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Dimethylthallium(III) Complexes with S,N and S,O Ligands: The Molecular Structure of Me_2TlL (L = 1-Oxidopyridinium-2-thiolato)

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The reaction of heterocyclic thiolic derivatives HL^n with dimethylthallium(III) hydroxide yields Me_2TlL compounds. The structure of dimethyl(1-oxidopyridinium-2-thiolato)thallium(III), Me_2TlL^5, has been determined by X-ray analysis. Me_2TlL^5 crystals are monoclinic, space group $P2_1/c$, with $a = 9.812$ (3) Å, $b = 7.616$ (1) Å, $c = 12.851$ (3) Å, $\beta = 97.48$ (3) °, and $Z = 4$. The structure was refined to $R = 0.016$ for 929 unique data. In this compound the thallium atom is six-coordinate, if weak bridging interactions are considered, in lattices with polymeric chains. Spectroscopic data for the complexes (^1H, ^{13}C, and ^{205}Tl NMR, IR, and Raman) are discussed in order to determine possible structural/spectroscopic correlations.

Introduction

Although Me_2Tl^+ (dimethylthallium(III)) is one of the most stable organometallic species, its coordination chemistry is scarcely known.[1] Only a few compounds with monoanionic organic ligands have been studied by X-ray diffraction in the solid state, and coordination numbers (CN) between four and seven have been found with O, N, and S as donor atoms (ref 2 and references therein). Coordination number four is reached through bridging atoms for monodentate ligands while CN of up to seven are reached with bidentate ligands using bridging O and S atoms.

On the other hand, unlike in other methylated organometallic cations (e.g., Me_2Sn^{2+} (ref 3) or $MeHg^+$ (ref 4)),

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(2) Garcia-Tasende, M. S.; Suarez, M. I.; Sanchez, A.; Casas, J. S.; Sordo, J.; Castellano, E.; Mascarenhas, Y. P. *Inorg. Chem.* **1987**, *26*, 3818.

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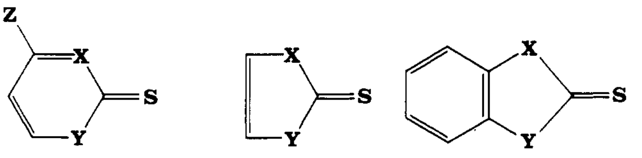
Table I. Analytical and Some Physical Data for the Dimethylthallium Complexes

compd	C^2	N	H	color	mp, °C	Λ,[b] Ω^{-1} cm^2 mol^{-1}
Me_2TlL^1	28.1 (28.0)		3.3 (3.2)	white	187	8
Me_2TlL^2	24.5 (24.4)	3.7 (4.1)	2.9 (2.9)	white	158	2
Me_2TlL^3	20.6 (20.8)	8.0 (8.1)	2.5 (2.6)	white	225	1
Me_2TlL^4	23.3 (23.4)	7.6 (7.8)	2.9 (3.1)	white	200	3
Me_2TlL^5	23.0 (23.3)	3.8 (3.9)	2.7 (2.8)	yellow	147	1
Me_2TlL^6	20.9 (20.7)	7.9 (8.1)	3.0 (3.2)	white	206	1
Me_2TlL^7	28.1 (28.2)	7.3 (7.3)	3.0 (2.9)	white	196	1
Me_2TlL^8	17.1 (17.0)	4.0 (4.0)	2.9 (2.8)	white	158	2
Me_2TlL^9	26.9 (26.9)	3.3 (3.5)	2.2 (2.5)	white	236	2
Me_2TlL^{10}	27.3 (28.1)	3.4 (3.6)	2.4 (2.6)	white	139	2

[a] Theoretical values in parentheses. [b] Molar conductivity for 10^{-3} M solutions in acetonitrile.

useful relations between spectroscopic parameters, measured in the solid state or in solution, and structural features have not been established. Only the vibrational data measured in compounds with oxygen- and sulfur-bonded ligands[5] seem to suggest some correlation between the nature of the atom bonded to thallium and the position of $\nu(TlC_2)$ and $\delta(CH_3)$.

As a part of a research program dedicated to the structural and spectroscopic study of the coodination chemistry of dimethylthallium(III), we describe in this work the synthesis and study of the compounds obtained by reactions of Me_2TlOH with HL^2–HL^{10} ligands.



HL^2: X = CH;
Y = NH; Z = H
HL^3: X = N;
Y = NH; Z = H
HL^4: X = N;
Y = NH; Z = CH_3
HL^5: X = CH;
Y = N-OH; Z = H

HL^6: X = N-Me;
Y = NH
HL^8: X = S;
Y = NH

HL^7: X = NH;
Y = NH
HL^9: X = S;
Y = NH
HL^{10}: X = O;
Y = NH

(The compound Me_2TlL^1, where HL^1 is thiophenol, was also prepared for comparative purposes.) These ligands, once deprotonated and bonded through the thiolic sulfur atom, have other donor atoms that can also coordinate to the metal. In some cases two different donor atoms are available. To our knowledge, only two thiolate derivatives of Me_2Tl^+ have been prepared (Me_2TlSMe (ref 6) and Me_2TlL^1 (ref 7)) before, and a dimer structure with bridging sulfur atoms was proposed for both. This proposal was confirmed for the thiophenol compound by X-ray diffraction in the solid state.[8]

Experimental Section

Chemicals. Thiophenol (HL^1), 2-mercaptopyridine (HL^2), 2-mercaptopyrimidine (HL^3), 2-mercapto-4-methylpyrimidine (HL^4), 4-mercaptopyridine *N*-oxide (HL^5), 2-mercapto-1-methylimidazole (HL^6), 2-mercaptobenzimidazole (HL^7), 2-mercaptothiazoline (HL^8), 2-mercaptobenzothiazole (HL^9), and 2-mercaptobenzoxazole (HL^{10}) were all commercial products and used as received. Dimethythallium iodide was obtained according to the method of Gilman and Jones.[9] Dimethylthallium hydroxide was prepared by stirring Me_2TlI with an excess of freshly precipitated silver oxide for 48 h in deionized water and removing the AgI by filtration.

