Proton and Thallium-203 and -205 Nuclear Magnetic Resonance and INDOR Studies of Dimeric Dimethylthallium Derivatives

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Variable-temperature ^{203}Tl and ^{205}Tl n.m.r. spectra (with and without ^{1}H-decoupling) and ^{1}H-{^{205}Tl} INDOR spectra of dimeric dimethylthallium ethoxide provide evidence of chemical exchange. The ^{1}H and ^{1}H–{^{205}Tl} INDOR spectra of dimethylthallium dimethylamide have also been analysed in terms of superimposed spectra of homonuclear and heteronuclear species. The thallium–thallium coupling constant in both compounds has been determined. Thallium chemical shifts are also reported for related compounds.

MOLECULAR-WEIGHT determinations and ^{1}H n.m.r. studies[1] indicate that Me_2TlX ($X = NMe_2$, OEt, or SMe, *etc.*) are dimeric in solution with bridging X groups. On the other hand trimethylthallium is monomeric in solution, but exhibits intermolecular methyl-group exchange on an n.m.r. time scale.[2] There are two $I = \frac{1}{2}$ isotopes of thallium (^{203}Tl, natural abundance 30% and ^{205}Tl, 70%) with magnetogyric ratios differing by *ca.* 1%; thus the abundances of isotopic species in $(Me_2TlX)_2$ are: $^{205}Tl_2$, 49%; $^{203}Tl_2$, 9%; $^{203}Tl^{205}Tl$, 42%. The n.m.r. spectra consist of superimposed complex

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[1] A. G. Lee and G. M. Sheldrick, *Trans. Faraday Soc.*, 1971, **67**, 7.

[2] J. P. Maher and D. F. Evans, *J. Chem. Soc.*, 1963, **5543**.

spectra from the homonuclear molecules and first-order spectra from the heteronuclear molecules. These considerations have enabled a more complete analysis to be made of the ^1H spectrum of $(Me_2TlNMe_2)_2$. The ^{203}Tl and ^{205}Tl n.m.r. spectra of $(Me_2TlOEt)_2$ reported here throw some light on the puzzling temperature-dependence of the ^1H spectrum.[1]

EXPERIMENTAL

Dimethylthallium dimethylamide was prepared[3] from lithium dimethylamide and dimethylthallium iodide, and purified by sublimation *in vacuo*. Dimethylthallium ethoxide was prepared[1] *in situ* from trimethylthallium and ethanol and $[Tl(S_2C_2H_2)_2]^-$ and $Me_2TlSSCNEt_2$ were prepared by literature methods.[4,5] The spectra were recorded with a Varian XL-100-15 spectrometer operating at 100·101 MHz for ^1H and 57·92 MHz for ^{203}Tl and ^{205}Tl; a ^2H field/frequency lock was employed for the ^1H and $^1H-\{Tl\}$ spectra only.

RESULTS AND DISCUSSION

Dimethylthallium Dimethylamide.—The ^1H n.m.r. spectrum of Me_2TlNMe_2 in benzene has been reported[3] to consist of a doublet ($J = 342{\cdot}4$ Hz) arising from methyl groups bonded to thallium and a triplet ($J = 94{\cdot}0$ Hz) from the amide methyl groups coupling to two equivalent thallium nuclei, from which it was deduced that the compound is dimeric in solution. We find that although the compound is indeed dimeric, the observed spectrum and its analysis are more complicated than previously reported.

We consider first the homonuclear dimers, which can be classified as $X_6AY_{12}A'X'_6$, because the amide methyl group protons are magnetically equivalent if $J_{AY} = J_{A'Y}$ and $J_{XY} = J_{X'Y} = 0$, and because the two geometrically different $J_{XX'}$ are also zero. Harris[6] has derived analytical expressions for the X transition frequencies of an $X_nAA'X'_n$ system of spin-$\frac{1}{2}$ nuclei with $J_{XX'} = 0$ (the A spectrum has subsequently been obtained[7]); we shall show how this analysis can be extended to the present example assuming that $J_{XY} = J_{X'Y} = 0$, without making any assumption about the chemical-shift difference between X and Y.

