH_3$, and $CdCl_2$ has been determined by x-ray diffraction. The crystal has a monoclinic unit cell of the space group $P2_1/a$, containing four TGM and eight $CdCl_2$, and the cell constants are a = 14.877, b = 7.468, c = 17.621 Å, and β = 103.73°. One TGM is coordinated to two Cd atoms, having the conformation III. Four $CdCl_2$ are combined to one another through Cl bridges. Interatomic distances are 2.409–2.735 Å for the O··Cd and 2.425–2.682 Å for the Cd–Cl distances.

Introduction

Blumberg et al. first reported complex formation of polyethylene oxide (PEO) with $HgCl_2$ on the basis of the observation of the infrared spectrum and x-ray diffraction pattern.[2] Iwamoto et al. found the existence of two kinds of complexes that have different compositions and determined the molecular and crystal structures of the complexes by x-ray diffraction.[3,4] PEO was found to have conformations of

$$\begin{array}{l} -CH_2-CH_2-O-CH_2-CH_2-O \\ \ \ \mathrm{T}\quad\ \mathrm{T}\quad\ \mathrm{T\,T}\quad\ \mathrm{G}\quad\ \mathrm{T} \end{array} \quad \text{and} \quad \begin{array}{l} -CH_2-CH_2-O \\ \ \ \mathrm{T}\quad\ \mathrm{G}\quad\ \mathrm{G'} \end{array}$$

where G and T mean gauche and trans,[3] respectively, and G′ is a torsional angle of about 90°,[4] for the repeating unit in the two complexes, whereas PEO consists of a succession of

$$\begin{array}{l} -CH_2-CH_2-O \\ \ \ \mathrm{T}\quad\ \mathrm{G}\quad\ \mathrm{T} \end{array}$$

in the pure polymer.[5] According to conformational studies of ethers consisting of CH_2CH_2O units, a gauche form is about 400 cal/mol more stable than a trans form for a CH_2-CH_2 bond,[6] whereas a trans form is 1100 cal/mol more stable than a gauche form for a CH_2-O bond.[7] This implies that coordination to Hg has the dominating influence on the molecular conformation of PEO in the $HgCl_2$ complexes. Iwamoto investigated further the effect of coordination on molecular conformations in a series of structural studies of the complexes of ethylene oxide oligomers $RO(CH_2CH_2O)_mR$ with $HgCl_2$.[8-10] He found that the

$$\begin{array}{l} -CH_2-CH_2-O-CH_2-CH_2-O \\ \ \ \mathrm{T}\quad\ \mathrm{G}\quad\ \mathrm{T\,T}\quad\ \bar{\mathrm{G}}\quad\ \mathrm{T} \end{array}$$

I

form ($\bar{G}$: gauche opposite to G), which is considered most stable on the basis of what was mentioned above, is at the same time most suitable for coordination to a Hg atom, so long as the degree of polymerization $m \leq 4$.[9] This is just the case of a 1:1 complex of tetraethylene glycol dimethyl ether (TGM)[8] or tetraethylene glycol diethyl ether (TGE)[9] with $HgCl_2$, in which five coplanar oxygen atoms of the circular molecule are coordinated inwardly to one Hg. If $m > 4$, the molecule is too long to surround just one Hg atom and is coordinated to more than one Hg, and consequently G′ O-CH_2 bonds enter into the molecular chain to bring about intimate coordinations to Hg.[10] This is the case with a 1:2 complex of hexaethylene glycol diethyl ether (HGE) with $HgCl_2$.[10] In this complex one HGE is coordinated to two Hg and a

$$\begin{array}{l} -CH_2-O-CH_2- \\ \qquad\ \ \mathrm{G'}\ \mathrm{G'} \end{array}$$

form occurs at the turning position of HGE in which the coordinating Hg changes from one to the other.