Table II. Crystal and Refinement Data for Me_2TlL^5

formula	$C_7H_{10}NOSTl$
fw	360.61
cryst system	monoclinic
cryst size, mm	0.05 × 0.1 × 0.4
space group	$P2_1/c$
a, Å	9.812 (3)
b, Å	7.616 (1)
c, Å	12.851 (3)
α, deg	90
β, deg	97.48 (3)
γ, deg	90
V, Å^3	952.2 (6)
Z	4
D(calcd), g·cm^{-3}	2.52
μ, mm^{-1}	17.1
F(000)	656
2θ range, deg	48
h,k,l range	−10→10,0→8,0→14
reflctns measd	1396
obsd reflctns	929 ($I \geq 2.5\sigma(I)$)
R	0.016

Syntheses of the Complexes. A solution of the corresponding ligand in methanol (or ethanol for HL^{10}) was added dropwise to a stirred aqueous solution of Me_2TlOH. In all cases, except for HL^4 and HL^5, a white solid precipitated that was removed by filtration, washed with a mixture of methanol/water, and dried in vacuo. When HL^4 or HL^5 were used, it was necessary to eliminate the solvent to obtain a solid. These products were also dried in vacuo. Analytical and some physical data for the complexes are shown in Table I.

Physical Measurements. The elemental analyses were carried out on a Perkin-Elmer 240B microanalyzer. Conductometric and vibrational studies were done as has been described previously.[2] ^1H and ^{13}C NMR spectra were recorded on a Bruker WM250 spectrometer as DMSO-d_6 solutions. Due to broadening of the ^1H and ^{13}C signals of the methyl groups bonded to thallium in a high magnetic field,[3] the NMR spectra were also recorded on a Varian FT-80A apparatus. ^{205}Tl NMR spectra were recorded on a Bruker MSL90 NMR spectrometer at 27 °C, and the chemical shifts are given in parts per million toward high frequency of an infinitely dilute aqueous solution of $TlClO_4$.

X-ray Study of Me_2TlL^5. (a) Data Collection. Colorless crystals of the compound Me_2TlL^5 were grown by slow evaporation from a DMSO solution. A suitable single crystal was mounted on an Enraf-Nonius CAD-4 automated four-circle diffractometer. Cell parameters were determined by a least-squares refinement based on 25 reflections ($5 \leq \theta \leq 13°$).

Intensity data were collected on the diffractometer by the $\omega/2\theta$ scan technique, using graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å). The intensity of one check reflection recorded after every 100 measurements showed no significant variation. The intensities were corrected for Lorentz, polarization, and absorption effects.

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Table III. Fractional Atomic Coordinates (×10^4; Tl × 10^5) and Isotropic Thermal Parameters[a] for Me_2TlL^5

	x/a	y/b	z/c	B(eq), Å^2
Tl	-1192 (4)	-14934 (5)	36703 (3)	3.52 (2)
S	1709 (3)	-39 (3)	2305 (2)	4.03 (11)
O	1082 (6)	1379 (9)	4333 (5)	4.71 (31)
N	2386 (7)	1572 (10)	4152 (5)	3.46 (31)
C(2)	2848 (9)	945 (11)	3279 (7)	3.75 (43)
C(3)	4207 (9)	1258 (14)	3158 (8)	4.89 (50)
C(4)	5081 (11)	2163 (14)	3936 (10)	5.62 (56)
C(5)	4555 (10)	2748 (14)	4809 (9)	4.97 (53)
C(6)	3213 (9)	2481 (11)	4930 (7)	4.05 (44)
C(7)	-1937 (9)	-136 (12)	3001 (8)	4.76 (50)
C(8)	1433 (9)	-3100 (12)	4538 (7)	4.77 (50)

[a] Numbers in parentheses are esd's in the least significant digit. $B_{eq} = {}^8/_3\pi^2\sum_i\sum_j V_{ij}a_i{}^*a_j{}^*\vec{a}_i\cdot\vec{a}_j$.

Table IV. Bond Distances (Å) and Angles (deg) for Me_2TlL^5[a]

	Bond Distances		
S-Tl	2.889 (2)	C(6)-N	1.388 (10)
O-Tl	2.577 (6)	C(3)-C(2)	1.383 (12)
C(7)-Tl	2.143 (9)	C(4)-C(3)	1.410 (13)
C(8)-Tl	2.148 (8)	C(5)-C(4)	1.369 (15)
C(2)-S	1.736 (9)	C(6)-C(5)	1.360 (13)
N-O	1.338 (8)	S′-Tl	3.284 (6)
C(2)-N	1.351 (10)	O′-Tl	2.849 (13)
	Bond Angles		
O-Tl-S	65.3 (1)	C(6)-N-O	114.3 (7)
C(7)-Tl-S	97.0 (3)	C(6)-N-C(2)	123.1 (8)
C(7)-Tl-O	92.5 (3)	N-C(2)-S	119.8 (7)
C(8)-Tl-S	94.5 (3)	C(3)-C(2)-S	122.2 (7)
C(8)-Tl-O	92.8 (3)	C(3)-C(2)-N	117.7 (8)
C(8)-Tl-C(7)	168.5 (4)	C(4)-C(3)-C(2)	120.7 (10)
C(2)-S-Tl	96.9 (3)	C(5)-C(4)-C(3)	118.7 (10)
N-O-Tl	116.2 (5)	C(6)-C(5)-C(4)	121.2 (10)
C(2)-N-O	122.6 (7)	C(5)-C(6)-N	118.4 (9)

[a] Numbers in parentheses are esd's in the least significant digit. For numbering scheme, see Figure 1.

