

COORDINATION COMPOUNDS OF DIMETHYL- AND DIETHYL-THALLIUM (III)

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INTRODUCTION

Relatively little has been reported on the coordination chemistry of the dialkyl thallium cations. Investigation of the acidity of these species has been complicated by the fact that these compounds are usually prepared as halides and the halide ion (with the possible exception of iodide) coordinates quite effectively. A partial X-ray structure determination¹ indicates a linear C-Tl-C configuration with four bridging halides in the plane of the thallium atom. The Raman spectra of dimethylthallium nitrate, perchlorate, and hydroxide² in aqueous solution have been assigned on the basis of a linear C-Tl-C configuration. A similar structure has been proposed for the dimethyltin(IV) cation³.

Coordination complexes of dialkylthallium cations with β -diketones are known⁴ and bis(perfluorophenyl)thallium cation has been found⁵ to form a coordination complex with 2,2'-bipyridine. Dimethylthallium methylmercaptide, methylselenide and dimethylamide have been shown to be dimeric in boiling benzene, indicating coordinate bridging through the donor atoms⁶. Several new and interesting coordination compounds of this cation are reported in this article.

The PMR spectra of organothallium compounds show large splitting due to proton-thallium spin coupling^{7,8,9,10,11}. In the diethylthallium cation $J(\text{Tl}-\text{CH}_2-\text{CH}_3)$ is found to be larger than $J(\text{Tl}-\text{CH}_2-\text{CH}_3)$ and of the opposite sign⁷. Similar results for the heavy metal spin coupling to the α - and β -protons of ethyl groups have been reported for mercury, lead, and tin¹². An investigation of thallium-proton spin coupling in the dimethylthallium and diethylthallium cations has been made, and the coupling constants were found to be sensitive to the solvent employed and to the anion in the dialkylthallium salt¹¹.

The coupling constants of the complexes reported here have been examined, and the solvent dependence of $J(\text{Tl}-\text{H})$ has been discussed in terms of the effect of the donor strength of the solvent on d - s mixing.

EXPERIMENTAL

A. Thallium compounds

Dialkylthallium halides. The basic procedure of Gilman and Jones¹³ was used for the preparation of dimethylthallium and diethylthallium halides. The procedure was modified by solvolyzing the trimethylthallium solution with methanol instead of

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aqueous acid. This modification gave a more tractable precipitate. Pyridine was used for recrystallization.

Dimethylthallium perchlorate. Two g of recrystallized dimethylthallium halide was stirred with silver oxide in water and the resulting basic solution was neutralized with perchloric acid. The neutralized solution was diluted with an equal volume of isopropanol and evaporated on a steam bath. Isopropanol was added at intervals as the water was azeotroped off, and the final solution was filtered and crystallized. Recrystallization was carried out from isopropanol or from dioxane solution with a very small quantity of water added.

The preparation of this compound was carried out several times with no difficulty. However, on one occasion when the crude product was being scraped from an evaporating dish with a stainless steel spatula, a violent explosion resulted. (Found: C, 7.36; H, 1.84. $C_2H_6ClO_4Tl$ calcd.: C, 7.19; H, 1.80 %.)

Dimethylthallium nitrate. The hydroxide, which was made from reaction of dimethylthallium halide with silver oxide in water, was neutralized with nitric acid to produce the nitrate. This compound was recrystallized from aqueous solution. (Found: C, 8.39; H, 2.10. $C_2H_6NO_3Tl$ calcd.: C, 8.10; H, 2.04 %.)

Dimethylthallium tetrafluoborate. The compound was made from the hydroxide by neutralization of an aqueous solution with fluoboric acid and recrystallized from tetrahydrofuran. (Found: C, 7.63; H, 1.87. $C_2H_6BF_4Tl$ calcd.: C, 7.47; H, 1.87 %.)

