Preparation and ^{1}H-NMR Spectra of Dialkyl{tetrakis(1-pyrazolyl)borato}thallium(III) Complexes

Masayoshi Onishi,* Katsuma Hiraki,* and Shigeki Nakagawa

Department of Industrial Chemistry, Faculty of Engineering, Nagasaki University, Bunkyo-machi, Nagasaki 852

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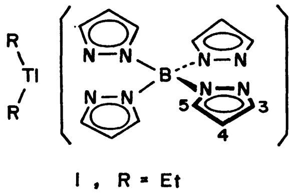
Synopsis. Diethyl- and dibuthyl{tetrakis(1-pyrazolyl)borato}thallium(III) complexes were prepared and characterized. The ^{1}H-NMR spectra of pyrazolyl protons of the BPz_4 ligand as well as the coupling constants between thallium and alkyl protons are discussed.

Trofimenko[1] reported several pyrazabole compounds, *i.e. boron* compounds of poly(1-pyrazolyl)borate. Storr *et al.* prepared sodium poly(1-pyrazolyl)aluminates and -indates,[2] and a few transition metal complexes of poly(1-pyrazolyl)gallates(III).[2,3] Some pyrazolyl-*N,N'*-bridged complexes of aluminum, gallium,[4] and thallium(III)[5] have also been reported. However, no study seems to have been reported on poly(1-pyrazolyl)borate complexes of IIIB group metals except boron[1] and thallium(I).[6]

This note deals with the preparation and ^{1}H-NMR study of two new dialkyl{tetrakis(1-pyrazolyl)borato}thallium(III) complexes, $[TlR_2(BPz_4)]$ {Pz=1-pyrazolyl, R=Et (**1**), and R=n-C_4H_9 (**2**)}.



1, R = Et
2, R = n-C_4H_9

Experimental

General Procedure and Materials. Melting points were determined in capillary tubes on a Yanagimoto MP-S3 microstage apparatus and are uncorrected. IR spectra were recorded on a Hitachi model 285 spectrometer, and ^{1}H-NMR spectra on a JEOL model JNM-MH-100 spectrometer (100 MHz) using tetramethylsilane as an internal standard. Molecular weight was determined in dichloromethane using a Mechrolab model 301 vapor pressure osmometer. Molar conductivities were measured with a Toa Denpa CM-6A instrument. Solvents were dried and distilled by the standard methods, all the preparative operations being performed in an atmosphere of dry nitrogen.

Sodium tetrakis(1-pyrazolyl)borate, $\{Na(BPz_4)\}$[7] and dialkylthallium(III) bromides[8] were prepared according to reported procedures.

Reactions of Dialkylthallium(III) Bromides with $Na(BPz_4)$. Sodium tetrakis(1-pyrazolyl)borate (1.66 mmol) was added to a THF solution of diethylthallium(III) bromide (1.46 mmol). After the mixture had been heated under reflux for 4 h, the solvent was evaporated under reduced pressure. The resulting residue was recrystallized from dichloromethane and hexane, affording a white powder of $[TlEt_2(BPz_4)]$ (**1**). A white powder of $[Tl(n\text{-}C_4H_9)_2(BPz_4)]$ (**2**) was prepared using dibuthylthallium(III) bromide in a similar way to that for **1**.

Results and Discussion

Diethyl- and dibutylthallium(III) bromides reacted with $Na(BPz_4)$ in THF under reflux to give **1** and **2**, respectively.[9] Complex **1** is considerably soluble in the usual organic solvents, the yield after recrystallization being fairly low. The molecular weight of **1** determined in dichloromethane was 526, in line with the monomeric structure formulated as $[TlEt_2(BPz_4)]$ (calcd 542). The non-ionic character of these two complexes was confirmed by low conductivity in common organic solvents (Table 1).

Mass spectra of **1** and **2** showed several peak-groups,

TABLE 1. YIELDS AND PROPERTIES OF THE NEW THALLIUM(III) COMPLEXES

Complex	Yield[a)]	Mp	$\Lambda/(\Omega^{-1}\,cm^2/mol)$[b)]				Found (Calcd), %		
	%	°C	CH_2Cl_2	THF	MeCOMe	EtOH	C	H	N
1	8.8	194	0.25	—	0.55	2.7	35.66(35.48)	4.00(4.09)	21.01(20.69)
2	40	89—90	0.18	0.03	0.26	2.06	40.27(40.19)	5.03(5.06)	18.87(18.75)

a) Based on dialkylthallium(III) bromide. b) Molar conductivity in mol m^{-3} solution, at 25 °C.

