Electron Spin Resonance Studies of Electron Addition to Bis(cyclopentadienyl)titanium(IV) Dichloride and Cyclopentadienyltitanium(IV) Trichloride

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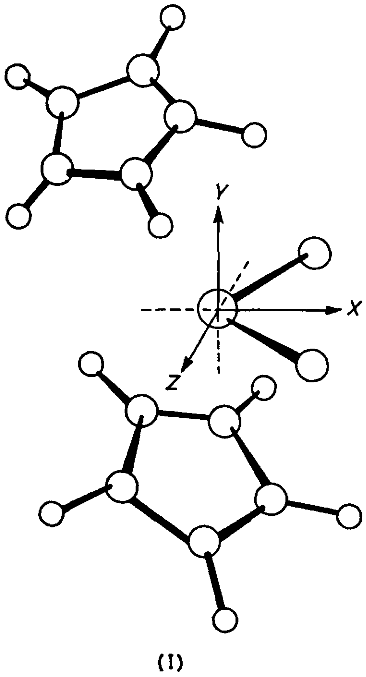
Exposure of [Ti(cp)$_2$Cl$_2$] (cp = cyclopentadienyl) in various media to ^{60}Co γ-rays at 77 K gives the corresponding titanium(III) complex, [Ti(cp)$_2$Cl$_2$]$^-$, characterised by its e.s.r. spectrum. On warming glassy solutions in methanol, this species changes irreversibly into a second titanium(III) complex, thought to be [Ti(cp)$_2$Cl]. This identification has been confirmed by comparison with the e.s.r. spectrum of authentic [Ti(cp)$_2$Cl] in methanol. The structures of these complexes are discussed with particular reference to [V(cp)$_2$Cl$_2$]. Similar treatment of [Ti(cp)Cl$_3$] gives the anion [Ti(cp)Cl$_3$]$^-$. The e.s.r. features for this complex suggest a major contribution from a $d_{x^2-y^2}{}^1$ configuration rather than a $d_{z^2}{}^1$ configuration as found for the previous complexes. Again, on annealing above 77 K, chloride ions are lost and the [Ti(cp)Cl$_2$] complex was detected. This was formed directly at 77 K in methanol glasses. A brief study of TiCl$_4$ in the pure state at 77 K suggested the formation of [TiCl$_4$]$^+$ ions, having an e.s.r. spectrum comparable with that for Cl$_2^-$, together with [TiCl$_4$]$^-$ ions, which have a distorted structure with the extra electron in a predominantly d_{z^2} orbital.

THERE has been much recent interest in the structures of M(cp)$_2$L$_2$ complexes (cp represents the cyclopentadienyl ligand and L$_2$ a variety of other ligands including halide), but it now seems well established that for the d^1 and d^2 complexes the ground state is largely $d_{z^2}{}^1$ or $d_{z^2}{}^2$ although, for the d^1 complexes, the form of the e.s.r. spectra suggests significant admixtures of $d_{x^2-y^2}$ orbitals.[1-3] The original suggestion of Ballhausen and Dahl[4,5] was that the z axis was the bisector of the L–M–L angle, but, following Alcock's suggestion,[6] there is now good evidence in favour of the alternative arrangement depicted in (I).[1,2] A major factor is that, since the L–M–L angle is much less than the tetrahedral angle, this will reduce the degree of antibonding for a $d_{z^2}{}^1$ structure based on (I), but would increase the antibonding interaction for the original postulate [$d_{x^2}{}^1$, based on (I)]. In a fully T_d structure d_{z^2} and $d_{x^2-y^2}$ are degenerate, and electron addition results in distortions which may favour predominant occupancy of either orbital. The e.s.r. results leave little doubt that d_{z^2} is favoured for M(cp)$_2$L$_2$ d^1 complexes. However, this is not clear from the results of Bakalik and Hayes,[7] for [V(cp)$_2$Cl$_2$] in single-crystal [Ti(cp)$_2$Cl$_2$]. When a ground state is predominantly $d_{z^2}{}^1$, g_z is usually close to the free-spin value of 2.0023. However, the principal values reported (1.946, 1.967, and 1.965) are too far removed from this value to conform with expectation, or indeed with g_z values reported for other M(cp)L$_2$ d^1 complexes. Their calculations suggest an almost equal admixture of the z^2 and $x^2 - y^2$ orbitals as a possible structure. However, we consider that this is unlikely since minor distortions and fluctuations would lead to a modulation in the extent of admixture and hence to broad lines except at very low temperatures: this was not observed.[7] Our own results for [Ti(cp)$_2$Cl$_2$]$^-$ discussed below, and those for the methylated derivative [V(C$_5$H$_4$Me)$_2$Cl$_2$] in single-crystal [Ti(C$_5$H$_4$Me)$_2$Cl$_2$],[2] both give g_z close to 2.0023. Thus the results of Bakalik and Hayes are anomalous, for reasons that we do not understand.