(b) Structure Solution and Refinement. The space group $P2_1/c$ was determined unequivocally from systematic absences. The structure was solved by direct methods using the MULTAN program.[10] The refinement was carried out by full-matrix least-squares methods (SHELX[11]).

The structure was refined anisotropically for all non-H atoms. Attempt for locate hydrogen atoms or refinement from computed positions gave unsuccessfull results. Data corresponding to the crystal and the refinement are given in Table II.

Calculations were performed on a Data General Eclipse MV-8000, Digital-Vax 785, and IBM-3082. The final atomic positions and equivalent thermal parameters are given in Table III. The scattering factors have been taken from ref 12. Table IV lists some significant bond distances and angles.

Results and Discussion

Crystal and Molecular Structure. Figure 1[13] shows the asymmetric unit of the Me_2TlL^5 structure with the numbering scheme. The ligand is bonded through the oxygen and sulfur atoms. The Tl-O, Tl-S, and Tl-C distances are similar to the values found in other dimethylthallium(III) complexes with anionic organic ligands (ref 2 and references therein). The C-Tl-C angle is also quite normal. The values for the N-O, C-S, and C(2)-N bond distances indicate a partial double-bond character,[14,15] suggesting that the formal negative charge of the sulfur atom is delocalized over these three bonds as was also found in $UO_2L^5{}_2$·DMSO.[15] The coordination of the thallium atom in the asymmetric unit is increased through bridging oxygen and sulfur atoms of vicinal units, as shown in Figure 2. The Tl···O and Tl···S bridging distances are quite large [2.849 (13) and 3.284 (6)Å, respectively] but smaller than the sum of the van der Waals radii.[16] On the other hand, these weak thallium-oxygen interactions are shorter than the weak interactions previously found in Me_2Tl(L)-PHE),[17] Me_2Tl(acac),[18] and $Me_2TlS_2COCH_3$.[19]

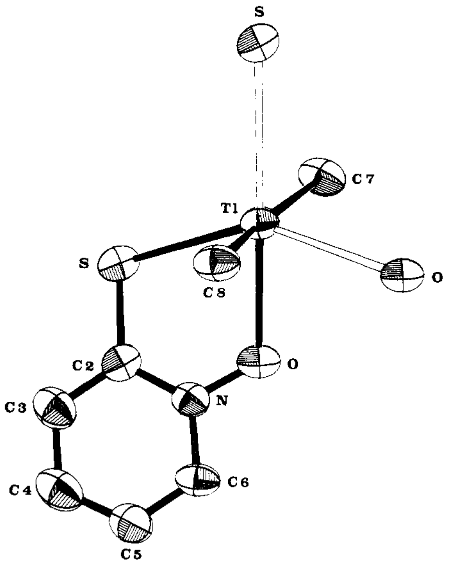

Figure 1. The environment of thallium atom in Me_2TlL^5 and numbering scheme of the compound.

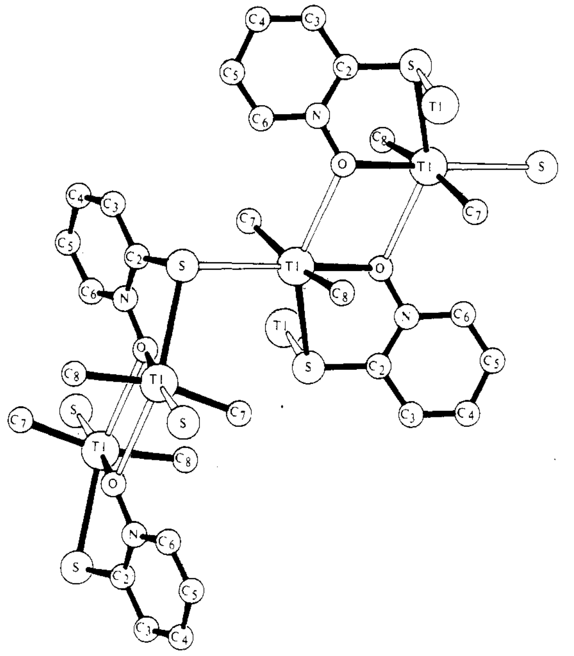

Figure 2. Polymerization of Me_2TlL^5 through Tl···O and Tl···S weak bonds.

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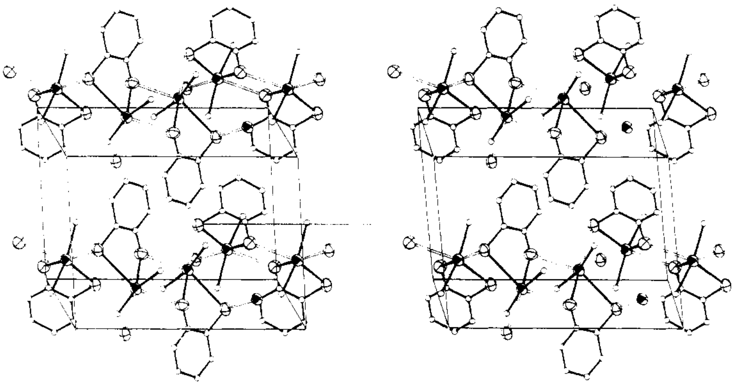

Figure 3. Stereoview of the packing arrangement of Me_2TlL^5 units within the unit cell.

