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DIMETHYLTHALLIUM COMPLEXES OF DICYCLOHEXYL-18-CROWN-6

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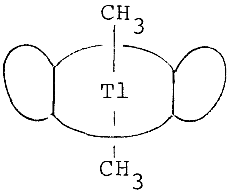
Dimethylthallium complexes of dicyclohexyl-18-crown-6, $[(CH_3)_2Tl(L)]$pic, L = DCC-A (1) and DCC-B (2), were prepared. The two methyl protons are not equivalent magnetically in 1, but equivalent in 2. A linear CH_3-Tl-CH_3 moiety was held strongly and perpendicularly in the quasi-planar ring of six oxygen atoms. The conformation of cyclohexyl groups of the complexes was discussed.

Numerous studies on macrocyclic polyether complexes of globular metal cations such as alkali and alkaline earth metals have been made in this decade.$^{1-4)}$ The complexes of cylindrical metal cations, however, have not been studied. In the present paper a dimethylthallium cation was used as a guest, since 1) the ionic radius of the thallium ion is about 1.25 Å$^{5)}$ and looks like to fit to the hole of a 18-crown-6 type of polyether,$^{6)}$ and 2) the ^1H NMR spectra can elucidate the CH_3-Tl-CH_3 moiety. Two isomers of dicyclohexyl-18-crown-6, DCC-A and DCC-B which have cis-syn-cis and cis-anti-cis forms, respectively, at the two bridge bonds,$^{7,8)}$ were taken as hosts. In a DCC-A complex, stereochemical environments above and below the quasi-plane made of six etherial oxygen atoms are different. Therefore, two methyl groups of the dimethylthallium ion are expectable to show different NMR signals, if the linear CH_3-Tl-CH_3 moiety is held perpendicularly in the ring.

To a solution of 400 mg(1.1 mmol) of DCC-A$^{9)}$ in 20 cm^3 of isopropanol, 500 mg (1.1 mmol) of $(CH_3)_2Tl\cdot pic^{10)}$ was added. The solution was heated under reflux for 4 hr. After solvent was removed under reduced pressure, the residual solid recrystallized from acetone/n-hexane gave yellow crystals of 1, which were washed with n-hexane and dried in vaccuo, m.p. 145 - 148°C. ^1H NMR($CDCl_3$):δ 0.87(d, J = 419 Hz, CH_3), 0.96(d, J = 428 Hz, CH_3),$^{11)}$ 1.4 - 1.9(broad, cyclohexyl protons), 3.36(m, CH_α-O), 3.64(three lines, CH_2-O), 8.79(s, picrate). Found: C, 40.06; H, 5.34; N, 5.01%. Calcd for $C_{28}H_{44}N_3O_{13}Tl$: C, 40.27; H, 5.31; N, 5.03%. The corresponding yellow DCC-B complex (**2**) was prepared by the same method and purified by recrystallization from isopropanol/acetone, by washing with n-hexane and drying in vaccuo, m.p. 167 - 171°C. ^{1}H NMR($CDCl_3$):δ 0.93(d, J = 423 Hz, CH_3), 1.4 - 1.7(broad, cyclohexyl protons), 3.35(dd,J = 9.5 and 4.8 Hz, CH_α-O), 3.65(four lines, CH_2-O), 8.79(s, picrate). Found: C, 40.02; H, 5.39; N, 5.08%. Calcd for $C_{28}H_{44}N_3O_{13}Tl$: C, 40.27; H, 5.31; N, 5.03%.

The J(Tl-CH_3) values observed in **1** and **2** are rather large and fall into a region where a linear CH_3-Tl-CH_3 moiety gives the value.[13)] Therefore, the CH_3-Tl-CH_3 skeltons in **1** and **2** are assumed to have a linear configuration. One of notable results in the NMR spectrum of **1** is that the two methyl groups are not equivalent magnetically, although they are equivalent in **2**. Two kinds of methyl signals have not been reported in dimethylthallium compounds. The above observation could be explained if the linear CH_3-Tl-CH_3 moiety is held perpendicularly in the quasi-planar ring of six etherial oxygen atoms and decomplexation is slow in an NMR time scale.



