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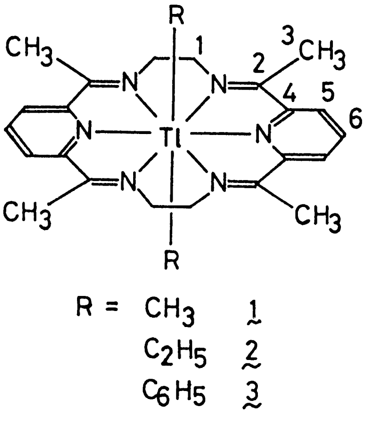
PREPARATION OF DIORGANOTHALLIUM(III) COMPLEXES WITH AN 'N_6' MACROCYCLIC LIGAND AND THEIR ^1H AND ^{13}C NMR SPECTRA

Yoshikane KAWASAKI* and Naoki OKUDA
Department of Petroleum Chemistry, Osaka University,
Yamadaoka, Suita, Osaka 565

Diorganothallium(III) complexes with an 'N_6' macrocyclic ligand were prepared by using Schiff base condensation of 2,6-diacetylpyridine with ethylenediamine. ^{13}C NMR signals of the ligand carbons were split by spin-spin coupling with the thallium nucleus. The dimethylthallium(III) complex shows the largest $^1J(\underline{Tl}\text{-}\underline{C}H_3)$ and $^2J(\underline{Tl}\text{-}C\underline{H}_3)$ values among dimethylthallium(III) compounds.

Recently attentions to organothallium(III) complexes with a macrocyclic ligand have been paid by several workers.[1 - 5] Monomethylthallium(III) ion, for example, forms complexes with tetradentate macrocyclic ligands such as tetraphenylporphyrin.[1] In these complexes, the large thallium ion cannot fit to the 'N_4' cavity of the ligands. As a result the thallium ion is located on the porphyrin ring plane.[1] If larger macrocyclic ligands were used, the organothallium(III) ions could enter into the ligand cavity. Really organothallium(III) ions are found in the center of the 'O_6' macrocyclic ligands.[2 - 5]



In this letter, preparation of diorganothallium(III) complexes with an 18-membered hexadentate 'N_6' macrocyclic ligand and interaction of the ligand nitrogen atoms with the thallium atom by using the ^1H and ^{13}C NMR spectra will be reported. The results are compared with the 'O_6' macrocyclic complexes.

The diorganothallium(III) complexes with an

Table 1. Relevant ^1H NMR data of the diorganothallium(III) complexes with an 'N$_6$' macrocyclic ligand in CD_3CN^3

	$\delta(CH_3)$	$J(\underline{Tl}-C\underline{H}_3)$	$\delta(CH_2)$	$J(\underline{Tl}-C\underline{H}_2)$	$\delta(H^1)$	$J(\underline{Tl}-\underline{H}^1)$	$\delta(H^3)$
1	0.22	516	——	——	3.83	8.1	2.42
2	0.90	666	0.93	495	3.86	9.3	2.42
3	——	——	——	——	3.72	8.4	2.20

a The separate ^{203}Tl and ^{205}Tl couplings are not resolving, presumably due to similarity of their magnetogyric ratios. The J values are expressed in the unit of Hz.

'N$_6$' macrocyclic ligand, diorgano(2,7,13,18-tetramethyl-3,6,14,17,23,24-hexaazatricyclo[17,3,1,1^{8,12}]tetracosa-1(23),2,6,8(24),9,11,17,19,21-decaene)thallium(III) perchlorates, were prepared by using the perchlorate salts of diorganothallium(III) as templates for '2 + 2' cyclic Schiff base condensation of 2,6-diacetylpyridine with ethylenediamine in CH_3CN solution.6) The solution was heated at reflux for about 7 h.7) Dialkyl(18-crown-6)thallium(III) perchlorates, $R_2Tl(18\text{-}C\text{-}6)ClO_4$ (R= CH_3, **4** and C_2H_5, **5**),8) were prepared by the same methods as reported in the literature.2) The complexes **1** - **5** are stable in air and soluble in polar solvents such as CH_2Cl_2 and CH_3CN. From the ^1H NMR spectrum of **1**, the two methyl groups bound to the thallium atom are found to be equivalent and the chemical shift of the signal was not disturbed by addition of dimethylthallium(III) perchlorate in CD_3CN solution. Therefore, the thallium ions are considered to be fixed in the 'N$_6$' cavity as shown in the figure and are inert to the demetallation reaction. In the 18-crown-6 complexes of dialkylthallium(III) the thallium ions are probably located also in the center of the 'O$_6$' cavity as are in the DBC and DCC complexes.2 - 4)

One of interesting results of the ^1H NMR spectra of the complexes is that spin-spin coupling between the thallium nucleus (^{203}Tl and ^{205}Tl) and the methylene protons (H^1) of the 'N$_6$' ligand was observed (see Table 1), although it was not detected in the methyl protons (H^3) and pyridine ring protons (H^5, H^6). Similar coupling was observed in **5** ($^3J(\underline{Tl}-O-C\underline{H}_2)$= 2.3 Hz), but not in **4**. The appearance of these spin-spin couplings indicates that interaction between the nitrogen atoms and the thallium atom is not completely electrostatic and the rate of demetallation reaction is smaller than the NMR time scale in consistent with the above observation. The appearance of these spin-spin couplings is unusual in diorgano-