On the other hand, much attention has recently been given to highly complexing macrocyclic polyethers[11] since first reported by Pedersen.[12] Among various macrocyclic polyethers, a crown ether $(CH_2CH_2O)_6$, 18-crown-6, is especially interesting from the viewpoint of conformational comparison with the linear ethers $RO(CH_2CH_2O)_mR$. Dunitz et al.[13] reported the crystal structures of the complexes of 18-crown-6 with alkali metal salts. It was found that a K^+ ion is most suitable for coordination to the cavity of the molecule, whose conformation is

$$\begin{array}{l}(\text{-CH}_2\text{-CH}_2\text{-O-CH}_2\text{-CH}_2\text{-O})_3\\ \;\text{T}\qquad\text{G}\qquad\text{T}\;\;\text{T}\qquad\bar{\text{G}}\qquad\text{T}\end{array}$$

The molecular conformation and the spatial arrangement of O atoms and a K^+ ion as well as the molecular shape are strikingly similar to the TGM-$HgCl_2$ complex.[8] When an ionic radius is larger than a K^+ ion, such as Rb^+ and Cs^+ ions, the ion is displaced from the coplanar plane including six O atoms, and if an ionic radius is smaller, such as a Na^+ ion, some variations from the gauche CH_2-CH_2 and trans CH_2-O conformation occur in the cyclic chain, bringing about proper O···metal ion distances. Thus, the molecular conformations and the manner of coordination are very similar between the linear and cyclic polyethers.

In the present paper the molecular and crystal structure of a $CdCl_2$ complex of TGM has been determined by x-ray diffraction. In the course of the structural studies of the complexes of ethylene oxide oligomers with $HgCl_2$, the authors found that TGM also forms a complex with $CdCl_2$, but the infrared spectrum was markedly different from that of the $HgCl_2$ complex. It is very interesting to investigate how the spectral difference is correlated with molecular conformations in the complexes. Moreover, the nature of interatomic interactions is very different between $CdCl_2$ and $HgCl_2$ so that the former is ionic, while the latter is covalent. The study of the $CdCl_2$ complex is, therefore, considered to be helpful for further understanding of the nature of coordination between O and metal ions and its influence on the molecular conformations.

Experimental Section

Crystals of the TGM-$CdCl_2$ complex were prepared in the same way as the TGM-$HgCl_2$ complex.[8] The crystals are transparent needles grown along the *c* axis. The density of the crystal was 2.04 g/cm^3 by flotation in a liquid mixture of CCl_4 and $CHBr_3$. The composition is TGM:$CdCl_2$ = 1:2 according to the C and H analysis (Calcd for $C_{10}H_{22}O_5Cd_2Cl_4$: C, 20.4; H, 3.8. Found: C, 20.8; H, 4.0).

X-ray diffraction measurements were made by the use of a Rigaku Denki four-circle computer-controlled diffractometer equipped with a graphite monochromator and the Mo Kα radiation. A crystal with dimensions of about 0.3 × 0.3 × 0.4 mm was used for intensity measurements. Unit cell dimensions and orientation of the crystal were determined by a least-squares refinement of 2θ, ω, φ, and χ values for 13 reflections. Integrated intensities were measured by the θ-2θ technique up to $2\theta = 55°$. The standard reflections of 200, 110, and 002 were measured after every 50 reflections. Intensities of the standard reflections decreased by the factor 1.0 to 0.94 for the initial and final sets of the intensity measurements, indicating that the crystal suffers slight damage under irradiation of x rays. The damage was not serious and observed intensities were corrected for it based upon the standard reflections. Of 4326 independent reflections measured, 2528 reflections had nonzero intensities and these were reduced to structure amplitudes on an arbitrary scale by the application of Lorentz and polarization factors. The crystallographic data are given in Table I.