(I)

We have used ionizing radiation as a useful method for achieving electron addition at temperatures sufficiently low that primary addition products are obtained, even if these normally exhibit a strong tendency to undergo dissociation.[8] When pure materials are irradiated, electron-gain and electron-loss centres are usually formed in equal concentration, provided electron return is prevented. However, when solvents such as methyltetrahydrofuran (mthf) or methanol (usually CD$_3$OD) are used the major centre formed from the solute is the electron-gain centre, electron loss being predominantly from solvent molecules. Our aim was to form primary anions from [Ti(cp)$_2$Cl$_2$] and [Ti(cp)Cl$_3$] at 77 K and to probe their tendency to lose chloride ions at temperatures above 77 K.

This seemed to be particularly relevant in view of a current controversy relating to the reaction (1). Several

$$[\mathrm{Ti(cp)_2Cl_2}]^- \longrightarrow [\mathrm{Ti(cp)_2Cl}] + \mathrm{Cl}^- \qquad (1)$$

groups claim that this reaction is rapid at room temperature, so that cyclic voltammograms exhibit irreversible behaviour,[9] but El Murr *et al.*[10] maintain that the parent anions are relatively stable in solvents such as thf, the cyclic voltammograms showing complete reversibility. It also seemed of interest to compare results for the isoelectronic titanium and vanadium derivatives.

EXPERIMENTAL

The compounds $[\mathrm{Ti(cp)_2Cl_2}]$, $[\mathrm{Ti(cp)Cl_3}]$, and $\mathrm{TiCl_4}$ were of the highest grades available, and were used as supplied. Dilute solutions were prepared in degassed dried solvents in a dry-box, and samples were prepared for irradiation either in Supracil tubing or as small beads obtained by adding small droplets directly into liquid nitrogen.

Samples were irradiated in a Vickrad ^{60}Co γ-ray cell at 77 K for up to 2 h at a dose rate of *ca.* 1 Mrad $\mathrm{h^{-1}}$.*

E.s.r. spectra were recorded at 77 K using a Varian E109 spectrometer. Samples were annealed by decanting the liquid nitrogen from the insert Dewar and allowing the samples to warm slowly with constant monitoring of the spectra. Whenever significant changes were detected the samples were recooled to 77 K for careful study.

RESULTS AND DISCUSSION

$[\mathrm{Ti(cp)_2Cl_2}]$.—Good e.s.r. spectra were obtained from solutions in mthf, especially after the glasses had been warmed until the mthf radicals were destroyed (Figure 1). This spectrum was unchanged on warming to the glass point of the system. Our spectral analysis is indicated, the resulting g and hyperfine coupling parameters being listed in Table 1. (^{47}Ti is 7.75% abundant with $I = \frac{5}{2}$, and ^{49}Ti is 5.51% abundant, with $I = \frac{7}{2}$. In the present spectra, the six inner components of the ^{49}Ti octet exactly superimpose on the sextet from ^{47}Ti.) By analogy with $[\mathrm{V(cp)_2Cl_2}]$, the signs of all three components are expected to be the same. This leads to the $A_{\mathrm{iso.}}$ and $2B$ values given in Table 1, $2B$ being the major component of the traceless part of the hyperfine tensor components. The only reasonable alternative is that A_z is of opposite sign to A_x and A_y. This leads to $2B$ values (*ca.* 11 G) that are greater than expected since the $2B^0$ value for unit spin density is *ca.* 12.1 G.[11] Whilst this cannot be excluded, we prefer $2B$ values of *ca.* 8.2, corresponding to spin densities of *ca.* 68%. Note that the $3d$-orbital population for $[\mathrm{V(cp)_2Cl_2}]$ using the same approach is *ca.* 74%. (These are highly approximate values since they assume axial symmetry.) Furthermore, the $A_{\mathrm{iso.}}(^{47}\mathrm{Ti})$ coupling constant for a species which is probably $[\mathrm{Ti(cp)_2Cl_2}]^-$ (see below) is 13.14 G which agrees well with our value of 13.5 G, but not at all with the value of 10 G obtained if A_z is of opposite sign to A_x and A_y.