Other dimethylthallium salts. Dimethylthallium fluoride was made by neutralization of dimethylthallium hydroxide with hydrofluoric acid in a polyethylene container. The crude product was used to make the tetraphenylborate salt by double decomposition in ethanol, methanol, or acetonitrile with sodium tetraphenylborate. The tetraphenylborate was not isolated, but was used to make coordination compounds of various ligands. Dimethylthallium thiocyanate, cyanide, and acetate were made by double decomposition of dimethylthallium fluoride and sodium thiocyanate, cyanide, and acetate in ethyl alcohol; these salts were not analyzed.

Diethylthallium perchlorate. The same procedure was used as for dimethylthallium perchlorate, but the compound was less stable and appeared to decompose somewhat upon standing. The compound was recrystallized from a dioxane/water mixture. (Found: C, 14.0; H, 2.68. $C_4H_{10}ClO_4Tl$ calcd.: C, 13.3; H, 2.77 %.)

2,2'-Bipyridinedimethylthallium(III) perchlorate. Dimethylthallium perchlorate (0.5 g, 1 mole) and 2,2'-bipyridine (0.5 g, 2 moles) were combined in 20 ml of isopropanol giving a white precipitate. The air-dried crystals had a melting point of 200°. (Found: C, 29.47; H, 2.08. $C_{12}H_{14}ClN_2O_4Tl$ calcd.: C, 29.40; H, 2.10 %.)

Bis(tetramethylguanidine)dimethylthallium(III) perchlorate. The compound was made by dissolving dimethylthallium perchlorate in the minimum amount of tetramethylguanidine, TMG, and precipitating with ether. The non-hygroscopic salt had a melting point of 93°. (Found: C, 24.75; H, 5.61; N, 12.39. $C_{12}H_{32}ClN_6O_4Tl$ calcd.: C, 25.60; H, 5.68; N, 14.95 %.)

Ethylenediaminedimethylthallium(III) perchlorate. Dimethylthallium perchlorate was dissolved in a minimum amount of ethanol and added to an excess of ethylenediamine in a dry atmosphere. White crystals formed which were deliquescent and had a melting point of 183°. (Found: C, 12.14; H, 3.74; N, 6.94. $C_4H_{14}ClN_2O_4Tl$ calcd.: C, 12.10; H, 3.56; N, 7.12 %.)

Bispyridinedimethylthallium(III) tetraphenylborate. Sodium tetraphenylborate

in ethanol was added to an equal molar amount of dimethylthallium fluoride in ethanol giving a white precipitate. The white precipitate of sodium fluoride and dimethylthallium tetraphenylborate was extracted with a small amount of pyridine and filtered to separate the sodium fluoride. Addition of ether to the pyridine solution gave a white precipitate. The compound decomposed without melting. (Found: C, 59.94; H, 5.09. $C_{36}H_{36}BClN_2O_4Tl$ calcd.: C, 60.80; H, 5.07 %.)

Bis(dimethylsulfoxide)dimethylthallium(III) perchlorate. The compound was prepared by dissolving 0.5 g dimethylthallium perchlorate in the minimum amount of dimethylsulfoxide, DMSO, and precipitating with ether. A two-phase system was formed, and the upper phase was discarded. The remaining viscous oil was diluted with a small volume of ethanol and precipitated with ether. The resulting hygroscopic crystals had a melting point of 92° . (Found: C, 14.54; H, 3.58. $C_6H_{18}ClO_6Tl$ calcd.: C, 14.70; H, 3.68 %.)

Attempted preparation of an HMPA solvate of dimethylthallium cation. An attempt was made to prepare a hexamethylphosphoramide, HMPA, adduct of dimethylthallium perchlorate by precipitation from an HMPA solution with ether. The product analyzed for unsolvated dimethylthallium perchlorate.

(Acetylaceton)dimethylthallium(III). Three g of dimethylthallium halide was stirred with 2 g of silver oxide in 10 cc of water. The resulting solution was diluted with an equal volume of ethanol, evaporated to a small volume, and taken to small volume with equal amounts of ethanol two more times. One cc of acetylacetone in 10 cc of benzene was added to the concentrated solution of dimethylthallium hydroxide in ethanol and boiled, resulting in white crystals easily soluble in hot benzene and slightly soluble in cold benzene. The crude product was sublimed at 20 mm, 160° . (Found: C, 25.50; H, 3.99. $C_7H_{13}O_2Tl$ calcd.: C, 25.40; H, 3.90 %.)