Structure Determination

Atomic coordinates of the two Cd atoms contained in an asymmetric unit were determined fom a three-dimensional Patterson function. A Fourier synthesis was made on the basis of the signs of the structure factors calculated for the Cd atoms only, the *R* factor being 33.8%. All the remaining atoms of the asymmetric unit except hydrogens were easily located in the Fourier function. The *R* factor was improved to 17.5% for the structure, including all the atoms except hydrogens with appropriate isotropic temperature factors. Finally, the atomic coordinates and the temperature factors were refined by the block-diagonal least-squares method and the anisotropic temperature factors of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ were taken into account. The *R* factor was 6.0% for the final results given in Table II. Hydrogen atoms were not considered for the calculation. Atomic scattering factors were referred to the "International Tables for X-Ray Crystallography", Vol. III, 1960. The atomic scattering factors of cadmium and chlorine were taken from those of Cd and Cl but not of Cd^{2+} and Cl^-. Anomalous dispersion correction was applied to Cd only ($\Delta f' = -0.90$, $\Delta f'' = 1.40$). All the calculations were carried out on a TOSBAC 3400-41 computer by the use of a Fourier program made by Dr. S. Kuribayashi of this Institute and the UNICS block-diagonal least-squares program originally programmed by Professor T. Ashida of Nagoya University and modified properly for the computer.

Table I. Crystallographic Data of the TGM-$CdCl_2$ Complex

Chemical formula	$C_{10}H_{22}O_5Cd_2Cl_4$, M = 588.89
Crystal system	Monoclinic
Space group	$P2_1/a$
a	14.877 ± 0.003 Å
b	7.468 ± 0.001 Å
c	17.621 ± 0.004 Å
β	103.73 ± 0.01°
Z	4
Volume	1901.8 Å^3
D_c	2.058 g/cm^3
D_0	2.04 (25 °C)
Radiation	Mo Kα_1 (0.70926 Å)
μ (Mo Kα_1)	27.88 cm^{-1}
$F(000)$	1144

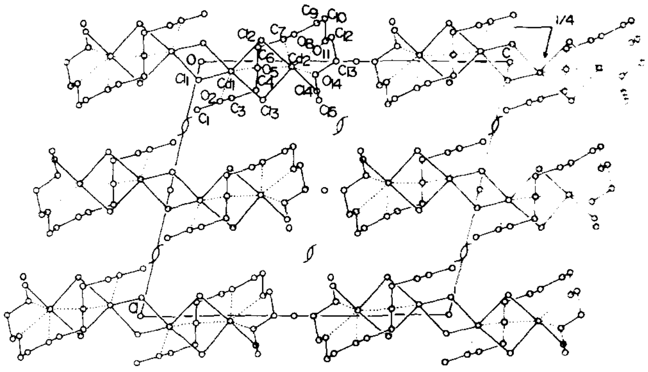

Figure 1. Crystal structure of the TGM-$CdCl_2$ complex projected on the *ac* plane. The asymmetric unit is indicated by numbered atoms.

Description of the Structure and Discussion

The crystal structure of the TGM-$CdCl_2$ complex is shown in Figure 1, where an asymmetric unit consisting of one TGM and two $CdCl_2$ is indicated by numbered atoms. The two asymmetric units that are related to each other by the symmetry of inversion are combined through Cl bridges, making a cluster. Two of the clusters are contained in the unit cell. Figure 2 shows the spatial arrangement of TGM, Cd, and Cl in the cluster. Figure 2a is the projection onto the *ac* plane and