The Tl···S distance falls within the range of the sulfur–thallium bridging distances found in dimethylthallium methylxanthogenate.[19] Due to these weak interactions the thallium atom has a very deformed octahedral environment with the two methyl groups in apical positions, a S atom and an O atom from a chelating ligand in equatorial positions, and a S atom and an O atom from another asymmetric unit at a greater distance. This configuration is similar to that described by Chow and Britton in $Me_2Tl(acac)$.[18] In fact, the S–Tl–O angle in Me_2TlL^5 is smaller than the O–Tl–O angle in the acetylacetonate compound owing to the smaller chelate "bite" of the thiolate ligand. The weak interactions polymerize the Me_2TlL^5 asymmetric units forming infinite chains along the *c* axis (Figure 3).

Vibrational Spectra. The use of IR and Raman spectra to determine the type of ligand coordination present is difficult since disagreement among different authors regarding the assignment of the free ligand bands (see, for example, ref 20) is further complicated by the fact that in some of the ligands coordination may produce a thione–thiol transformation that reduces the utility of these assignments. Therefore, the spectra of those complexes whose structures were not possible to determine by X-ray diffraction methods have been compared with those of other systems that have been studied by using this technique. For clarity we discuss first the 4000–600 cm^{-1} range for each ligand in which significant vibrations are expected; the 600–180 cm^{-1} range is then discussed for all the complexes jointly.

The IR and Raman spectra of Me_2TlL^1 failed to exhibit the bands assigned[21] to stretching and deformation modes of the SH group, which shows that deprotonation of this group has occurred. There are no significant changes in the ring stretching vibrations. In Me_2TlL^5 the ν(N–O) band (1199 cm^{-1}, IR; 1190 cm^{-1}, Raman) is shifted toward lower wavenumbers than in NaL^{22} (1219 cm^{-1}); the δ(N–O) and ν(C–S) bands are in positions close to those observed in other systems[22] in which the ligand is coordinated via its S and O atoms.

The ring stretching bands of Me_2TlL^2 are shifted toward higher wavenumbers than in L–L appearing close to those detected in $MeHgL^2$ (ref 23) and the C–H in-plane deformation and ring breathing modes are located at even higher wavenumbers than in this mercury compound; therefore, the coordination must be similar in both compounds. When the ligand is 2-mercaptopyrimidine (HL^3), the shifts exhibited by the ring stretching bands ν(C=S) and by the ring breathing and C–H deformation modes are very similar to those observed in 4-methyl-2-mercaptopyrimidine (HL^4), and the same kind of coordination is postulated for both complexes. We believe coordination takes place through the sulfur and nitrogen atoms in view of the similar position of these bands in $MeHgL^4$, in which the Hg–S and Hg···N bonds have been detected.[24]

Table V. ν(Tl–C$_2$) and ρ(CH$_3$) (cm^{-1}) for the Me$_2$TlL Complexes

	ν(C–Tl–C)			
	asym	sym	$\rho(CH_3)$	
Me_2TlL^1	532 s	480 m	785 m	IR
	535 w	480 s		Raman
Me_2TlL^2	530 vs	470 w	790 h	IR
	535 w	475 vs		Raman
Me_2TlL^3	540 m, 530 m	475 m	790 m	IR
		480 vs		Raman
Me_2TlL^4	530 s	480 m	785 s	IR
	530 w	485 vs		Raman
Me_2TlL^5	540 s	485 w	805 m	IR
	540 w	485 s		Raman
Me_2TlL^6	520 s	465 w	775 m, b	IR
Me_2TlL^7	525 s	470 m	790 m	IR
		475 vs		
Me_2TlL^8	530 s	475 m	790 m	IR
	540 w	480 s		Raman
Me_2TlL^9	540 m		790 m	IR
	540 w	480 s		Raman
Me_2TlL^{10}	550 m, 540 m		obscured	IR
		485 vs		Raman

In Me_2TlL^6 and Me_2TlL^7, the bands normally used[25,26] to identify the coordinated ligand atoms undergo very small shifts and are useless in obtaining any information.

In Me_2TlL^8 the ring stretching bands ν(C–S) are unchanged, showing that the endocyclic S atom is not involved in coordination. The other significant bands (at 1520, 1430, 1300, 1290, and 660 cm^{-1}) are puzzling since they appear to imply coordination via the N atom without showing the effects reported[25] for coordination via the S atom.

In Me_2TlL^9 the bands lie at positions close to those found in other systems with additional interactions to the