(1,3-Diphenyl-1,3-propanedione)dimethylthallium(III). Five g of dimethylthallium halide was stirred with 3.5 g of silver oxide in water, and the water was azeotroped off with isopropanol. 1,3-Diphenyl-1,3-propanedione (3.1 g) was dissolved in 10 cc of benzene and added to the isopropanol solution. The solution was boiled to reduce the volume and the resulting solid crystallized from benzene/hexane. The recrystallized product was sublimed at 0.025 mm, 150° . (Found: C, 44.8; H, 3.87. $C_{17}H_{17}O_2Tl$ calcd.: C, 44.5; H, 3.74 %.)

Dimethylthallium phenoxide. A solution of dimethylthallium hydroxide was prepared from 3 g of dimethylthallium halide and 2 g of silver oxide, and the water was removed by azeotroping with ethanol. A solution of phenol in 10 cc of benzene was added. The volume of the benzene/ethanol solution was reduced, and hexane was added causing a white precipitate to form. The initial product was recrystallized twice from benzene/hexane with precautions taken against the entry of moisture. This compound has a melting point of 202° . (Found: C, 29.74; H, 3.76. $C_7H_{11}OTl$ calcd.: C, 29.4; H, 3.39 %.)

Dimethylthallium methylmercaptide. A solution of dimethylthallium hydroxide was made in water from 3 g of dimethylthallium halide and 2 g of silver oxide, and the water was removed by azeotroping with isopropanol. An excess of methanethiol was added to the isopropanol solution, and the solution was evaporated to near dryness. The solid was extracted with benzene and recrystallized twice from this solvent. The nonhygroscopic white solid decomposed at 190° . (Found: C, 13.0; H, 3.24. C_2H_5TlS calcd.: C, 12.78; H, 3.19 %.)

B. Spectra

Infrared spectra of heavy metal compounds in the potassium bromide region were obtained on a Beckman IR-5A spectrophotometer with cesium bromide optics. The cell material was cesium bromide except for solutions of high dielectric constant solvents such as DMSO where silver chloride plates were used. This material has low transmittance below 350 cm^{-1} . Nujol mulls were recorded between cesium bromide plates. Some experiments in the potassium bromide region were repeated on a Perkin-Elmer 521 instrument.

Nuclear magnetic resonance spectra were obtained with a Varian Associates A-60 spectrometer. Separate splitting of proton signals by the ^{203}Tl and ^{205}Tl nuclei, which have only slightly different gyromagnetic ratios, was not resolved.

Solvents were either reagent grade or distilled prior to use.

RESULTS

The results of infrared and Raman studies in the C-Tl-C stretching frequency region are tabulated in Table I for these systems. The effect of the solvent on $J(\text{Tl-CH}_3)$

TABLE I

THALLIUM-CARBON STRETCHING FREQUENCIES^a

Compound	Solvent ^b	Frequencies (cm^{-1})		
		Asym. str.	Sym. str.	Other bands
$(\text{CH}_3)_2\text{TlClO}_4$		557		
	Acetonitrile	557		
	Methanol	554		
	Pyridine	548	484	
			487 ^c	
	DMSO	552	486 ^c	
	DMA	554		
$(\text{CH}_3)_2\text{TlNO}_3$	HMPA	553		
		557		
		524	469 (s)	
		552	507 (s)	544 (m)
				478 (w)
$[(\text{CH}_3)_2\text{TlSCH}_3]_2$ $[(\text{CH}_3)_2\text{TlOC}_6\text{H}_5]_2$		552	498 (w)	532 (vs)
		552	503 (w)	532 (s)
		540	483 (w)	515 (m)
	Benzene	545		515 (m)
	Benzene + 10% DMSO	548		515 (m)
	DMSO	542	484 (w)	515 (m)
	Pyridine	556		462 (vw)
$[(\text{CH}_3)_2\text{Tl}(\text{DMSO})_2]\text{ClO}_4$ $[(\text{CH}_3)_2\text{Tl}(\text{pyridine})_2](\text{C}_6\text{H}_5)_4\text{B}$		545		466 (m)
				479 (m)
		549	493 (w)	461 (w)
		539	485 (w)	473 (m)
		535	485 (w)	460 (vw)
$[(\text{CH}_3)_2\text{Tl}(2,2'\text{-bipyridine})]\text{ClO}_4$ $[(\text{CH}_3)_2\text{Tl}(\text{ethylenediamine})]\text{ClO}_4$				553 (vs)
				525 (m)

