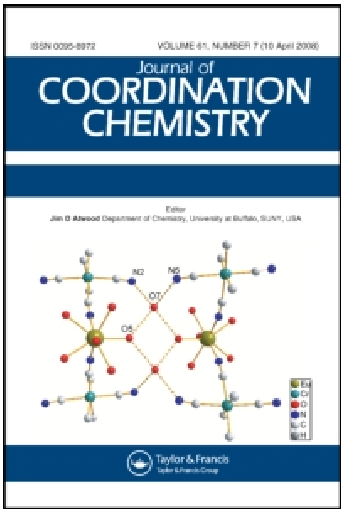

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^{1}H NMR Spectra of Phenylthallium (III) Crown-Ether Complexes, $[C_6H_5Tl(III)(Crown)X]n(ClO_4)$ (n=1 OR 2); Trans Influence of The X Groups

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^{1}H NMR SPECTRA OF PHENYLTHALLIUM(III) CROWN-ETHER COMPLEXES, $[C_6H_5Tl(III)(CROWN)X]n(ClO_4)$ (n=1 OR 2); TRANS INFLUENCE OF THE X GROUPS

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Abstract Trans influence of the X groups on the spin-spin coupling constants between the thallium nucleus and the meta protons of the phenyl group attached to the thallium atom, $J(Tl\text{-}H_m)$, were studied for a number of phenylthallium(III) crown-ether complexes, $[C_6H_5Tl(III)(crown)X]n(ClO_4)$(n=1 or 2).

Keywords: Transinfluence, X-groups, thallium

INTRODUCTUION

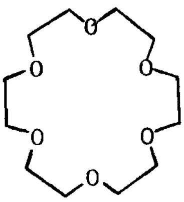
Many monophenylthallium(III) compounds are rather unstable and decompose into thallium(I) ion and organic compounds. These properties are appreciably modified in the presence of crown-ethers. For example, $C_6H_5Tl(III)^{2+}$ ion gives $Tl(I)^+$ ion and C_6H_5I imediately by the reaction of a soft I^- ion,[1] but the $C_6H_5Tl(III)I^+$ ion was isolated as a stable crown-ether complex, $[C_6H_5Tl(III)(DBC)I]ClO_4$, where DBC= dibenzo-18-crown-6.[2] The stabilizing effect of the crown-ether in the phenyl thallium(III) crown-ether complexes may be due to a) compelling the I^- ion to the trans position of the phenyl group, which makes the reductive elimination reaction affording C_6H_5I difficult, and b) inhibiting sterically the approach of the two thallium atoms in close proximity by the crown-ether coordinated to the thallium atom. Several other stable phenylthallium(III) crown-ether complexes having Tl-X bond,otherwise unstable, have been obtained. In this paper, trans influence of the X groups on the spin-spin coupling constants between the thallium nucleus and the meta protons of the phenyl group attached to the thallium atom, $J(Tl\text{-}H_m)$ were investigated for a number of complexes, $[C_6H_5Tl(III)(crown)X]n(ClO_4)$ (n= 1 or 2) by means of the ^1H NMR spectra. The order of the trans influence of the X groups of the phenylthallium(III) crown-ether complexes was compared with that of the low valent transition metal complexes, in which a considerable amount of π back bonding was possible.

PREPARATION OF PHENYLTHALLIUM(III) CROWN-ETHER COMPLEXES

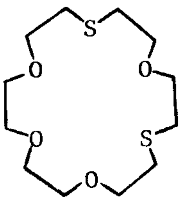
$[C_6H_5Tl(III)(crown)]2(ClO_4)\cdot m(H_2O)$ (**1**). These complexes were prepared according to eq. 1. To the suspension of C_6H_5TlO

$$C_6H_5TlO + 2HClO_4(aq.) + crown \xrightarrow{THF} [C_6H_5Tl(III)(crown)]2(ClO_4)\cdot m(H_2O) \qquad (1)$$

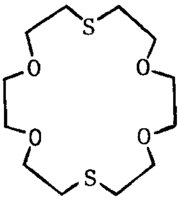
crown; 18C6(a) (m= 3), 1,7-DTC(b) (m= 0), 1,10-DTC(c) (m=0)



18C6



1,7-DTC



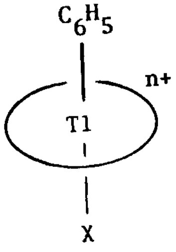
1,10-DTC

in THF was added a dilute THF solution of 2 - 2.5 equivalent $HClO_4$ (aq.) slowly to give a clear light brown solution. This solution was added dropwise to the THF solution of crown-ether on a ice bath. The mixture was stirred overnihgt at ambient temperature giving white precipitates. These were purified by recrystallization from acetonitrile/ether for **1a** and **1b**, and acetone/n-hexane for **1c** giving air stable white(**1a** and **1c**) and light yellow(**1b**) crystals. These are soluble in acetonitrile, acetone and methanol, and sparingly soluble in methylene chloride and chloroform. Acetone is not a suitable solvent for 1a and 1b, as hydoxo complex, $[C_6H_5Tl(III)(18C6)OH]ClO_4$ and α-keto complex, $[C_6H_5Tl(III)(1,7\text{-DTC})CH_2C(O)CH_3]ClO_4$ were recovered form acetone solutions of 1a and 1b, respectively, after partial evaporation of the solvent at reduced pressure.