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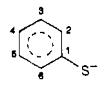
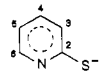
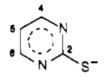
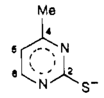
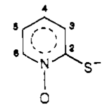
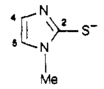
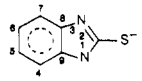
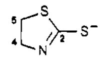
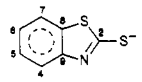
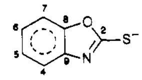
Table VI. NMR (^1H, ^{13}C, and ^{205}Tl)[a] Data for Me_2Tl Complexes (δ from TMS and J (Hz))

compd		^1H		^{13}C			other signals from the L	
		$\delta(CH_3)$	$^2J(Tl-H)$	$\delta(CH_3)$	$^1J(Tl-C)$	^{205}Tl	^1H	^{13}C
Me_2TlL^1		0.68	400.0	20.31	2895.0	3856.1	7.21 (H2, H6, d) 7.01 (H3, H5, t) 6.81 (H4, t)	133.5 (C2, C6) 127.3 (C3, C5) 121.8 (C4) 145.3 (C1)
Me_2TlL^2		0.86	417.0	22.59	3005.0	3690.8	7.0–6.8 (H5, H3, m) 7.3 (H4, t) 8.0 (H6, dd)	175.2 (C2) 129.7 (C3) 136.0 (C4) 116.4 (C5) 147.0 (C6)
Me_2TlL^3		0.92	417.4	23.07	3004.0	3596.3	8.2 (H4, H6, d) 6.8 (H5, t)	185.6 (C2) 156.3 (C4, C6) 114.4 (C5)
Me_5TlL^4		0.91	417.2	22.60	3003.0	3622.7	6.7 (H5, d) 8.1 (H6, d) 2.2 (CH_3, s)	165.5 (C2) 113.9 (C5) 156.1 (C6) 24.0 (CH_3)
Me_2TlL^5		0.80	419	22.70	2995.0	3741.1	6.8 (H5, td) 7.0 (H4, td) 7.5 (H3, dd) 8.1 (H6, dd)	163.9 (C2) 117.8 (C3) 132.5 (C4) 127.4 (C5) 140.4 (C6)
Me_2TlL^6		0.83	422.6	22.50	2983.2	3602.8	6.7 (H5) 6.6 (H4) 3.4 (CH_3)	156.7 (C2) 118.9 (C4) 123.1 (C5) 32.7 (CH_3)
Me_2TlL^7		0.93	424.3	23.66	2966.9	3592.6	7.2 (H4, H7, d) 6.9 (H5, H6, d)	165.4 (C2) 111.0 (C4, C7) 119.6 (C5, C6) 138.9 (C8, C9)
Me_2TlL^8		0.89	426.7	23.24	2965.6	3584.4	3.9 (H4, t) 3.2 (H5, t)	180.5 (C2) (?) 62.4 (C4) 35.1 (C5)
Me_2TlL^9		0.95	425.7	25.32	2948.7	3542.0	7.6 (H4, H7, m) 7.2 (H5, t) 7.1 (H6, t)	182.6 (C2) 119.8 (C4)[b] 125.0 (C5) 121.8 (C6) 117.7 (C7)[b] 135.5 (C8) 153.5 (C9)
Me_2TlL^{10}		0.97	435.3	25.21	2926.5	3508.7	7.24–7.19 (H4, H7, m) 7.06–6.92 (H5, H6, m)	179.5 (C2) 114.6 (C4) 122.5 (C5) 120.5 (C6) 107.6 (C7) 150.9 (C8)

[a] In ppm toward higher frequency from infinitely dilute aqueous solution of $TlClO_4$ (27 °C). [b] Can be reversed.

M–S bond[27] or with S,N-coordination;[28] as in the latter type of compounds, the free ligand bands at 1604 and 1505 cm^{-1} disappear. The positions of the ν_{asym} (C–O–C) and ν_{sym} (C–O–C) stretching bands in Me_2TlL^{10} show that the oxygen atom of the ring is not involved in coordination. The thioamide stretching bands I, II, and III lie close to those observed in complexes of the unprotonated ligand with S,N-coordination,[29] though the situation is not so clear in the case of the thioamide band IV.

The 600–180 cm^{-1} range show bands due to ν(C–Tl–C) (Table V). The location of metal–ligand stretching modes is occluded by the complexity of the ligand bands in this region. In this sense the simplest compounds are Me_2TlL^1 in which a weak band at 275 cm^{-1} (IR; Raman) has been assigned to ν(Tl–S), and Me_2TlL^5, in which bands at 410 cm^{-1} (IR; 405 cm^{-1} in the Raman) and 265 cm^{-1} (IR) have been assigned to ν(Tl–O) and ν(Tl–S), respectively.

The values of the $\nu(TlC_2)$ and $\rho(CH_3)$ modes found in the compounds prepared in this work and also those obtained by Walter et al.,[30] in derivatives of Me_2Tl^{III} with Tl–N bonds, were plotted together with the Kurosawa and Okawara data.[5] As figure 4 shows, some lineality is observed, except for the Me_2TlNEt_2 and $Me_2TlNMeEt$ compounds, but the point position in the plot seems to maintain any relation with the ligand donor atom identity.

NMR Spectra. Table VI lists the positions of the ^1H, ^{13}C, and ^{205}Tl NMR peaks. Our assignment of the coordinated ligand signals of Me_2TlL^5 agrees with that of Barnett et al.[31] As those of the Zn(II)[31] and n-Bu_3Sn^{IV}[32] compounds, these signals are clearly different from those