Table II. The Atomic Coordinates and Temperature Factors of the Final Results[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cd(1)	0.0416 (1)	0.0286 (2)	0.1077 (1)	0.0052 (1)	0.0134 (2)	0.0021 (0)	−0.0004 (1)	0.0013 (0)	0.0000 (1)
Cd(2)	0.0238 (1)	0.0408 (2)	0.2997 (1)	0.0043 (1)	0.013 (2)	0.0022 (0)	0.0004 (1)	0.0012 (0)	0.0001 (1)
Cl(1)	0.0711 (3)	−0.1877 (5)	0.0069 (2)	0.0065 (3)	0.0156 (8)	0.0023 (1)	0.0030 (4)	0.0014 (1)	0.0001 (3)
Cl(2)	−0.0823 (3)	−0.0928 (5)	0.1774 (2)	0.0049 (2)	0.0153 (7)	0.0025 (1)	−0.0020 (3)	0.0013 (1)	−0.0004 (2)
Cl(3)	0.1553 (3)	−0.0774 (5)	0.2310 (2)	0.0043 (2)	0.0163 (8)	0.0028 (1)	0.0005 (3)	0.0011 (1)	0.0005 (3)
Cl(4)	0.1202 (3)	0.2273 (6)	0.3994 (2)	0.0061 (3)	0.0213 (9)	0.0030 (1)	−0.0039 (4)	0.0011 (1)	−0.0021 (3)
C(1)	0.1876 (15)	0.2698 (35)	0.0264 (12)	0.0078 (14)	0.0418 (68)	0.0046 (9)	−0.0031 (26)	0.0032 (9)	0.0027 (20)
O(2)	0.1551 (8)	0.2514 (15)	0.0970 (6)	0.0060 (7)	0.0172 (23)	0.0038 (5)	−0.0031 (11)	0.0020 (5)	0.0003 (9)
C(3)	0.1446 (15)	0.4219 (25)	0.1295 (10)	0.0093 (14)	0.0189 (40)	0.0040 (7)	−0.0034 (19)	0.0027 (8)	0.0015 (14)
C(4)	0.1149 (14)	0.3955 (26)	0.2029 (11)	0.0085 (14)	0.0202 (40)	0.0050 (8)	−0.0083 (20)	0.0021 (9)	−0.0030 (16)
O(5)	0.0272 (8)	0.2944 (13)	0.1885 (6)	0.0073 (7)	0.0112 (19)	0.0030 (4)	0.0015 (10)	0.0015 (5)	−0.0012 (7)
C(6)	−0.0577 (12)	0.3988 (25)	0.1717 (9)	0.0066 (11)	0.0219 (38)	0.0031 (6)	0.0042 (17)	0.0020 (7)	0.0008 (13)
C(7)	−0.0866 (13)	0.4378 (21)	0.2476 (9)	0.0086 (12)	0.0137 (32)	0.0029 (5)	0.0049 (16)	0.0023 (7)	0.0029 (11)
O(8)	−0.1056 (8)	0.2674 (14)	0.2762 (6)	0.0075 (8)	0.0151 (22)	0.0026 (4)	0.0022 (11)	0.0019 (4)	0.0003 (7)
C(9)	−0.1488 (11)	0.2800 (22)	0.3413 (9)	0.0048 (9)	0.0167 (33)	0.0036 (6)	0.0010 (14)	0.0019 (6)	−0.0014 (12)
C(10)	−0.1705 (11)	0.0890 (24)	0.3578 (10)	0.0037 (8)	0.0201 (37)	0.0047 (7)	0.0030 (14)	0.0008 (6)	0.0020 (14)
O(11)	−0.0860 (7)	−0.0053 (13)	0.3809 (5)	0.0043 (5)	0.0150 (21)	0.0027 (3)	−0.0006 (9)	0.0010 (3)	0.0005 (7)
C(12)	−0.0958 (12)	−0.1896 (20)	0.3983 (10)	0.0065 (10)	0.0105 (27)	0.0041 (7)	−0.0021 (14)	0.0022 (7)	−0.0006 (11)
C(13)	−0.0007 (13)	−0.2596 (23)	0.4340 (9)	0.0077 (12)	0.0180 (35)	0.0032 (6)	0.0018 (17)	0.0029 (7)	0.0012 (12)
O(14)	0.0560 (8)	−0.2350 (14)	0.3784 (6)	0.0064 (7)	0.0119 (20)	0.0030 (4)	0.0016 (10)	0.0014 (4)	0.0009 (7)
C(15)	0.1524 (12)	−0.2781 (26)	0.4127 (11)	0.0045 (9)	0.0232 (42)	0.0052 (8)	0.0055 (17)	0.0004 (7)	0.0014 (16)

[a] The anisotropic temperature factors are expressed by the form of $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The values in parentheses denote the estimated standard deviations (×10⁴).

