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Structure of Ethylene Oxide Oligomer Complexes. IV. Infrared Study of $CH_3O(CH_2CH_2O)_mCH_3$-$HgCl_2$ Complexes

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Infrared spectra of $CH_3O(CH_2CH_2O)_mCH_3$ ($m=1$—4) in their crystalline complexes with $HgCl_2$ have been measured. There is no significant regular variation of band frequencies depending upon m. Molecular conformations of the compounds in the complexes have been concluded to be $CH_3\text{-}O\underset{T}{-}CH_2\underset{G}{-}CH_2\underset{T}{-}O\underset{T}{-}CH_2\underset{\bar{G}}{-}CH_2\underset{T}{-}O\text{-}CH_3$ for $m=2$ and $CH_3\text{-}O\underset{T}{-}CH_2\underset{G}{-}CH_2\underset{T}{-}O\underset{T}{-}CH_2\underset{\bar{G}}{-}CH_2\underset{T}{-}O\underset{T}{-}CH_2\underset{G}{-}CH_2\underset{T}{-}O\text{-}CH_3$ for $m=3$ from molecular structures for $m=1$ and 4.

Molecular and crystal structures of the molecular complexes of $CH_3O(CH_2CH_2O)_4CH_3$,[1] $CH_3CH_2O(CH_2CH_2O)_4CH_2CH_3$,[2] and $CH_3CH_2O(CH_2CH_2O)_6CH_2CH_3$[3] with $HgCl_2$ have been studied by means of X-ray diffraction. It has been found that the conformational unit of $O\underset{T}{-}CH_2\underset{G}{-}CH_2\underset{T}{-}O\underset{T}{-}CH_2\underset{\bar{G}}{-}CH_2\underset{T}{-}O$ is favorable for the coordination between the molecules

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

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

[3] R. Iwamoto, *ibid.*, **46**, 1123 (1973).

and $HgCl_2$. The ethylene oxide oligomer molecules enclose the $HgCl_2$ molecules with close interatomic distances between the Hg and O atoms (2.66—2.97 Å).[1-3]

According to Snyder and Zerbi[4] the molecular conformation of $CH_3OCH_2CH_2OCH_3$ in the crystalline state is of TGT form. In a previous paper,[5] the $CH_3OCH_2CH_2OCH_3$ molecule in the crystalline complex with $HgCl_2$ was concluded to have the TGT form from analogy with the molecular conformation of the $CH_3O(CH_2CH_2O)_4CH_3$-$HgCl_2$ complex[1] and from a comparison of the infrared spectrum of the $CH_3OCH_2CH_2OCH_3$–$HgCl_2$ complex with that of the pure crystalline compound of $CH_3OCH_2CH_2OCH_3$.[4] Therefore, the molecular structures of $CH_3O(CH_2CH_2O)_mCH_3$ for m=2 and 3 in the complexes with $HgCl_2$ may be inferred by infrared spectroscopy, since it has been found that the $\mathrm{O\underset{T}{-}CH_2\underset{G}{-}CH_2\underset{T}{-}O\underset{T}{-}CH_2\underset{\bar{G}}{-}CH_2\underset{T}{-}O}$ conformation is favorable for coordination between Hg and O in the complexes. From this view-point the infrared spectra of the $CH_3O(CH_2CH_2O)_mCH_3$-$HgCl_2$ complexes have been studied.

Experimental

Commercial $CH_3O(CH_2CH_2O)_mCH_3$ was used (Tokyo Kasei Kogyo Co., Ltd.). Crystalline complexes of these compounds with $HgCl_2$ were prepared by dissolving powdered crystals of $HgCl_2$ in an ethanol solution containing the compounds in volume ratio about 4: 1 at 35 °C and by cooling the saturated solution to room temperature. In the case of $CH_3OCH_2CH_2OCH_3$, crystalline powder of $HgCl_2$ was dissolved directly in the pure liquid, the crystalline complex being precipitated in the solution. Infrared spectra were measured by a Japan Spectroscopic Co., Ltd. Model IR-G grating infrared spectrometer by means of Nujol mull method. Frequencies were calibrated by the standard bands of polystyrene.

TABLE 1. INFRARED ABSORPTION BANDS OF CH_3O-$(CH_2CH_2O)_mCH_3$–$HgCl_2$ COMPLEXES IN THE 1500—700 cm^{-1} REGION[a)]

m=1	m=2	m=3	m=4
1472 s	1469 s	1473 m	1471 m
1455 s	1453 s	1455 m	1454 m
1442 sh			
1414 m	1424 vw	1394 vw	1383 vw
1377 sh	1378 m	1382 vw	1370 vw
1371 m	1366 sh	1365 m	1355 m
	1346 m	1350 m	1345 m
1288 m	1283 m	1300 w	1296 w
		1288 m	1285 w
1243 s	1245 m	1250 m	1248 m
1202 sh	1200 m	1201 m	1198 m
1194 s			
1157 m	1160 w	1160 vw, sh	1160 vw, sh
1154 sh			
1123 vs	1129 s	1129 s	1126 s
1091 vs	1101 vs	1106 vs	1112 vs
	1095 sh		
	1078 vs	1085 vs	1096 vs
1064 sh	1051 vs, sh		
1028 m	1029 w	1030 sh	1044 vw
1016 s	1013 s	1023 m	1025 m
982 w		984 w	983 w
	940 m	944 m	943 m
		932 sh	937 sh
			921 sh
852 sh	859 s	861 m	862 m
841 vs	835 m	847 m	848 m
	831 m	834 m	835 m

a) vs: very strong, s: strong, m: medium, w: weak, vw: very weak, sh: shoulder.