The total spin-Hamiltonian matrix can be factorised into three submatrices because the A chemical shifts are very different from the X and Y shifts; these correspond to $F_z(A) = \sum_i I_z(A_i) = 1, 0, -1$, *i.e.* (i) AA′ spin state $|\alpha\alpha\rangle$, (ii) $|\alpha\beta\rangle$ and $|\alpha\beta\rangle$, (iii) $|\beta\beta\rangle$. Submatrices (i) and (iii) have no internal off-diagonal elements because couplings between magnetically equivalent nuclei can be ignored and because J_{XY} and $J_{XX'}$ are assumed to be zero. Therefore the differences between diagonal elements corresponding to $\Delta F_z(X \text{ or } X') = \pm 1$ give X transitions at frequencies $\nu_X \pm \frac{1}{2}N$, where $N = |J_{AX} + J_{AX'}|$. For $\Delta F_z(Y) = \pm 1$ we obtain the Y transitions at $\nu_Y \pm J_{AY}$. Half of the spectrum arising from each homonuclear species thus resides in these two doublets. Submatrix (ii) has off-diagonal elements of $\frac{1}{2}J_{AA'}$ which mix states identical except for an interchange of A and A′ spins. The coupling J_{AY} cannot appear in the matrix because it cancels with $J_{A'Y}$ for an AA′ state of $|\alpha\beta\rangle$ or $|\beta\alpha\rangle$. Thus (ii) can be factorised into a series of 2 × 2 submatrices. The X transitions appear as a set of 12 symmetrical doublets (of varying intensities) given by:

$$\nu = \nu_X \pm \tfrac{1}{2}[\chi^2L^2 + J^2{}_{AA'}]^{\frac{1}{2}} \pm \tfrac{1}{2}[(\chi - 1)^2L^2 + J^2{}_{AA'}]^{\frac{1}{2}} \quad (1)$$

where $L = |J_{AX} - J_{AX'}|$ and $\chi = 1, 2 \ldots 6$. The Y transitions all appear at ν_Y. Combining the transition in submatrices (i), (ii), and (iii), we obtain for the Y spectrum a 1 : 2 : 1 triplet with splitting J_{AY}. Half the X intensity resides in a doublet of splitting $|J_{AX} + J_{A'X}|$, the remainder in the lines given by equation (1). The two sets of spectra arising from homonuclear ^{205}Tl pairs and ^{203}Tl pairs overlap except for the outermost lines.

We now consider the spectrum arising from heteronuclear dimers, which can be classified as $X_6AY_{12}MX'_6$, with A = ^{203}Tl and M = ^{205}Tl. If we assume that $J_{XX'}$, J_{XY}, and $J_{X'Y}$ are all zero, and since there is a large frequency difference between resonances of different isotopes, the spin-Hamiltonian matrix becomes diagonal. Y Transitions occur at $\nu_Y \pm J_{YA}/2 \pm J_{YM}/2$, and X transitions at $\nu_X \pm J_{X'A}/2 \pm J_{X'M}/2$.

Summing the spectra of all the species present gives a 69-line spectrum for $(MeTlNMe_2)_2$. In practice many of these lines are not resolved, but overlap to give typical half-height linewidths of 4 Hz. Experimental verification of features of the theoretical spectrum was obtained by, (*a*) integration of peak intensities, which revealed that one half of the X intensity arising from the homonuclear species did not reside in the main X doublet; (*b*) observation of a number of the X transitions (Table 1)

TABLE 1

^1H N.m.r. parameters for $(Me_2TlNMe_2)_2$ in C_6D_6 solution

Doublet splittings (in Hz)

		Observed[a]	Calculated[b]
$\chi = 1$	Inner	100	99·6
	Outer	1172·5[c]	1172·0
$\chi = 2$	Inner	234	232·7
	Outer	1503·5	1504·3
$\chi = 3$	Inner	288	288·1
$\chi = 4$	Inner	312	311 2

Derived parameters (in Hz)

$L = |J(^{205}TlH) - J'(^{205}TlH)| = 341{\cdot}6$

$N = |J(^{205}TlH) + J'(^{205}TlH)| = 346{\cdot}0$

$|J(^{205}Tl^{205}Tl)| = 536{\cdot}2$

$J(^{205}TlH) = \mp 343{\cdot}8 \qquad J'(^{205}TlH) = \mp 2{\cdot}2$

$|J(^{205}TlH(\text{amide}))| = 94{\cdot}5$ (from amide methyl group triplet).