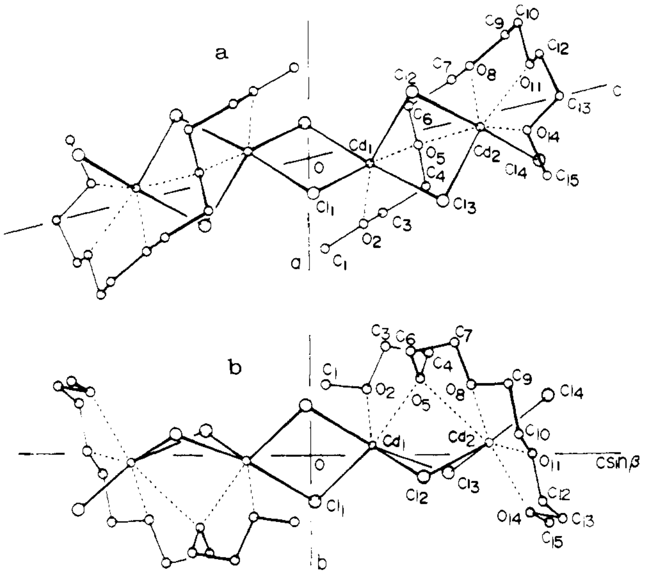

Figure 2. Molecular arrangement of TGM and $CdCl_2$ in the cluster projected on (a) the *ac* plane and (b) the plane perpendicular to the *a* axis. The right half that is the asymmetric unit and is indicated by numbered atoms is related to the left half by the symmetry of inversion.

Figure 2b shows the molecule projected on the plane perpendicular to the *a* axis.

Bond lengths and angles of TGM in the complex are given in Table III. C-C bonds are a little shorter (1.48-1.53 Å) than the normal value (1.54 Å). The shortening of C-C bonds was also reported for 18-crown-6 ether in the complexes with alkali metal salts.[13] C-O bonds range from 1.41 to 1.48 Å, while the normal value is 1.43 Å. C-O-C angles (110.7-116.8°) are relatively larger than C-C-O angles (104.3-110.7°). It should be noted that the bonds, C(3)-C(4) (1.48 Å) and C(4)-O(5) (1.48 Å), and the angle C(4)-O(5)-C(6) (116.8°), which deviate appreciably from their normal values, are directly or indirectly concerned with the O(5) atom.

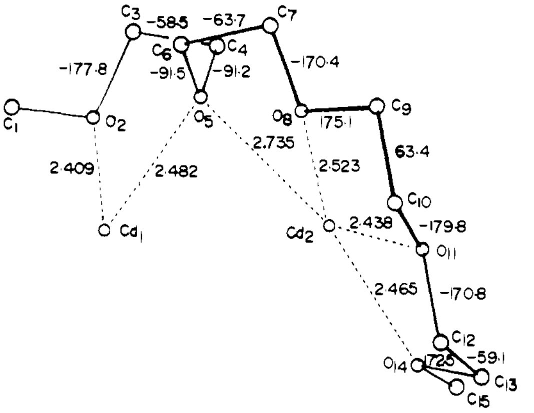

Figure 3. The molecular conformation of TGM in relation to the manner of its coordination to Cd in the $CdCl_2$ complex.

Table III. Bond Lengths and Angles of TGM in the TGM-$CdCl_2$ Complex[a]

Bond lengths, Å		Bond angles, deg	
C(1)-O(2)	1.45 (3)	C(1)-O(2)-C(3)	110.7 (1.5)
O(2)-C(3)	1.42 (2)	O(2)-C(3)-C(4)	108.6 (1.5)
C(3)-C(4)	1.48 (3)	C(3)-C(4)-O(5)	110.7 (1.5)
C(4)-O(5)	1.48 (2)	C(4)-O(5)-C(6)	116.8 (1.2)
O(5)-C(6)	1.45 (2)	O(5)-C(6)-C(7)	109.6 (1.3)
C(6)-C(7)	1.53 (3)	C(6)-C(7)-O(8)	105.1 (1.3)
C(7)-O(8)	1.42 (2)	C(7)-O(8)-C(9)	112.7 (1.2)
O(8)-C(9)	1.44 (2)	O(8)-C(9)-C(10)	104.3 (1.3)
C(9)-C(10)	1.51 (2)	C(9)-C(10)-O(11)	108.1 (1.3)
C(10)-O(11)	1.41 (2)	C(10)-O(11)-C(12)	114.4 (1.2)
O(11)-C(12)	1.43 (2)	O(11)-C(12)-C(13)	107.0 (1.3)
C(12)-C(13)	1.50 (3)	C(12)-C(13)-O(14)	108.4 (1.3)
C(13)-O(14)	1.45 (2)	C(13)-O(14)-C(15)	111.5 (1.3)
O(14)-C(15)	1.45 (2)		

[a] Numbers in parentheses mean the estimated standard deviations (in the last digit for bond lengths).