Results and Discussion

Infrared spectra of the $CH_3O(CH_2CH_2O)_mCH_3$–$HgCl_2$ (m=1—4) complexes in the region 1500—700 cm^{-1} are shown in Fig. 1. The absorption bands are listed in Table 1. The absorption spectra of these complexes are, on the whole, very similar to each other.

The band around 940 cm^{-1} which is not observed for m=1 appears as a well-defined and fairly strong band when m is equal to or greater than 2. The band becomes stronger with increasing m, no significant frequency change being observed. The band is observed for crystalline diethyl ether.[4] The band should be characteristic when the chain molecule is composed of a sequence of two or more CH_2CH_2O units. The spectral feature around 850 cm^{-1} changes depending on m until m=3. The absorption bands are similar for m=3 and 4 in this region. In the other regions, the absorption bands of these complexes correspond to

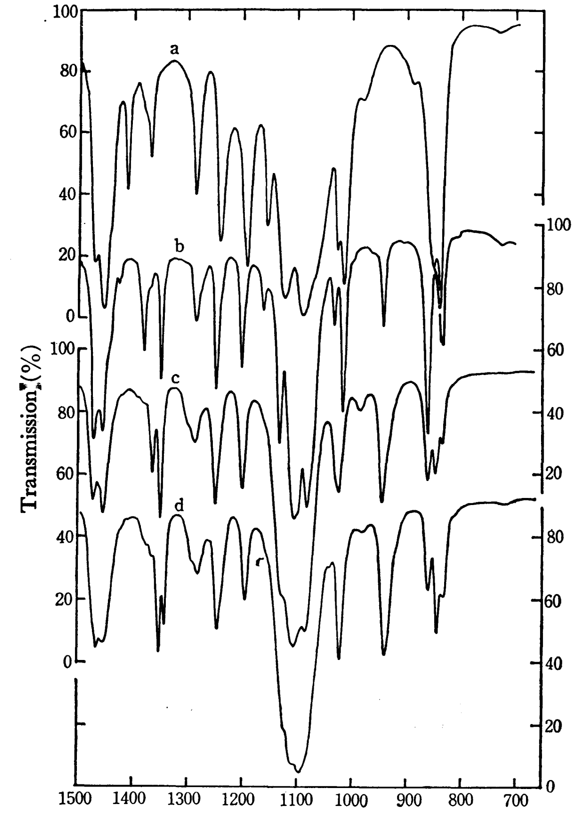

Fig. 1. Infrared spectra of $CH_3O(CH_2CH_2O)_mCH_3$-$HgCl_2$ complexes for (a) m=1, (b) m=2, (c) m=3, and (d) m=4 in the crystalline state.

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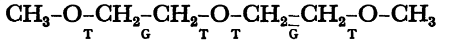
4) R. G. Snyder and G. Zerbi, *Spectrochim. Acta*, **23A**, 391 (1967).

5) R. Iwamoto, *ibid.*, **27A**, 2385 (1971).

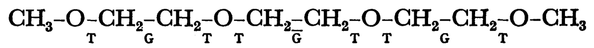
each other, especially when m is equal to or greater than 2. The two bands at 1150 and 1200 cm^{-1} are associated with the terminal CH_3 groups[4] and display different behavior with increasing m. The 1200 cm^{-1} band decreases in intensity very gradually with increasing m. It appears as a fairly strong and well-defined band even for $m=4$, while the 1150 cm^{-1}, band which is weak but well-defined for $m=1$ and 2, is hardly observable for $m=3$ and 4.

Thus, the infrared spectra of these complexes for $m=2$ and 3 are very similar to those of the $CH_3O(CH_2CH_2O)_4CH_3$–$HgCl_2$ complex in the whole region. In the $CH_3O(CH_2CH_2O)_4CH_3$–$HgCl_2$ complex, the conformation was found to be essentially a sequence of $\mathrm{O\underset{T}{-}CH_2\underset{G}{-}CH_2\underset{T}{-}O\underset{T}{-}CH_2\underset{\bar{G}}{-}CH_2\underset{T}{-}O}$.[1] From the similarity of the infrared spectra of the members of $m=2$ and 3 to those of the $CH_3O(CH_2CH_2O)_4CH_3$–$HgCl_2$ complex, the following conformations can be assumed in the complexes:



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

for $m=2$, and



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

for $m=3$.

It has been found reasonable to consider that the molecular conformation of $CH_3O(CH_2CH_2O)_mCH_3$ ($m=4$) in the complexes with $HgCl_2$ consists of a sequence of $\mathrm{O\underset{T}{-}CH_2\underset{G}{-}CH_2\underset{T}{-}O}$ with alternation of G and $\bar{G}$ in the adjacent chemical units. It is noticed that "band progression" or regular variation of band frequencies depending on m is not observed for these complexes, but their infrared spectra can be reasonably interpreted in terms of group characteristic vibrations.

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