[a] Some doublets were too weak to observe, and in other cases only one of the two lines was observed, due to overlap with other peaks. [b] Equation (1). [c] The doublet arising from the ^{203}Tl species was observed to have a splitting of 1152·5 Hz (calculated 1151·2 Hz).

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[3] B. Walther and K. Thiede, *J. Organometallic Chem.*, 1971, **32**, C7.

[4] E. Hoyer, W. Dietzsch, H. Müller, A. Zschunke, and W. Schroth, *Inorg. Nuclear Chem. Letters*, 1967, **3**, 457.

[5] F. Bonati, S. Cenini, and R. Ugo, *J. Organometallic Chem.*, 1967, **9**, 395.

[6] R. K. Harris, *Canad. J. Chem.*, 1964, **42**, 2275.

[7] P. J. Mowthorpe and A. C. Chapman, *Spectrochim. Acta* (*A*), 1967, **23**, 451.

predicted by equation (1); (*c*) a homonuclear INDOR experiment, which revealed the presence of one of the more intense inner doublets otherwise partly obscured by other peaks; (*d*) high-power frequency decoupling of ^{205}Tl, which gave a broad central line and a doublet with a splitting of 341 Hz arising from the methyl groups bonded to ^{203}Tl.

Values for L and $|J_{AA'}|$ were obtained by fitting the first two outer doublets (of the $^{205}Tl_2$ species) to splittings given by equation (1); this gave satisfactory agreement for the other observed lines. The ' long-range ' coupling, $J'(^1H^{205}Tl) = 2{\cdot}2$ Hz, and the ' short-range ' coupling, $J(^1H^{205}Tl) = 343{\cdot}8$ Hz, were calculated such that summing the 12 overlapping peaks which form the main doublet, each weighted according to its intensity, yielded the observed splitting of 343·5 Hz. Since $N > L$, the two H–Tl couplings have the same sign. Only the magnitude of $J(^{205}Tl^{205}Tl)$ (= 536·2 Hz) was determined, since the thallium spectrum (Table 2) was too broad to permit the ' spin-tickling ' experiments recently described for this type of system.[8]

Dimethylthallium Ethoxide.—Lee and Sheldrick[1] observed the ^{1}H n.m.r. spectrum of dimethylthallium ethoxide in [$^2H_8$]toluene. The broad doublet (from Me_2Tl–) at room temperature ($J = 371$ Hz) began to coalesce in a symmetrical fashion on cooling. Below −10 °C the trend was reversed, and at −60 °C the peaks had sharpened to give a doublet with the original separation. A sharp triplet and quartet arising from the ethoxide groups were observed over the entire temperature range, with no evidence of coupling to thallium. The Me_2Tl doublet lines were broader for more dilute solutions, and the addition of Me_3Tl or Me_2TlI had no significant effect on the spectrum.