Torsional angles are given in Table IV. The correlation between torsional angles around C-C and C-O bonds and the manner of coordination to Cd atoms is seen from Figure 3. All C-C bonds are gauche (58.5-63.7°), although the sign of the torsional angles changes alternatingly between the neighboring

Table IV. Torsional Angles of TGM in the TGM-$CdCl_2$ Complex

C(1)-O(2)-C(3)-C(4)	−177.8	C(7)-O(8)-C(9)-C(10)	175.1
O(2)-C(3)-C(4)-O(5)	−58.5	O(8)-C(9)-C(10)-O(11)	63.4
C(3)-C(4)-O(5)-C(6)	−91.2	C(9)-C(10)-O(11)-C(12)	−179.8
C(4)-O(5)-C(6)-C(7)	−91.5	C(10)-O(11)-C(12)-C(13)	−170.8
O(5)-C(6)-C(7)-O(8)	−63.7	O(11)-C(12)-C(13)-O(14)	−59.1
C(6)-C(7)-O(8)-C(9)	−170.4	C(12)-C(13)-O(14)-C(15)	172.5

Table V. Interatomic Distances and Angles Concerning Cd, Cl, and O Atoms in the TGM-$CdCl_2$ Complex[a]

O(2) . . Cd(1)	2.409 (11) Å	Cd(1)-Cl(1)	2.515 (6) Å
O(5) . . Cd(1)	2.482 (10)	Cd(1)-Cl(1)′	2.587 (17)
O(5) . . Cd(2)	2.735 (10)	Cd(1)-Cl(2)	2.607 (11)
O(8) . . Cd(2)	2.523 (12)	Cd(1)-Cl(3)	2.542 (18)
O(11) . . Cd(2)	2.438 (16)	Cd(2)-Cl(2)	2.553 (16)
O(14) . . Cd(2)	2.465 (11)	Cd(2)-Cl(3)	2.682 (12)
O(2) . . Cd(1) . . O(5)	69.5 (0.5)°	Cd(2)-Cl(4)	2.425 (13)
O(5) . . Cd(2) . . O(8)	63.9 (0.5)	Cl(1)′-Cd(1)-Cl(1)	86.1 (0.3)°
O(8) . . Cd(2) . . O(11)	66.4 (0.4)	Cl(1)′-Cd(1)-Cl(2)	97.3 (0.2)
O(11) . . Cd(2) . . O(14)	67.7 (0.4)	Cl(1)′-Cd(1)-Cl(3)	170.6 (0.1)
Cd(1) . . O(5) . . Cd(2)	82.9 (0.3)	Cl(1)-Cd(1)-Cl(2)	111.7 (0.3)
O(5) . . Cd(2)-Cl(4)	90.7 (0.4)	Cl(1)-Cd(1)-Cl(3)	102.2 (0.2)
O(8) . . Cd(2)-Cl(4)	91.8 (0.5)	Cl(2)-Cd(1)-Cl(3)	83.7 (0.2)
O(11) . . Cd(2)-Cl(4)	91.1 (0.3)	Cl(2)-Cd(2)-Cl(3)	82.0 (0.2)
O(14) . . Cd(2)-Cl(4)	94.0 (0.4)	Cl(2)-Cd(2)-Cl(4)	167.5 (0.2)
O(2) . . Cd(1)-Cl(1)	98.4 (0.5)	Cl(3)-Cd(2)-Cl(4)	98.5 (0.2)
O(2) . . Cd(1)-Cl(2)	149.7 (0.3)	Cd(1)-Cl(2)-Cd(2)	84.1 (0.2)
O(5) . . Cd(1)-Cl(2)	80.9 (0.4)	Cd(1)-Cl(3)-Cd(2)	82.8 (0.2)
Cd(1) . . Cd(1)′	3.729 (16) Å	Cd(1)′-Cl(1)-Cd(1)	93.9 (0.3)
Cd(1) . . Cd(2)	3.457 (4)	Cd(1)′ . . Cd(1) . . Cd(2)	156.3 (0.1)