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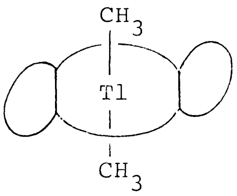


2

This assumption is consistent with the facts that 1) by an addition of large excess of aqueous HCl to **1** or **2** in acetonitrile, no precipitates of $(CH_3)_2TlCl$ were observed even after 1 hr, although the precipitates were obtained immediately in the case of $(CH_3)_2Tl\cdot pic$, and 2) the NMR spectra of mixtures of **1** and DCC-A, and **2** and DCC-B in $CDCl_3$ consist of superposition of each spectrum.

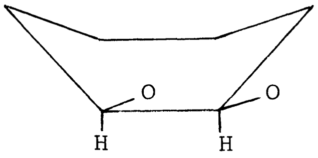
$$(CH_3)_2Tl(DCC)^+ \quad + \quad HCl_{aq} \xrightarrow{CH_3CN} \text{no precipitates}$$

$$(CH_3)_2Tl\cdot pic \quad + \quad HCl_{aq} \xrightarrow{CH_3CN} (CH_3)_2TlCl\downarrow$$

This observation indicates that exchange reaction of DCC shown below is slow in the NMR time scale.

$$(CH_3)_2Tl(DCC)^+ \quad + \quad DCC^* \xrightleftharpoons{\text{slow}} (CH_3)_2Tl(DCC^*)^+ \quad + \quad DCC$$

The chemical shifts of the methylene protons adjacent to oxygen(CH_2-O) do not show any appreciable change upon complex formation, but the signals split into three and four lines for **1** and **2**, respectively, although both of the free ethers give only single lines. The cyclohexyl protons bonded to bridge carbons (H_α) show, however, some upfield shifts in the complexes and a doublet of H_α in the free ethers becomes a multiplet and a bouble doublet in **1** and **2**,respectively. The upfield shift of H_α associates to the fact that H_α takes an axial position in the complexes, since the proton in the axial position is usually found to be shielded more than one in the equatorial position.$^{13,14)}$ The doublet of H_α in the free state indicates that conformational changes of the cyclohexyl groups are fast in the NMR time scale. On the other hand the double doublet of H_α in **2**, which arises from spin-spin couplings with nonequivalent two vicinal protons, suggests that the conformational changes of the cyclohexyl groups are slow and two H_α are equivalent. The large $^2J_{H-H}$(9.5 Hz) may correspond to $^2J_{ax-ax}$ and the small $^2J_{H-H}$ (4.8 Hz) to $^2J_{ax-eq}$.$^{15)}$ From the above results one of probable conformations of the cyclohexyl groups of **2** is deduced to be a boat form (**I**). In **I** the interference



(**I**)

of the methylene protons of the cyclohexyl groups with the methyl protons attached to the thallium atom is smaller than that of the other conformers in a model. This conformation is different from that of sodium-DCC-B complex, in which a chair form was reported from the X-ray crystallography.$^{8)}$ The conformation of the cyclohexyl groups of **1** could not be decided from spin-spin coupling constants.

References and Notes

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9) The two isomers of dicyclohexyl-18-crown-6 supplied form Nakarai Chemicals were separated chromatographycally and purified according to the procedure given by Frensdorff. (H. K. Frensdorff, J. Am. Chem. Soc., 93, 4684 (1971).) Thus obtained cis-syn-cis isomer has a melting point of 61 - 62°C(liter. value 61 - 62°C). ^1H NMR($CDCl_3$): δ 1.2 - 1.9(broad, cycloheyxl protons), 3.55(d, J = 6.8 Hz, CH_α-O), 3.67(s, CH_2-O). The cis-anti-cis isomer has a melting point of 65.5 - 68.5°C (69 - 70°C). ^1H NMR($CDCl_3$): δ 1.2 - 1.9(broad, cyclohexyl protons), 3.58(d, J = 7.5 Hz, CH_α-O), 3.67(s, CH_2-O).

10) After stirring a mixture of 1 g of $(CH_3)_2TlCl$ and 0.4 g of Ag_2O in H_2O (30 cm^3) over night, 0.9 g of picric acid was added to the solution and AgCl was filtered off. Yellow solid obtained by spontaneous evaporation of the filtrate at room temperature was recrystallized form acetone/h-hexane giving yellow crystals of $(CH_3)_2Tl\cdot pic$. ^1H NMR(acetone-d_6): δ 1.23(d, J = 411 Hz, CH_3), 8.65(s, picrate). Found: C, 40.60; H, 3.98; N, 5.13%. Calcd for $C_8H_8N_3O_7Tl$: C, 40.87; H, 3.92; N, 5.11%.

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