Table 2. $J(\underline{\mathrm{Tl}}\text{-}\underline{\mathrm{C}})$ and ^{13}C chemical shifts of the diorganothallium(III) complexes with an 'N_6' macrocyclic ligand[a]

	C^1	C^2	C^3	C^4	C^5	C^6	CH_3	CH_2
1[b]	27(53.0)	39(166.2)	21(17.3)	42(155.3)	15(124.5)	2.1(139.5)	4425(20.4)	———
2[c]	22(52.8)	32(166.3)	23(17.4)	39(154.8)	16(124.3)	<1(139.4)	4010(35.5)	229(12.9)
3[b]	27(52.2)	36(165.7)	21(17.2)	38(154.8)	21(124.3)	<1(139.7)	———	———

a Chemical shifts are shown in parentheses and the J values are expressed in the unit of Hz. J values of the CH_3 and CH_2 groups are with the ^{205}Tl nucleus.

b In CD_2Cl_2 solution. c In $CDCl_3$ solution.

thallium(III) complexes.[9)] As is shown in Table 2, spin-spin couplings with the thallium nucleus were detected in all carbons of the 'N_6' macrocyclic ligand in the ^{13}C NMR spectra. The result suggests that all six nitrogen atoms coordinate to the thallium atom, forming an eight-coordinate structure about the thallium atom. The $^2J(\underline{\mathrm{Tl}}\text{-O-}\underline{\mathrm{C}}H_2)$ values of **4** and **5** are 2.4 and <1 Hz, respectively. These values are smaller than those of monomethylthallium(III) complex of tetraphenylporphyrin[1)] or dimethylthallium(III) derivative of 4,4'-diethoxycarbonyl-3,3',5,5'-tetramethyl-dipyrromethylene,[9)] in which the C-Tl-C moiety is assumed to be bent and the thallium atom takes sp^3 hybridization.

Another notable observation of the ^{1}H NMR spectra of the complexes is that very large $^2J(\underline{\mathrm{Tl}}\text{-}C\underline{H}_3)$ value is obtained for **1** in CD_3CN solution (see Table 1). This fact indicates a presence of a linear C-Tl-C moiety in the complex. This value is almost independent of the solvents, i.e.,507, 510, and 515 Hz in CD_2Cl_2, pyridine, and DMSO-d_6 solutions, respectively. These values are larger than those of **4**(430 Hz in CD_3CN) and $(CH_3)_2TlClO_4$ (475 Hz in HMPA)[10)] and are the largest among the dimethylthallium(III) compounds hitherto reported. As is shown in Table 1, similar result was obtained in **2**, i.e., $^2J(\underline{\mathrm{Tl}}\text{-}C\underline{H}_2)$ and $^3J(\underline{\mathrm{Tl}}\text{-}C\underline{H}_3)$ values of 2 are larger than those of **5** (399 and 628 Hz in CD_3CN, respectively) and $(C_2H_5)_2TlClO_4$ (387 and 636 Hz in HMPA, respectively).[10)] Dimethylthallium ion with the linear C-Tl-C moiety gives large $^2J(\underline{\mathrm{Tl}}\text{-}C\underline{H}_3)$ values in polar coordinative solvents.[10,11)] The increase of the values is assumed as an indication of the increase of interaction of the solvent molecules to the thallium ion.[10)] On the basis of this criterion the thallium atom of **1** as well as **2** and **3** is considered to be coordinated strongly by the six nitrogen atoms and the interaction of the 'N_6' macrocyclic ligand to the thallium atom is stronger than that of 'O_6' macrocyclic ligands such as 18-crown-6, DCC and DBC. This assumption is consistent with the fact that relatively large spin-spin couplings of the ligand carbons as well as the methylene protons(H^1) with the thallium nucleus were observed in 1 - 3 compared with those in 4 - 5.

In the ^{13}C NMR spectra, $^{1}J(^{205}\underline{Tl}-\underline{C}H_3)$ value of 1 is markdely larger than that of 4 (2839 Hz in CD_3CN) or $(CH_3)_2TlNO_3$ (3080 and 2478 Hz in pyridine and H_2O, respectively).[12] In the diethyl complex 2 large $^{1}J(\underline{Tl}-\underline{C}H_2)$ and $^{2}J(\underline{Tl}-\underline{C}H_3)$ values are also found relative to those of 5 (2476 and 169 Hz, respectively, in CD_3CN). These observations may be explained on the same basis as discussed on the ^1H NMR spectra.

It is interesting that both $J(\underline{Tl}-\underline{C}_{alkyl})$ and $J(\underline{Tl}-\underline{C}_{ligand})$ values of 1 or 2 give larger values than those of 4 or 5. These results could not be explained by the d-s mixing model as proposed by Shier and Drago.[10] Further study is in progress to generalize these findings, which may give some informations on the spin-spin couplings and the electronic structutes of organothallium(III) compounds.

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7) These complexes were purified by recrystallization from hot methanol (1 and 2) or CH_2Cl_2/hexane (3). Elemental analyses of C, H, N of all complexes agree to the calculated values within 0.3 %. 1 % yield 50, mp 180 - 190° C decomp. 2 % yield 53, mp ~200° C decomp. 3 % yield 69, mp $>$200° C, solvated with $1/2CH_2Cl_2$.
8) These complexes were purified by recrystallization from CH_2Cl_2/hexane. Elemental analyses of C, H agree to the calculated values within 0.3%. 4 % yield 81, mp 200 - 230 °C decomp. 5 % yield 81, mp 200° C.
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