$[C_6H_5Tl(III)(crown)X]n(ClO_4)$ (n=1 or 2) (2). These complexes were prepared according to eqs. (2) and (3) in acetonitrile at ambient

$$1 \quad + \quad X(\text{or } HX) \xrightarrow{CH_3CN} [C_6H_5Tl(III)(crown)X]n(ClO_4) \qquad (2)$$

$$1c \quad + \quad 2P(OR)_3 \xrightarrow{\text{dry } CH_3CN} [C_6H_5Tl(III)(1,7\text{-DCT})P(O)(OR)_2]ClO_4 + RP(OR)_3ClO_4 \qquad (3)$$



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temperature, except for X= SCH_3 and $SC(O)CH_3$, in which the reactions were carried out at -40 °C, although the complexes isolated are stable at ambient temperature. Since the complexes with X= $P(OR)_3$ and $P(C_6H_5)_3$ are reactive, these were detected only as a transient species in solution by ^1H and ^{31}P NMR spectra. The complex with X= OCH_3 is rather hydrolytic giving easily the OH complex in solution. The other complexes studied are stable in air and soluble in polar solvent such as acetonitrile and methylene chloride.

Spectra

^1H, ^{31}P, and ^{77}Se NMR spectra were obtained by using JEOL-PS-100, -FX-90, and -GX-270 spectrometers,respectively, in CH_3CN or CD_3CN.

RESULTS AND DISCUSSION

In the phenylthallium(III) crowun-ether complexes 1 and 2, ortho, meta, and para protons give a double-boublet, a double-triplet, and a double-triplet with relative intensity of 2 : 2 : 1. The high field signal of the double-doublet of the ortho protons, however, are sometimes overridden by stong crown-ether signals, so that $J(Tl\text{-}H_o)$ values, which extend from 400 to 1200 Hz,could not be measured for some complexes. On the other hand, the spin-spin coupling constants observed for the para proton, $J(Tl\text{-}H_p)$, are not large, the value of which changes from 50 to 170 Hz with the X groups. Therefore, we concentrated our attention mainly on the meta proton spin-spin coupling constants, $J(Tl\text{-}H_m)$.

In the dicationic complexes, 1, the $J(Tl\text{-}H_m)$ values depend markedly on the kind of crown-ether and were found to be 498, 459, and 429 Hz for 1a, 1b, and 1c, respectively. 1a, in which a water molecule may coordinate to the thallium atom from the back side of the phenyl group, shows the largest $J(Tl\text{-}H_m)$ value and 1c gives the smallest one. The main reason for the decrease of the $J(Tl\text{-}H_m)$ value of 1c is that the sulfur atoms of the 1,10-DTC coordinate to the thallium atom at the trans position to the phenyl group. This explanation is compatible with the results that a) $J(Tl\text{-}H_m)$ value of the $(C_2H_5)_2S$ adduct, $[C_6H_5Tl(III)(18C6)S(C_2H_5)_2]^{2+}$, shows a simlar value(426 Hz) with that of 1c and b) in both complex, the protons of the methylene groups next to the sulfur atoms show splittings by spin-spin coupling with the thallium nucleus; $J(Tl\text{-}SCH_2)$= 139 and 171 Hz for the $(C_2H_5)_2S$ adduct and 1c, respectively. On the other hand the $J(Tl\text{-}H_m)$ of 1b takes an intermediate value of 1a and 1c. This result possibly indicates that the interaction of the sulfur atom of the 1,7-DTC with the thallium atom is not strong enough as in that of 1c, but sulfur atoms prevent the coordination of water molecule, which results in coloring of 1b by weak charge transfer interaction.

In Table I, the $J(Tl\text{-}H_m)$ values of a number of $[C_6H_5Tl(III)(crown)\text{-}X]n(ClO_4)$, 2, were given in the order of increasing value. The value changes, more or less, as the crown-ether changes. For example, in the chloro complexes, $J(Tl\text{-}H_m)$= 358, 369, 373, and 376

TABLE I The J(Tl-H$_m$) values of [C_6H_5Tl(III)(crown)X]n(ClO_4) in CH_3CN or CD_3CN solution.*