[a] Numbers in parentheses are the estimated standard deviations based on the last digit.

monomeric units concerning the molecular part coordinated to one Cd. All C–O bonds are trans (170.4–179.8°) except for the C–O bonds bonded to the O(5) atom, which have the torsional angles of −91.2 and −91.5° (the torsional angles are denoted as $\bar{G}'$ hereafter). O(2) and O(5) are coordinated to Cd(1), while O(5), O(8), O(11), and O(14) are coordinated to Cd(2). The only O atom that is coordinated to both Cd(1) and Cd(2) is O(5). One of the six coordinating distances, $O_5 \cdot\cdot Cd_2$ (2.735 Å), is significantly long in comparison with the other five O··Cd distances (the average, 2.463 Å).

The main part of the TGM conformation consists of unit I in the $CdCl_2$ complex as mentioned above. This is consistent with the fact that the same conformational unit favorably occurs in the $HgCl_2$ complexes of TGM,[8] TGE,[9] and HGE.[10] However, it should be noted that one TGM is coordinated to two Cd atoms and a unit such as

$$\mathrm{{-}CH_2{-}O{-}CH_2{-}}$$
$$\mathrm{G'\ G'}$$

II

occurs in the TGM chain of the $CdCl_2$ complex, giving rise to the conformation of the whole molecule as

$$\mathrm{CH_3{-}O{-}CH_2{-}CH_2{-}O{-}CH_2{-}CH_2{-}O{-}CH_2{-}CH_2{-}O{-}CH_2{-}CH_2{-}O{-}CH_3}$$
$$\mathrm{T\quad \bar{G}\quad \bar{G}'\,\bar{G}'\quad \bar{G}\quad T\ T\quad G\quad T\ T\quad \bar{G}\quad T}$$

III

On the other hand, the conformation of TGM in the $HgCl_2$ complex is

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

with coplanar coordination of five oxygen atoms to one Hg.[8] The difference of the TGM conformation between the two complexes may originate from different coordination radii of Cd and Hg atoms.[14] The conformational difference may also be related to the very different chemical nature of ionic $CdCl_2$ and covalent $HgCl_2$, as revealed in the way that the atomic configuration of Cd and Cl is completely changed on complexation from the configuration in the $CdCl_2$ crystal as will be described below. On the other hand, $HgCl_2$ keeps essentially the same molecular structure in the complexes of TGM,[8] TGE,[9] HGE,[10] and PEO,[3,4] as well as in the $HgCl_2$ crystal.[15]

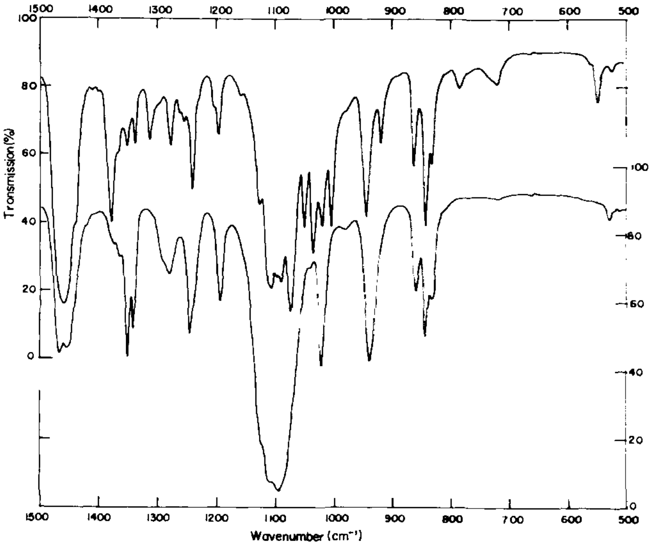

Figure 4. Infrared spectra of the TGM-$CdCl_2$ (upper) and TGM-$HgCl_2$ (lower) complexes.