^a All frequencies measured by infrared spectrophotometry except where noted. The asymmetric stretching frequency is assigned a qualitative intensity of strong (s), and other bands are assigned intensities of very strong (vs), strong (s), medium (m), weak (w), or very weak (vw).

^b Where no solvent is listed, the spectrum was obtained on a Nujol mull. ^c By Raman.

TABLE 2

 $J(\text{TI}-\text{CH}_3)$ AND τ FOR DIMETHYLTHALLIUM PERCHLORATE IN VARIOUS SOLVENTS

Solvent ^a	$J(\text{TI}-\text{CH}_3)$ (cps)	τ (ppm) ^b
Sulfolane	408	8.68
Acetonitrile	412	8.75
Deuterium oxide	413	
Deuterium oxide (60%)	407	
5 M NaOH	415	
Methanol (80%)	414	
2,6-Lutidine	416	8.62
Pyridine	416	8.30
Pyridine (30%)	425	
Pyridine (0.5 M NaClO ₄)	416	
2-Picoline	416	
Acetone	420	8.60
Acetone (0.5 M NaClO ₄)	414	
TMG	421	9.03
3-Picoline	426	8.34
Ethylenediamine	427	9.10
TMU	426	
DMF	434	8.90
DMSO	442	
DMSO (30%)	451	9.10
DMSO (0.5 M NaClO ₄)	444	
DMA	452	8.88
Tetramethylenesulfoxide	457	9.16
HMPA	475	9.05
HMPA (0.5 M NaClO ₄)	462	

^a Concentrations are 10% by weight except as noted after the solvent. ^b Referred to tetramethylsilane internal standard.

TABLE 3

COUPLING CONSTANTS FOR DIETHYLTHALLIUM PERCHLORATE IN VARIOUS SOLVENTS

Solvent ^a	$J(\text{TI}-\text{CH}_2-\text{CH}_3)$	$J(\text{TI}-\text{CH}_2-\text{CH}_3)$
Sulfolane	338	630
Acetonitrile	344	624
Acetone	353	631
2-Picoline	356	626
TMG	360	637
Pyridine	364	640
Methanol	371	644
Deuterium oxide	378	634
TMU	378	630
DMSO	384	633
DMF	387	641
Ethylenediamine	390	659
DMA	394	642
HMPA	399	628

^a All concentrations are 10% by weight.

TABLE 4
 $J(\text{TI}-\text{CH}_3)$ FOR $(\text{CH}_3)_2\text{TI}$ IN VARIOUS SOLVENTS

Anion	Solvent ^a	$J(\text{TI}-\text{CH}_3)$ (cps)	Anion	Solvent ^a	$J(\text{TI}-\text{CH}_3)$ (cps)
BF_4^-	Pyridine	417	CN^-	Pyridine	410
	DMSO	444		Pyridine	423.5 ^b
	HMPA	464	OH^-	Pyridine	421 ^b
ClO_4^-	Deuterium oxide	413		Pyridine	422.0 ^b
	Pyridine	416	MnO_4^-	Pyridine	421.5 ^b
	Pyridine	415.5 ^b		Pyridine (20 %)	414
	DMSO	442	OC_6H_5^-	Methylene chloride (20 %)	370
	HMPA	475		Methylene chloride (saturated)	371
NO_3^-	Deuterium oxide	411	$[\text{CH}(\text{COC}_6\text{H}_5)_2]^-$	Methylene chloride (30 %)	394
	Pyridine	433		DMSO	451
	Pyridine	433.5 ^b		Pyridine	421
	Pyridine (33 %)	438	$[\text{CH}(\text{COCH}_3)_2]^-$	Methylene chloride (saturated)	393
	Pyridine saturated with LiNO_3	426			
	DMSO (30 %)	450			
I^-	DMF (30 %)	442			
	Pyridine	418			
	Pyridine	413.4 ^b			
SCN^-	DMSO	441			
	Pyridine	426			
	Pyridine	426.5 ^b			
	Pyridine saturated with NaSCN	428			