If the compound is dimeric and in the slow-exchange limit at low temperatures, the ^{205}Tl spectrum (Figure 1) should be a superposition of $^{205}Tl_2$ and $^{205}Tl^{203}Tl$ spectra with an integrated intensity ratio of *ca.* 7 : 3. This spectrum has not been analysed because of its complexity, but it is clearly not that of a monomer, which would consist of seven evenly spaced lines with a binomial distribution of intensities. The ^{203}Tl spectrum should be dominated by that of the heteronuclear species (since it is more abundant and is split into fewer lines); it was indeed observed to have the general appearance of a doublet [$|J(^{203}Tl^{205}Tl)|$ *ca.* 1200 Hz] of septets [$|J(^1H^{203}Tl)|$ *ca.* 370 Hz], as expected for a dimer. Further evidence for the presence of a dimer in the slow-exchange limit at low temperatures is provided by the ^{1}H high-power frequency-decoupled ^{205}Tl and ^{203}Tl spectra (Figures 2 and 3). The centre peak arises from the homonuclear species, and the doublet from the heteronuclear species with a splitting $|J(^{203}Tl^{205}Tl)| = 1200 \pm 20$ Hz. The spectra are consistent with the calculated intensity ratios of 3 : 14 : 3 for the ^{205}Tl spectrum and 7 : 6 : 7 for the ^{203}Tl spectrum.

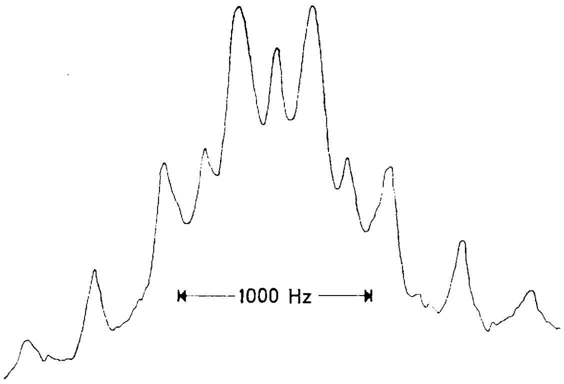

FIGURE 1 ^{205}Tl N.m.r. spectrum of $(Me_2TlOEt)_2$ in $C_6D_5CD_3$ at −70 °C

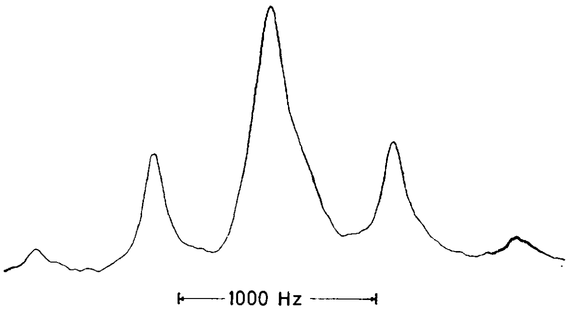

FIGURE 2 ^{205}Tl N.m.r. spectrum with high-power ^{1}H-decoupling of $(Me_2TlOEt)_2$ in $C_6D_5CD_3$ at −70 °C

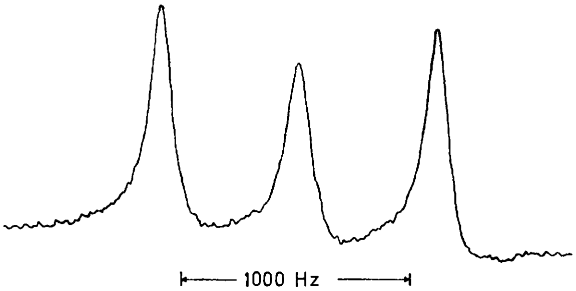

FIGURE 3 ^{203}Tl N.m.r. spectrum with high-power ^{1}H-decoupling of $(Me_2TlOEt)_2$ in $C_6D_5CD_3$ at −65 °C

At room temperature, the ^{1}H spectrum has a broad doublet with a splitting $|J_{TlH}| = 371$ Hz, and the $^1H\text{-}\{^{205}Tl\}$ INDOR spectrum is an equally spaced septet with the same splitting. These results are consistent with either a monomer, or a dimer approaching the fast-exchange limit. J_{TlH} and the ^{205}Tl chemical shift at room temperature for dimethylthallium ethoxide dissolved in both benzene and toluene are similar; moreover, they are similar to the parameters at low temperature in toluene (Table 2). In view of the sensitivity of these parameters to the co-ordination environment, this is strong evidence for a dimeric structure throughout the temperature range studied.