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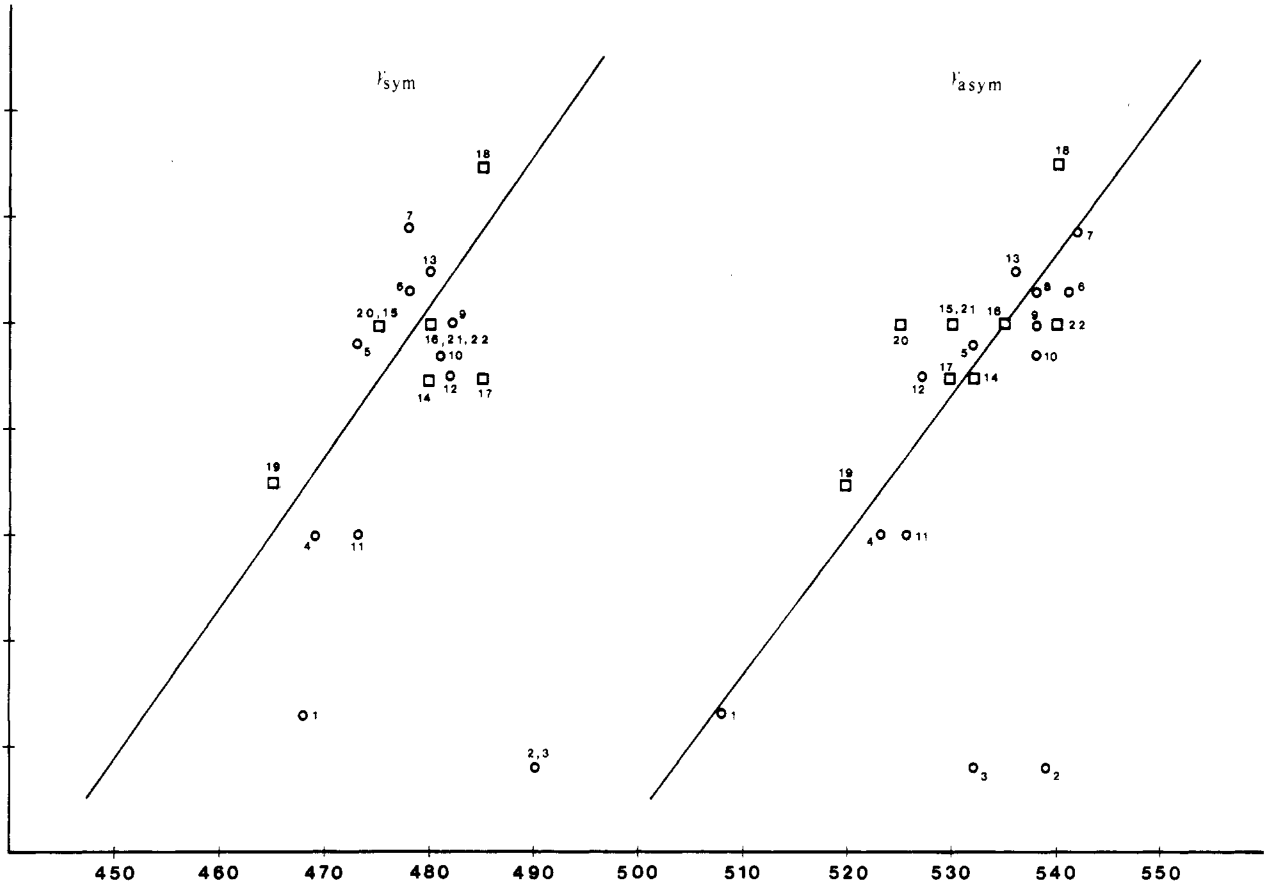

Figure 4. Plot of ν(C–Tl–C) versus $\rho(CH_3)$ for Me_2TlL: ○, L = NMe_2 (1), NEt_2 (2), NMeEt (3), SCH_3 (4), SC_6H_5 (5), OC_6H_5 (6), OC_6H_4Cl-*o* (7), OC_6H_4CHO-*o* (8), acac (9), ox (10), $C_5H_7N_2$ (11), $C_3H_3N_2$ (12), C_4H_4N (13) (values from ref 5 and 30); □, L = L^1 (14), L^2 (15), L^3 (16), L^4 (17), L^5 (18), L^6 (19), L^7 (20), L^8 (21), L^9 (22).

of $NaL^{5;31}$ the ^{13}C NMR spectra of the Tl, Zn, and Sn compounds exhibit shielding effects on the C(2) atom and deshielding effects on the C(3) and C(5) atoms compared with those of the sodium salt. This rules out the possibility of an ionic structure in DMSO-d_6 solution.

The interpretation of the spectra of the remaining complexes was done on the basis of the available data for the free ligands[33-39] and for the S-methylated derivatives.[40-44] The latter have structures close to the thiol form, whereas the free ligands are generally thiones. In their complexes with Me_2Tl^{III} the ligand region of the spectrum usually lies at a position intermediate between its location in HL and is L(S)Me. The great differences between the spectra of HL and L(S)Me affect the signals associated with C(2), whose strong shielding as the result of S-methylation has been attributed to the change from to N—C=S to N=C—S.[45] The same effect is observed in those complexes whose coordination involves solely the thiol group,[45] but if coordination takes place simultaneously via both the S and N atoms, the signal is shifted downfield.[45] Its position in the Me_2Tl complexes studied

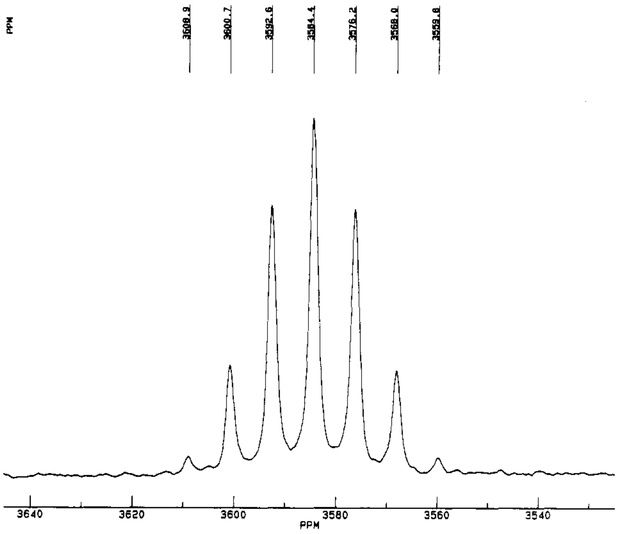

Figure 5. ^{205}Tl spectrum of Me_2TlL^8 in DMSO solution.