^a All concentrations are 10% by weight except as noted in parentheses after solvent. ^b Values from ref. 11; concentrations were 0.5 to 3.0%.

and τ for dimethylthallium perchlorate are reported in Table 2. The effect of solvent on $J(\text{TI}-\text{CH}_2-\text{CH}_3)$ and $J(\text{TI}-\text{CH}_2-\text{CH}_3)$ for dissolved diethylthallium perchlorate are reported in Table 3. The effect of the anion on the value of the coupling constant was studied and the results are tabulated in Table 4. The following abbreviations are employed in both the results and discussion sections: DMSO for dimethylsulfoxide; DMF for *N,N*-dimethylformamide; DMA for *N,N*-dimethylacetamide; HMPA for hexamethylphosphoramide; TMG for tetramethylguanidine; TMU for tetramethylurea.

DISCUSSION

A. Infrared indication of the structures of the dialkylthallium compounds

The infrared spectrum of dimethylthallium perchlorate was examined in the solvents acetonitrile, methanol, pyridine, DMSO, DMA, and HMPA (Table 1) and in all cases a strong absorption was observed near 550 cm^{-1} which was assigned to the C-Tl-C asymmetric stretching frequency. Strong lines appeared at 487 cm^{-1} and 486 cm^{-1} respectively in the Raman spectra of solutions of dimethylthallium per-

chlorate in pyridine and DMSO*, and these were assigned to the thallium-carbon symmetric stretch. This assignment is in reasonably good agreement with the Raman spectrum of dimethylthallium perchlorate and nitrate in aqueous solution where a strong line at 498 cm^{-1} was assigned to the thallium-carbon symmetric stretching mode². The infrared spectra of saturated dimethylthallium perchlorate solutions in acetonitrile, methanol, pyridine, DMSO, DMA, and HMPA were carefully examined. Only in pyridine could a weak band at 484 cm^{-1} be found which could be assigned to a symmetric carbon-thallium stretching frequency. In all instances the infrared spectrum in the perchlorate region indicated that this anion was not coordinated.

The absence of an observable symmetric stretching frequency in the infrared spectrum of dimethylthallium perchlorate dissolved in acetonitrile and the oxygen donor solvents which were studied indicates a linear structure for the dimethylthallium cation in those solvents. The symmetric stretching frequency is not allowed in the infrared spectrum for $D_{\infty h}$ symmetry (C-Tl-C ignoring the hydrogens) but this band should be Raman active. These predictions are in agreement with the experimental findings and provide strong support for a linear C-Tl-C arrangement in these solvents. Both the symmetric and asymmetric thallium-carbon stretching vibration should be observed for a bent carbon-thallium-carbon system. The infrared spectrum of a pyridine solution of dimethylthallium perchlorate differs from the infrared spectra of solutions of this salt in oxygen donor solvents by the strong shift of the asymmetric stretch toward lower frequency and the appearance of the symmetric stretch at 484 cm^{-1} . We attribute the difference in these structures to a stronger covalent interaction between thallium and pyridine than between thallium and those solvents in which the C-Tl-C system remained linear. In the interaction with pyridine, rehybridization of thallium occurs to provide orbitals that overlap effectively with pyridine. In the four coordinate complexes this results in a reduction in the *s* character of the thallium hybrid directed toward the methyl group, and a smaller C-Tl-C bond angle results.