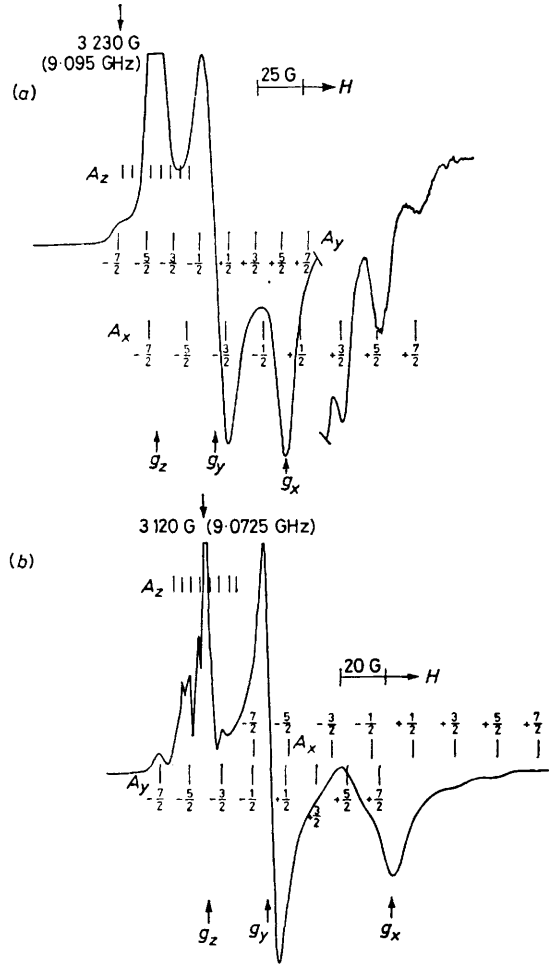


FIGURE 1 First-derivative X-band e.s.r. spectra for $[\mathrm{Ti(cp)_2Cl_2}]$ after exposure to ^{60}Co γ-rays at 77 K, (*a*) in methyltetrahydrofuran after slight annealing to remove features due to solvent radicals and (*b*) in $\mathrm{CD_3OD}$ also after annealing to remove features from solvent radicals

TABLE 1

E.s.r. parameters for radicals formed from $[\mathrm{Ti(cp)_2Cl_2}]$

	g values [a]				A values/G [b]				
Medium	x	y	z	*av.*	x	y	z	$A_{\mathrm{iso.}}$	$2B$
Pure	1.959	1.982	2.0017	1.981	(+) 21.0	(+) 14.3	(+) 5.3	(+) 13.5	(−) 8.2
mthf	1.959	1.982	2.0015	1.980	(+) 21.0	(+) 14.3	(+) 5.3	(+) 13.5	(−) 8.2
MeOH ($\mathrm{CD_3OD}$)	1.958	1.982	2.0015	1.980	(+) 21.0	(+) 14.3	(+) 5.3	(+) 13.5	(−) 8.2
MeOH [c]	1.950	1.984	2.001	1.978	(+) 18.0	(+) 14.0	(+) 4.0	(+) 12.0	(−) 8.0

[a] ±0.0004. [b] ±0.5 G. [c] After annealing. Almost identical with results for $[\mathrm{Ti(cp)_2Cl}]$ in MeOH at 77 and 273 K. This gave $g_{\mathrm{av.}} = 1.979$, $A_{\mathrm{iso.}} = 12.0$ G (ref. 13).

The form of the g-tensor components is comparable

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* Throughout this paper: 1 rad = 10^{-2} J kg^{-1}; 1 G = 10^{-4} T.

with those assigned to $[V(cp)_2Cl_2]$ for all workers except Bakalik and Hayes. The fact that g_z is close to 2.0023 fits with expectation for a predominantly d_{z^2} orbital,[11] in which case $2B$ must be negative. (Note that both ^{47}Ti and ^{49}Ti have negative magnetic moments.) Hence A_x, A_y, A_z, and $A_{iso.}$ are all positive. Values of *ca.* $+13.5$ are quite normal for titanium(III) complexes, so there can be very little admixture of the outer *s* orbital into the d_{z^2} function.