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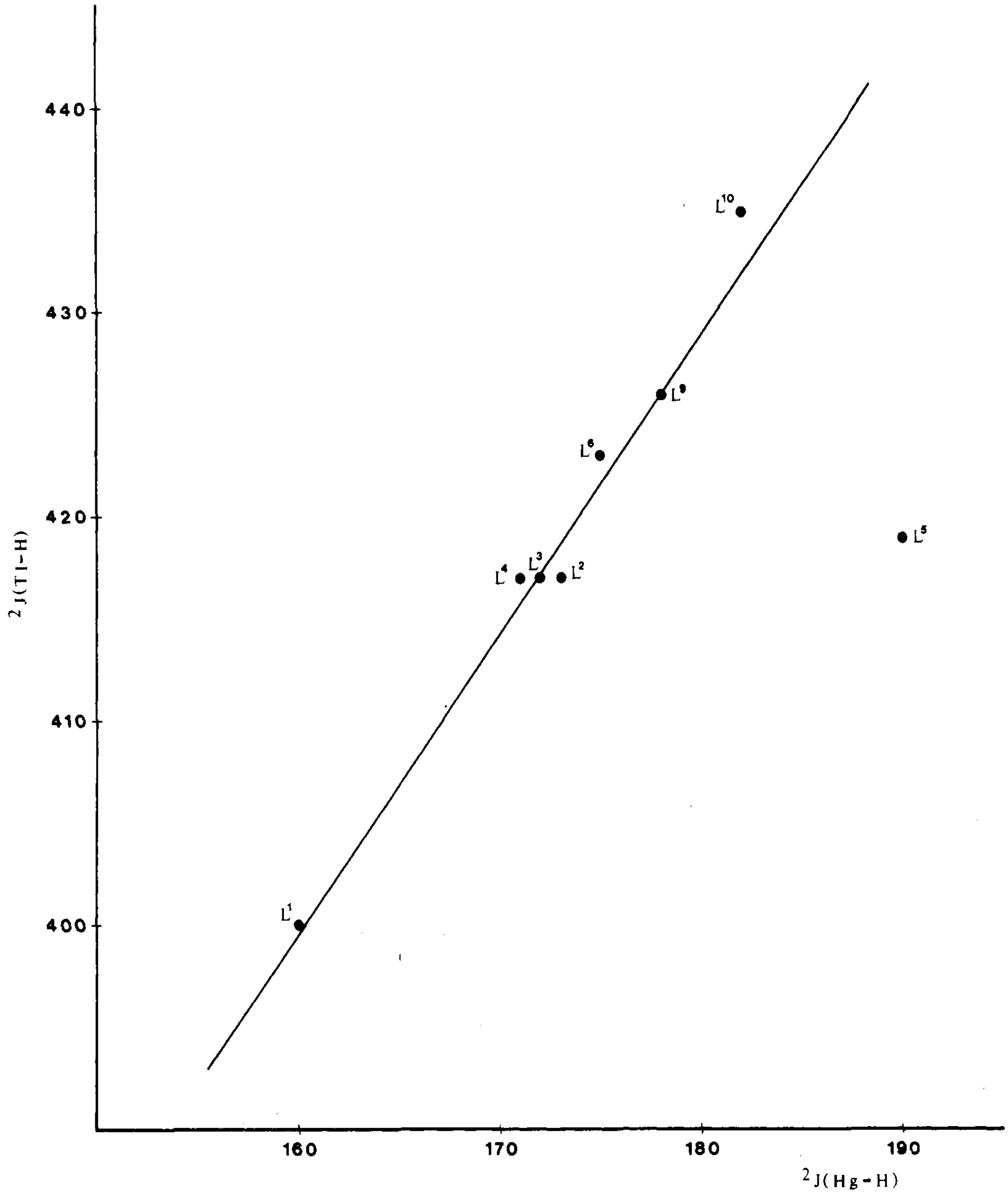

Figure 6. A plot of $^2J(^{205}\text{Tl–H})$ for Me_2TlL^n versus $^2J(^{199}\text{Hg–H})$ for $MeHgL^n$.

suggests that in all of them the nitrogen is involved in coordination.

The ^{1}H NMR spectrum of complex Me_2TlL^3 has only two signals, one integrates for two protons and the other for one. These signals have been attributed to the H(4) and H(6) atom and to the H(5) atoms, respectively (Table VI). In the ^{13}C NMR spectrum, the C(4) and C(6) atoms produce the same signal. This fact suggests that, unlike in the HL^3 complexes of Mo and W,[46] in the Me_2Tl compound the Tl–N bond is labile. The insolubility of the complex in low melting point solvents has impeded a low-temperature test.

The ^{205}Tl NMR spectra of the Tl complexes in DMSO exhibit the multiplicity and intensity ratios expected for monomers (see Figure 5 for Me_2TlL^8), and the absence of $^{205}\text{Tl} - {}^{205}\text{Tl}$ spin–spin coupling rules out a polymeric structure. The chemical shifts and ^2J(Tl–H) are of the same magnitude as those of other diorganothallium(III) compounds (e.g. ref 47). The difference of more than 300 ppm in the chemical shifts of the different complexes is difficult to interpret because of the lack of information concerning factors influencing this parameter in dimethylthallium(III)[48] but may be partially due to differences in the denticities of the ligands (see above).