Several adducts of the dimethylthallium cation were isolated. The infrared spectral assignments in the region of the thallium-carbon stretching frequency are given in Table 1. The infrared nujol mull spectra of the two β -diketone complexes and the dimeric phenoxide of $(\text{CH}_3)_2\text{Tl}^+$ show an asymmetric carbon-thallium stretch at 552 cm^{-1} and a symmetric stretch in the vicinity of 500 cm^{-1} . In both of the β -diketone complexes a strong band appears at 532 cm^{-1} in the infrared spectrum which is due to the complexed β -diketone system. An infrared spectrum of a benzene solution of (1,3-diphenyl-1,3-propanediono)dimethylthallium(III) contains the C-Tl-C asymmetric stretch at 540 cm^{-1} , the symmetric stretch at 483 cm^{-1} , and the β -diketone mode shifted to 515 cm^{-1} . In a benzene solution containing 10% DMSO by volume the band at 483 cm^{-1} disappears, indicating that DMSO is coordinating to thallium. If two DMSO molecules coordinate to thallium, the thallium atom would have four oxygen donors in the plane of the β -diketone ligand giving pseudotetragonal symmetry in which the intensity of the symmetric C-Tl-C vibration would be expected to be smaller because of the small dipole moment change during the vibration. In DMSO solution the infrared spectrum of (1,3-diphenyl-1,3-propanediono)dimethylthallium(III) shows an increase in the asymmetric stretching frequency and the absence of a

* The Raman spectra were kindly obtained for us by Professor R. C. TAYLOR, University of Michigan.

band assignable to the symmetric stretch. The infrared spectrum of a pyridine solution of the complex contains an asymmetric and a symmetric stretch at the same frequencies as the benzene solution within experimental error.

The spectrum of dimeric dimethylthallium methylmercaptide possessed symmetric and asymmetric stretching absorptions in the infrared that were of nearly equal intensity. The strong shift of both vibrational modes toward lower frequency relative to those in $(\text{CH}_3)_2\text{TlClO}_4$ is suggestive of a pronounced covalent interaction (*i.e.*, considerable charge transfer) between thallium and sulfur.

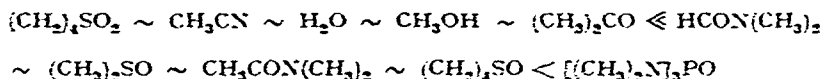
Attempts to isolate six-coordinate solvates of thallium were unsuccessful. The isolated products from solutions of dimethylthallium perchlorate appear to contain thallium with two methyl groups and two ligand donor atoms as nearest neighbors. However, thallium is reported to be six-coordinate in the crystalline dimethylthallium halides¹, and a complex of the isoelectronic and more highly charged $(\text{CH}_3)_2\text{Pb}^{2+}$ ion has been isolated containing four coordinated DMSO ligands in tetrakis(dimethylsulfoxide)dimethyllead(IV) perchlorate¹⁴. Inferences regarding the solvation number of $(\text{CH}_3)_2\text{Tl}^+$ in solution cannot be made from the stoichiometry of the crystalline solvates since crystal lattice effects can influence the stoichiometry and structure of the solid products isolated. It seems plausible, however, that in oxygen donor solvents $(\text{CH}_3)_2\text{Tl}^+$ remains nearly linear; and that in solvents such as pyridine and tetramethylguanidine the linear cation is somewhat distorted.

B. Thallium-proton spin-spin coupling

The $J(\text{Tl-H})$ and τ values from the PMR spectra of solutions of dimethylthallium perchlorate are reported in Tables 2 and 4 in a variety of solvents. The values for $J(\text{Tl-CH}_3)$ were found to be sensitive to the nature of the solvent, the concentration of dimethylthallium perchlorate, and the addition of sodium perchlorate to the solution (Table 2). These results can be interpreted in terms of the coordination model for non-aqueous solvent behavior^{15,16}. For example, the NMR results show that for solutions of the salts of dimethylthallium cation with several different anions and in the presence of excess anion the value for $J(\text{Tl-CH}_3)$ stays essentially constant for the solvents deuterium oxide and dimethylsulfoxide, but varies widely for less polar solvents such as pyridine (Tables 2 and 4). Anion coordination is less important for the solvating solvent, deuterium oxide, and the first coordination sphere of thallium will consist essentially of solvent molecules. In the poorer solvating solvents, such as acetone or pyridine, ion pairing is much more prevalent, and penetration of the first coordination sphere by the anion probably occurs, causing changes in the coupling constant when the anion is varied or the concentration changed. In view of the large concentrations employed in the NMR studies, it is difficult to draw anything but qualitative conclusions regarding the extent of anion dissociation.