X	J(Tl-H$_m$)/Hz	X	J(Tl-H$_m$)/Hz
$CH_3{}^{c}$	126	$SeCN^{a,*****}$	321
$4\text{-}C_6H_4OH^{a}$	140	$N_3{}^{c}$	330
$P(O)(OC_4H_9{}^{n})_2{}^{c,**}$	171	I^{c}	339
$CH_2C(O)CH_3{}^{b}$	174	SCN^{c}	357
$C{\equiv}CC_6H_5{}^{b}$	223	Br^{c}	368
$SCH_3{}^{d}$	225	Cl^{c}	373
$CH(CN)C(O)OCH_3{}^{b}$	246	$P(C_6H_5)_3{}^{c}$	381
SH^{d}	252	$OC(O)CH_3{}^{d}$	382
OH^{a}	262	F^{a}	389
$CH(CN)_2{}^{b}$	268	$S(C_2H_5)_2{}^{a}$	426
$SC(O)CH_3{}^{d}$	270	$OC(O)CF_3{}^{d}$	435
$OCH_3{}^{a,***}$	291	$CO^{a,******}$	493
CN^{c}	293	H_2O^{a}	498
$P(OC_4H_9{}^{n})_3{}^{c,****}$	304		

* The supescript on each X represents the kind of crown-ether, a;18C6, b;1,7-DTC, c;1,10-DTC, and d;DBC.

** J(^{205}Tl-^{31}P)= 22354 Hz

*** In CH_3OH solution

**** J(^{205}Tl-^{31}P)= 17530 Hz

***** J(^{205}Tl-^{77}Se)= 7260 Hz

****** Measured after bubbling CO gas for 1 min.

Hz for crown= 18C6, 1,7-DTC, 1,10-DTC, and DBC, respectively. This change, however, is smaller than that in the complexes 1.

The characteristic features of the trans influence of X groups on the J(Tl-H_m) values of $[C_6H_5Tl(III)(crown)X]n(ClO_4)$ are that the OH and OCH_3 groups show a strong trans influence in contrast to the carboxylato groups, which show the smallest trans influence. The J(Tl-H_m) value of the $P(C_6H_5)_3$ complex is rather large, indicating small trans influence. The CO group has almost no interaction with the thallium atom on the basis of the J(Tl-H_m) value. These results are marked contrast with those of corresponding transition metal complexes. One of the interesting results of the OH and OCH_3 complexes is the large splittings of these proton signals by spin-spin coupling with the thallium nucleus. These J(Tl-OH) and J(Tl-OCH_3) values are 330 and 455 Hz for the OH and OCH_3 complexes, respectively. The splitting of the OH signal is observed even after an addition of one drop of H_2O to the CH_3CN solution in an NMR tube. This signal, however, disappears when one drop of D_2O was added. The above results may be compared with similar splittings observed for the SH and SCH_3 complexes; J(Tl-SH)= 405 and J(Tl-SCH_3)= 453 Hz.[2]

As can be expected, the J(Tl-H_m) values of the complexes with the Tl-C bond belong to the group showing the smallest J(Tl-H_m) value, which indicates that the large trans influence of the carbon ligands. The J(Tl-H_m) values increase as the s content of the hybridization of the carbon atom increases; 126, 140, and 223 Hz for X= $CH_3(sp^3)$, 4-$C_6H_4OH(sp^2)$, and $CCC_6H_5(sp)$, respectively. Among the carbon ligands with sp^3 hybridization, J(Tl-H_m) values increase when electronegative groups such as $C(O)CH_3$ and CN groups are attached directly to this carbon; 174 and 268 Hz for X= $CH_2C(O)CH_3$ and $CH(CN)_2$, respectively. This may reflect the increase of the ionic character of the Tl-C bond.

In the three phosphorous ligands studied, the dibutylphosphonato ligand, $P(O)(OC_4H_9{}^n)_2$, shows one of the largest trans influence, but that of the neutral ligands $P(OC_4H_9{}^n)_3$, especially $P(C_6H_5)_3$ is small. In the ^{31}P NMR spectra, the $P(O)(OC_4H_9{}^n)_2$ group with the large trans influence gives large J(^{205}Tl-^{31}P) value of 22354 Hz. While P(OC_4H_9)$_3$ giving the smaller trans influenc shows small J(^{205}Tl-^{31}P) value of 17530 Hz, indicating the weaker interaction of the latter group with the thallium atom.

The N_3, SeCN, and SCN groups show similar J(Tl-H_m) values with an intermediate trans influence. On the basis of the IR spectra, the SeCN and SCN groups were concluded to coordinate to the thallium atom with the selenium and sulfur atoms. The presence of the Tl-Se bond in the SeCN complex was confirmed also by the ^{77}Se NMR spectra. The large J(^{205}Tl-^{77}Se) value of 7260 Hz was observed for this complex. The J(^{205}Tl-^{77}Se) values reported for Zintl compounds, $TlSe_3^{3-}$ and $Tl_2Se_2^{2-}$ are 7250 and 2260 Hz, respectively.[3]

In conclusion, the trans influence of the X group is large when the group could form covalent bond with the thallium atom. The halogen groups show an intermediate trans influence with following order; I > Br > Cl > F.

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