TABLE 2. ^{1}H-NMR DATA OF THE THALLIUM(III) COMPLEXES[a)]

Complex	Alkyl group							BPz₄ group[b)]		
	α-CH_2			β-$\underline{H}$		γ-$C\underline{H}_2$	δ-$C\underline{H}_3$	3-H	4-H	5-H
	δ/ppm	J_{HTl}/Hz	$J_{\alpha\beta}$/Hz	δ/ppm	J_{HTl}/Hz	δ/ppm	δ/ppm	δ/ppm	δ/ppm	δ/ppm
1[c)]	1.41(dq)	306	8.0	1.14(dt)	638	—	—	6.94(d)	6.28(t)	7.65(d)
2[d)]	1.49(dt)	338	7.0	1.70(dm)[e)]	538	1.25(m)[e,f,g)]	0.86(t)[g)]	6.94(d)	6.28(t)	7.65(d)

a) TMS as an internal standard. Abbreviations used; d=doublet, dm=double multiplet, dq=double quartet, dt=double triplet, m=multiplet, t=triplet. b) $^3J_{3,4}$ and $^3J_{4,5}$ are actually 2.0 Hz. c) In CD_2Cl_2. d) In $CDCl_3$. e) $^3J_{\alpha\beta}$ was not distinguished. f) The coupling to thallium was not distinguished. g) $^3J_{\gamma\delta}$=7.0 Hz.

TABLE 3. SOLVENT EFFECT OF THE PYRAZOLYL PROTON RESONANCES OF **2**[a)]

Solvent	3-H	4-H	5-H
C_6D_6	7.21	6.12	7.48
CD_2Cl_2	6.88	6.25	7.59
$(CD_3)_2CO$	6.87	6.22	7.68

a) δ value (ppm) from TMS, at 25 °C. See Table 2, concerning the values in $CDCl_3$.

the pattern of each being characteristic of the isotopes of thallium (^{203}Tl and ^{205}Tl) and boron (^{11}B and ^{10}B). The highest peak of each peak-group, corresponding to a species containing both ^{205}Tl and ^{11}B was characterized as follows. Complex **1** showed four peaks at *m/e* 475, 513, 542, and 747 ascribable to the ethylthallium species, $[TlEt_2(BPz_3)]^+$, $[TlEt(BPz_4)]^+$, $[TlEt_2(BPz_4)]^+$ (the weak parent peak), and $[Tl_2Et_2(BPz_4)]^+$, respectively, and six peaks at *m/e* 350, 417, 484, 555, 622, and 689 to the dealkylated thallium species, $[Tl(BPz_2)]^+$, $[Tl(BPz_3)]^+$, $[Tl(BPz_4)]^+$, $[Tl_2(BPz_2)]^+$, $[Tl_2(BPz_3)]^+$(weak), and $[Tl_2(BPz_4)]^+$, respectively, the peak at *m/e* 614 not being ascribable to any species. Complex **2** showed four peaks at *m/e* 531, 541, 598, and 803 ascribable to the butylthallium species, $[Tl(C_4H_9)_2(BPz_3)]^+$, $[Tl(C_4H_9)(BPz_4)]^+$, $[Tl(C_4H_9)_2(BPz_4)]^+$ (weak parent peak), and $[Tl_2(C_4H_9)_2(BPz_4)]^+$, respectively, in addition to the six peaks ascribed to the dealkylated species and the unknown one at *m/e* 614 shown for complex **1**. It seems that the {poly(1-pyrazolyl)borato}dithallium fragments are formed in a considerable amount.

The pyrazolyl region in the ^{1}H-NMR spectrum of both **1** and **2** showed a virtual triplet for four 4-H's and two doublets for four 3-H's and 5-H's (Table 2). This indicates that the four pyrazolyl groups of the BPz_4 ligand are magneto-spectroscopically equivalent and fluxional in solution, similar to the case of $[Zn(BPz_4)_2]$[10)] and $[Pd(1\text{-}3\text{-}\eta^3\text{-}C_3H_5)(BPz_4)]$.[10)] On cooling to −31 °C,[11)] the three signals broadened slightly, no slow-exchange limiting spectrum being obtained even at this temperature. ^{1}H-NMR data of the pyrazolyl protons of **2** in C_6D_6, CD_2Cl_2, and $(CD_3)_2CO$ are given in Table 3. Two doublets at δ 6.88 and 7.59 in CD_2Cl_2 were attributed to the 3-H's and the 5-H's, respectively, considering the fact that the environment of the outer 3-H's changes more significantly on switching the NMR solvent, than that of the inner 5-H's located near boron atom.

In the ^{1}H-NMR signals of alkyl groups, couplings to ^{203}Tl and ^{205}Tl were virtually identical (Table 2). Similar large and actually equal coupling constants of these two thallium isotopes were reported on some alkyl- or arylthallium(III) compounds by Maher and Evans, who found that a positive charge delocalized on the thallium atom increases the magnitude of the J(Tl-H) values, through the enhancement of s character upon the thallium atom.[12)] The coupling constants of the α- and β-protons in **1** are actually comparable with the respective values [$^2J(H_\alpha Tl)=340$ Hz and $^3J(H_\beta Tl)=628$ Hz] of diethylthallium(III) sulfate,[12)] this being the case with the dibutylthallium(III) homologues. This suggests that there is nearly one positive charge on the thallium atom in **1** or **2**, and the bonds between the thallium atom and the pyrazolyl-nitrogens are a kind of contact ion pair. This is in line with the fluxional behavior of the BPz_4 ligand in **1** and **2** at low temperature.

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9) The analytical data of **1** and **2** are satisfactory, as seen in Table 1. Their IR spectra were also consistent with the proposed formulae.

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