The data in Table 2 are a composite from systems in which there is good evidence for a near linear C-Tl-C arrangement, those in which the system is known not to be linear and those which are uncertain because overlapping infrared bands or other physical limitations prevented structural assignments from the infrared. The NMR discussion will be restricted to those systems in which there is good evidence for the linear arrangement. The data (Table 2) show that the increase in $J(\text{Tl-CH}_3)$ over the series of solvents: methanol, deuterium oxide, sulfolane, acetonitrile, acetone, DMF, DMA, DMSO, and HMPA is greater than changes due to different concen-

trations of dimethylthallium perchlorate or the addition of excess anion. It is possible to divide these solvents into three groups with the following order of increasing $J(\text{Tl}-\text{CH}_3)$:



This increase in $J(\text{Tl}-\text{CH}_3)$ is in the same order as the increase in solvent donor strength. This latter property is indicated by the enthalpy results where available for the formation of adducts of these donors with iodine and phenol in the solvent CCl_4 (see ref. 16 for a summary). Therefore, the magnitude of $J(\text{Tl}-\text{CH}_3)$ may be regarded as an indication of increasing interaction between the solvent molecule and thallium. It is impossible to further subdivide the solvent order listed above for $J(\text{Tl}-\text{CH}_3)$ because minor effects, such as incomplete perchlorate dissociation in some solvent or minor contributions to J from terms other than the Fermi contact terms, may be operative. Consequently, only large differences in $J(\text{Tl}-\text{CH}_3)$ can be considered to be significant.

It is of interest to see whether various models can adequately explain the indicated effect of solvent on $J(\text{Tl}-\text{CH}_3)$. If the change in $J(\text{Tl}-\text{CH}_3)$ were caused by increasing covalency in the thallium-solvent bonds, it would be expected that solvents of increasing donor strength would cause redistribution of the $6s$ orbital from the axial carbon-thallium bonds to the equatorial solvent-thallium bonds. This should cause a decrease in the coupling constant, but $J(\text{Tl}-\text{CH}_3)$ increases with the increasing donor character of the solvent. Basic solvent molecules might decrease the effective electronegativity of thallium by an inductive effect and increase the carbon-thallium bond polarity; but this would also cause $J(\text{Tl}-\text{CH}_3)$ to decrease, contrary to the observed effect. A proposed explanation of the solvent dependence of $J(\text{Tl}-\text{CH}_3)$ in dimethylthallium perchlorate can be made in terms of a d - s mixing scheme. According to this proposal, a strong axial field such as that in dimethylthallium cation causes polarization of thallium and mixing of the filled $5d_{z^2}$ and the empty $6s$ orbitals resulting in two new hybrid orbitals, one in the xy plane and one directed along the z axis. This allows distribution of thallium electron density from d_{z^2} into the xy plane away from the methyl groups in the cation. The difference in the ligand field along the z axis and in the xy plane will govern the degree of d - s mixing and the thallium s character in the bonds to the carbons. The thallium p_z orbital is most probably involved in bonding the methyl groups but its role is of no direct consequence to the problem at hand. Increased field difference will give increased mixing, reduced s character in the $\text{Tl}-\text{C}$ bonds, and a lower $J(\text{Tl}-\text{CH}_3)$. The ligand field along the z axis can be considered to be approximately constant due to the presence of the "methide ligands", but in the xy plane it will depend on the nature of the solvent. With increasing strength of interaction between the solvent molecules and thallium the difference in field on the axis and in the plane will be reduced, mixing will be reduced, and the s character of the $\text{Tl}-\text{C}$ bonds will increase, thus increasing $J(\text{Tl}-\text{CH}_3)$ as observed.