We now consider the interpretation of the ^{1}H spectrum of dimethylthallium ethoxide at −60 °C in the light of the thallium n.m.r. results and the analysis of the dimethylthallium dimethylamide spectrum. The broadness of the ^{1}H lines indicates that although we are

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[8] W. McFarlane and D. S. Rycroft, *J.C.S. Faraday II*, 1974, 377.

TABLE 2

^{205}Tl Chemical shifts

Compound	Solvent	t/°C	$\nu(^{205}Tl)/\nu(Me_4Si)$	Chemical shift from Me_2TlNO_3 in p.p.m
$(Me_2TlNMe_2)_2$ [a]	Benzene	37	0·5785215	+509
$(Me_2TlOEt)_2$ [b]	Benzene	37	0·5784181	+330
$(Me_2TlOEt)_2$ [b]	Toluene	37	0·5784143	+323
$(Me_2TlOEt)_2$ [b]	Toluene	−60		+353
$Me_2TlSSCNEt_2$ [b,c]	Chloroform	−50		+212
Me_2TlNO_3 [b]	D_2O	37		(0)
Me_2TlBr [d]	Liquid ammonia	−30	0·5788824	+1133
$[Et_4N][Tl(S_2C_2H_2)_2]$	Acetone	56		+559
Me_3Tl [d]	Acetone	−70	0·5794364	+2091
$(TlOEt)_4$	Benzene	37		+111

[a] The INDOR spectrum, obtained by monitoring the central peak of the triplet in the ^{1}H spectrum, was several thousands of Hz broad, and, at higher power levels of the thallium-irradiating frequency, exhibited indistinct multiplet structure extending over 25 kHz. Whether this is an instrumental artefact or due to coupling to the quadrupolar nitrogen is not known. [b] Measured as the centre of the lowest frequency set of (three) INDOR resonances. [c] The methyl doublet (J_{TlH} = 357 Hz) broadened at low temperature. [d] K. Hildenbrand and H. Dreeskamp, *Z. phys. Chem.*, 1970, **69**, 171.

approaching the ' slow-exchange ' limit, chemical exchange (or some other relaxation mechanism) must still be taken into account. We can describe the 42% of dimers which are heteronuclear by the notation $X_6AMX'_6$; the uncoupled ethoxide groups can be ignored in the discussion which follows. Since the two thallium isotopes have very similar magnetogyric ratios, $J_{AX} \simeq J_{XM'}$, and by analogy with the dimethylamide, $|J_{AX}| \gg |J_{MX}|$. Thus the heteronuclear dimers will give a broad ^{1}H doublet with a splitting equal to the mean $|J_{TlH}|$. The homonuclear dimers constitute a $X_6AA'X'_6$ system. Half of the X intensity resides in a doublet of separation $|J_{AX} + J_{AX'}|$; because of the line broadening the difference between $J(^{203}TlH)$ and $J(^{205}TlH)$ will not be resolved, and this doublet will merge with the heteronuclear doublet. The remaining intensity (29% of the total) will reside in 48 lines whose positions and intensities depend on J_{Tl-Tl} as well as J_{Tl-H}.

Thus the low-temperature (slow-exchange) ^{1}H limiting spectrum should consist of a strong doublet, splitting approximately $|^2J_{TlH}|$, and 48 weaker lines. The high-temperature (fast-exchange) limiting spectrum should consist of a simple doublet, separation $|^2J_{TlH}|$. Between these two extremes exchange of monomer units should cause all the low-temperature lines to broaden, coalesce, and eventually sharpen again as the high-temperature limit is reached. It is a general feature of systems undergoing exchange that the weaker lines (with low transition moments) are broader than the stronger in the intermediate temperature region. This qualitative picture accounts for the observed temperature dependence, and the fact that the 48 weak lines are not seen at −60 °C. It is doubtful whether the information content of the spectra justifies a full density matrix treatment.

Thallium chemical shifts are presented for several related compounds in Table 2; these illustrate the wide range of thallium chemical shifts, and their sensitivity to the co-ordination environment.

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