The different molecular conformation of TGM causes drastic changes in the infrared spectrum of the $CdCl_2$ complex in comparison with that of the $HgCl_2$ complex as shown in Figure 4, where the upper spectrum is of the $CdCl_2$ complex and the lower is of the $HgCl_2$ complex. The $CdCl_2$ complex has many more absorption bands, especially in the 1000–1100 cm^{-1} region, than the $HgCl_2$ complex. The frequency region

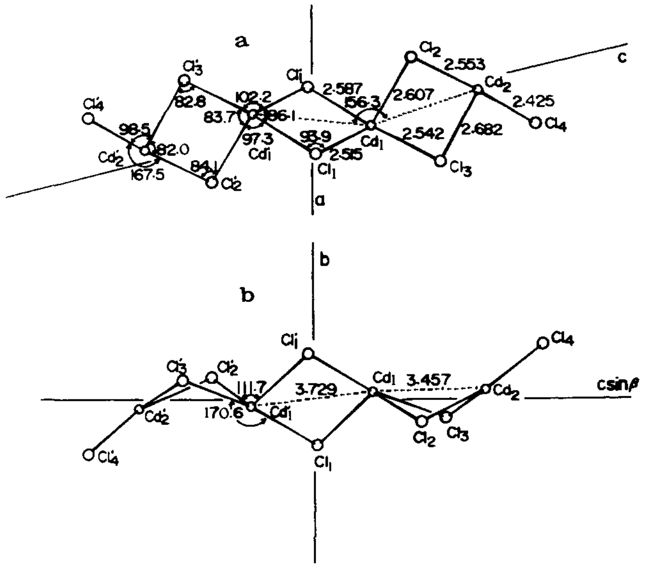

Figure 5. Atomic arrangement of Cd and Cl in the complex projected on (a) the *ac* plane and (b) the plane perpendicular to the *a* axis. Each atom of the right half is related to the primed counterpart of the left half by the symmetry of inversion.

is mainly associated with skeletal stretching vibrations of TGM. The occurrence of the II unit brings about distortion in the molecular chain consisting of a uniform succession of unit I, and this may cause different vibrational coupling modes, especially if the vibrations are associated with nonlocalized modes like skeletal vibrations. Therefore, the complication of the spectrum may reasonably be associated with the unit II conformation.

Interatomic distances and angles concerning Cd, Cl, and O are given in Table V. Figure 5 shows the spatial arrangement of Cd and Cl in the complex. In the figure, the right half is related to the left half by the symmetry of inversion. Cd(1) and Cd(2) are combined to each other through Cl(2) and Cl(3) bridges. Cd(1) is further combined to the symmetrically related Cd(1)′ through Cl(1) and Cl(1)′ bridges. Thus, four $CdCl_2$ are combined together through Cl bridges. The atomic arrangement is remarkably changed from that in the $CdCl_2$ crystal, in which a Cd atom is coordinated to six symmetrically equivalent Cl atoms and a layer of Cd is sandwiched between two Cl layers.[16] The Cd(1)··Cd(2) distance (3.457 Å), which is, in addition, "bridged" by O(5) as is seen in Figure 2, is shorter than the Cd(1)··Cd(1)′ distance (3.729 Å). We note that the four atoms, Cd(1), Cl(2), Cd(2), and Cl(3), make approximately a tetragon when they are projected on the *ac* plane, but they are not coplanar as is seen in Figure 5b, and the four corner angles are in the 82.0-84.1° range. The plane through Cd(1), Cl(2), and Cd(2) makes an angle of 124.9° with the plane through Cd(1), Cl(3), and Cd(2), while the angle between the plane through Cl(2), Cd(1), and Cl(3) and the plane through Cl(2), Cd(2), and Cl(3) is 125.2°. The Cd-Cl distances range from 2.425 to 2.682 Å, which are considerably shorter than that (2.74 Å) in the $CdCl_2$ crystal.[16] The Cd-Cl distances are longer for bridging Cl (2.515-2.682 Å) than for a nonbridging Cl (2.425 Å), while the Cd-Cl distance is 2.235 Å in the gaseous molecule.[17] The coordination number of Cd(1) is six including four with Cl and two with O, whereas that of Cd(2) is seven including three with Cl and four with O.

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