If one wishes to describe the dimethylthallium cation as being bonded by essentially sp hybrids an equivalent result to that stated above is obtained. The electron density in the thallium-carbon bond (which shall be located on the z axis of our coordinate system) causes a splitting of the d orbitals raising the energy of d_{z^2} .

Using some of d_{zz} in the bonding of the free ion enables one to distribute inner shell electron density in the x - y direction by releasing some of the s orbital to accommodate inner shell electron density. Solvent interaction on the x and y axes decrease the extent to which this occurs and increases the s character in the thallium carbon bond*, causing an increase in $J(\text{Tl}-\text{CH}_3)$ as observed.

This model provides an interpretation of the changes in $J(\text{Tl}-\text{CH}_3)$ and implies that changes in the hybridization of the thallium bonding orbitals are responsible for changes in the Fermi contact contributions to $J(\text{Tl}-\text{CH}_3)$ which result in the observed changes in the coupling constants. It has been proposed by Klose¹² that there is significant direct interaction between a heavy metal and the α - and β -protons of a bonded ethyl group. The coupling constants between thallium and the methylene and the methyl protons in the diethylthallium cation have been shown to be of the opposite sign⁷. Recent experimental work shows that H-H spin coupling, in which the Fermi term should be dominant, alternates in sign when transmitted through an odd or an even number of bonds¹⁹. In $\text{Tl}(\text{C}_2\text{H}_5)_2^+$, the Fermi term transmitted through the thallium-carbon bond will be of the opposite sign from that due to direct thallium-proton interaction for the methylene protons and of the same sign for the methyl protons. The fact that $J(\text{Tl}-\text{CH}_2-\text{CH}_3)$ is greater than $J(\text{Tl}-\text{CH}_2-\text{CH}_3)$ can be explained by $J(\text{Tl}-\text{CH}_2-\text{CH}_3)$ being the difference of two large Fermi contact terms and $J(\text{Tl}-\text{CH}_2-\text{CH}_3)$ being the sum. Taking into consideration the usual attenuation of the contact term when transmitted through several bonds, it is necessary that the contact term for direct thallium-methylene proton interaction be relatively large compared to $J(\text{Tl}-\text{CH}_2-\text{CH}_3)$. A comparison of $J(\text{Tl}-\text{CH}_2-\text{CH}_3)$ vs. $J(\text{Tl}-\text{CH}_2-\text{CH}_3)$ indicates that the latter varies in an apparently random fashion within the narrow range of 635 ± 10 cps while the former varies with solvent donor order over a range of 60 cps. This suggests that the solvent effect changes are due predominantly to the Fermi contact term at the CH_2 position of $\text{Tl}(\text{CH}_2\text{CH}_3)_2^+$ and by analogy also at the CH_3 position of $\text{Tl}(\text{CH}_3)_2^+$. The interpretation of the changes in $J(\text{Tl}-\text{CH}_2-\text{CH}_3)$ and $J(\text{Tl}-\text{CH}_3)$ in terms of a Fermi contact term is given further support by a recent study of the thallium-proton spin-spin coupling constants for a whole series of organothallium compounds¹⁹. However, the random variation in $J(\text{Tl}-\text{CH}_2-\text{CH}_3)$ further emphasizes the point that other effects are operative and only large differences in donor strength can be distinguished by this technique on solutions as concentrated as those employed here.

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SUMMARY

The coordination chemistry of the dimethylthallium(III) cation in solution has been investigated by infrared, Raman and nuclear magnetic resonance spectroscopy.

* These kinds of arguments have been applied in other systems, e.g. see refs. 17 and 18.

Several solid compounds have also been isolated. In oxygen donor solvents, a linear C-Tl-C arrangement results, but in pyridine solution, a bent arrangement is found. The thallium-proton coupling constants for the linear complexes of dimethyl- and diethylthallium(III) are found to vary considerably with solvent. The results have been interpreted in terms of the way the donor strength of the solvent affects the mixing of the filled d_{z^2} and empty s orbitals of the thallium cations.

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