The organometallic signals are of interest in view of the information that NMR spectra provide regarding the coordination of cations such as CH_3Hg^+, in which ^2J(H–Hg) dominated by the Fermi contact contribution has been related to the acidity constants of the ligands or the stability constants of the complexes.[4,49] Although the factors affecting ^1J(C–Tl) and ^2J(H–Tl) in organometallic Tl(III) compounds are not all the same,[48] it seems clear that these constants are also dominated by the Fermi contact contribution.[50] It is, therefore, relevant to see whether the

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Table VII. Coupling Constants ^2J(H-M) (Hz) for the Dimethylthallium and Methylmercury Complexes

compd	^2J(H-Tl)	^2J(H-Hg)	ref (MeHg$^+$ compds)
Me_2TlL^1	400	160	49
Me_2TlL^2	417	173	49
Me_2TlL^3	417	172	24
Me_2TlL^4	417	171	24
Me_2TlL^5	419	190	49
Me_2TlL^6	423	175	51
Me_2TlL^9	426	178	51
Me_2TlL^{10}	435	182	51

relationships observed in the case of methylmercury also hold for dimethylthallium(III). In order to answer this question, we have made use of the fact that most of the methylmercury(II) complexes of the ligands used in the present study have already been studied and the corresponding values of ^2J(H-Hg) determined.[49,51] In Figure 6 these values are plotted against the values of ^2J(H-Tl) for complexes of the same ligands with Me_2Tl^+ (Table VII). Least-squares analysis shows the correlation among these data to be poor ($r = 0.714$) if the totality of the points are taken into account but very good ($r = 0.9915$) if the data for the ligand HL^5 are omitted. Though the number of systems considered is small, it would be desirable to investigate a wider range of complexes of different structural ligands, Figure 6 suggests that ^2J(H-Tl) and ^2J(H-Hg) are affected in the same way by the same ligands. The exceptional case of Me_2TlL^5 may be due to the second bond being Tl-O in Me_2TlL^5, whereas it is Tl-N in the other complexes considered.

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Registry No. HL^1, 108-98-5; HL^2, 2637-34-5; HL^3, 1450-85-7; HL^4, 35071-17-1; HL^5, 33486-07-6; HL^6, 60-56-0; HL^7, 583-39-1; HL^8, 96-53-7; HL^9, 149-30-4; HL^{10}, 2382-96-9; Me_2TlL^1, 16834-15-4; Me_2TlL^2, 114928-71-1; Me_2TlL^3, 114944-20-6; Me_2TlL^4, 114928-72-2; Me_2TlL^5, 114928-73-3; Me_2TlL^6, 114928-74-4; Me_2TlL^7, 114928-75-5; Me_2TlL^8, 114928-76-6; Me_2TlL^9, 114928-77-7; Me_2TlL^{10}, 114928-78-8; Me_2TlOH, 53759-11-8; ^{205}Tl, 14280-49-0.

Supplementary Material Available: A table of thermal parameters (1 page); a listing of observed an calculated structure factors (4 pages). Ordering information is given on any current masthead page.

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Theoretical Investigation of the Platinum Ketene Complex $Pt(PR_3)_2(CH_2{=}C{=}O)$ and Carbene Complex $Pt(PR_3)_2(CH_2)(CO)$

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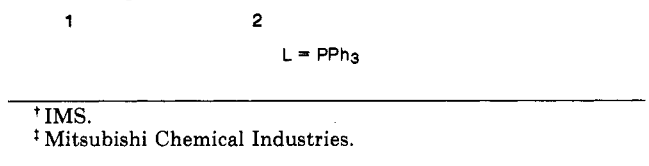
Received July 20, 1987

An ab initio MO study has been carried out on the structure and energetics of the platinum ketene complex $Pt(PR_3)_2(CH_2{=}C{=}O)$, the carbene carbonyl complex $Pt(PR_3)_2(CH_2)(CO)$, and the possible transition state connecting them, taking R = H as the model. The most stable ketene complex has been calculated to have the η^2(C-C) square-planar structure with the CH_2 group perpendicular to the molecular plane. Comparison between η^2(C-C) and η^2(C-O) coordination and between perpendicular CH_2 and in-plane CH_2 orientations has been made. The carbene carbonyl complex has been found to have a square-planar structure with its CH_2 group in the molecular plane, stabilized by the strong CH_2 π-Pt π interaction. The transition state connecting the ketene complex and the carbene carbonyl complex has a structure in which CH_2 is twisted halfway from the perpendicular to the in-plane conformation. The possibility of the existence of the carbene carbonyl intermediate in thermolysis of the ketene complex is discussed as well.

I. Introduction

Carbon-carbon bond formation and cleavage is one of the central objectives of modern catalytic chemistry. The reaction of transition-metal ketene complexes[1] is currently drawing considerable attention in this regard, as consisting of elementary steps[2] relevant to models for heterogeneous[3] and homogeneous carbon monoxide reduction.[4] Recently Miyashita et al.[5] have synthesized unsubstituted ketene complexes $M(PPh_3)_2(CH_2{=}C{=}O)$ (**1**, M = Ni, Pd, and Pt) and have reported thermolysis of these complexes that produced hydrocarbons such as C_2H_4 and C_3H_6. To explain this reaction, they proposed a carbene carbonyl intermediate, **2**. Although there exist several examples[1d,2,6]



[†] IMS.

[‡] Mitsubishi Chemical Industries.

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