It is not clear from the e.s.r. data that the species is indeed $[Ti(cp)_2Cl_2]^-$ rather than $[Ti(cp)_2Cl]$. However, since the added electron is largely non-bonding with respect to the two chloride ligands (if this were not the case, we would expect to detect $^{35,37}Cl$ hyperfine coupling) there is no strong reason for reaction (1) to occur, and since mthf is a very poor anion-solvating medium, loss of Cl^- at 77 K is not to be expected.

This conclusion is reinforced by our results for solutions in $[^2H_4]$methanol. (These were prepared at *ca.* 213 K followed by freezing to 77 K, to prevent solvolysis.) The species formed at 77 K is clearly the same as that formed in mthf. However, on annealing the glass to *ca.* 120 K the spectrum underwent a well defined change, to that shown in Figure 1(*b*). The resulting data are not very different from those for the parent anion, but we feel that, in view of the gain and loss of two well defined species, the change is unlikely to be simply due to an increase in the outer-sphere solvation of $[Ti(cp)_2Cl_2]^-$ ions. We favour the postulate that reaction (1) has occurred. In previous work on systems capable of undergoing such dissociative electron capture we have often found that this only occurs in protic media, the driving force being clearly solvation of the leaving anion. That this can occur rapidly in glassy methanol is now well established.[12]

It is noteworthy that the *z* and *y* features are much narrower than the *x* feature for this species, in marked contrast with the results for mthf systems. Since a major source of linewidth must be unresolved hyperfine coupling to $^{35,37}Cl$ nuclei, this result accords well with loss of one chloride ligand. If the structure is $d_{z^2}{}^1$, as seems highly probable because of the marked similarity with the results for $[Ti(cp)_2Cl_2]^-$ anions, then the TiCl bond probably lies along *x*. This conclusion is based on the assumption that coupling occurs largely *via* spin polarization of the Ti–Cl σ electrons. This would lead to a maximum coupling along *x* and very small interactions along *y* and *z*.

Results for the pure compound in the absence of solvent were less satisfactory since the features were unusually broad. Nevertheless, a broad free-spin signal could be assigned to some organic radical formed by electron loss, together with $[Ti(cp)_2Cl_2]^-$ anions with *g* values equal to those listed in Table 1. This means that $[Ti(cp)_2Cl_2]^-$ anions in a $[Ti(cp)_2Cl_2]$ lattice have normal parameters, there being no marked changes induced by the crystalline host. This makes the results for $[V(cp)_2Cl_2]$ and $[Ti(cp)_2Cl_2]$ [7] even more remarkable, and it seems unlikely that the host lattice is responsible for the unexpected and drastic modification of the e.s.r. parameters.

The assignment of this spectrum to $[Ti(cp)_2Cl]$ complexes is strongly supported by the work of Myatt [13] on solutions prepared directly from dicyclopentadienyltitanium(III) monochloride. The isotropic spectrum, shown in Figure 2, gives $g_{av} = 1.978$ and $A(^{47,49}Ti) = 12.0$ G, in excellent agreement with the present results. Furthermore, *g* values obtained from frozen solutions in methanol were identical with those given in Table 1. It is of interest to note the very large linewidth variation obtained at −30 °C (Figure 2). This result is directly understandable in terms of the hyperfine parameters given in Table 1. It arises because the *x*, *y*, and *z* features for the $-\frac{7}{2}$, $-\frac{5}{2}$, and $-\frac{3}{2}$ features are quite close together, whereas the $+\frac{7}{2}$, $+\frac{5}{2}$, and $+\frac{3}{2}$ features are well separated [*cf.* Figure 1(*b*)].[11]

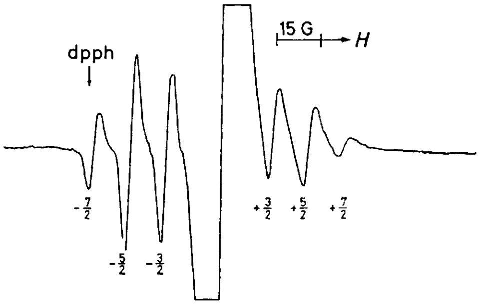


FIGURE 2 First-derivative *X*-band e.s.r. spectrum for $[Ti(cp)_2Cl]$ in methanol at −30 °C showing isotropic hyperfine features from coupling to ^{47}Ti and ^{49}Ti nuclei. The arrow indicates the position of the diphenylpicrylhydrazyl (dpph) signal

$[Ti(cp)Cl_3]$.—Irradiated solutions in mthf gave nearly axial spectra [Figure 3(*a*)]: absence of a third feature that might have been hidden under those due to mthf radicals was confirmed by studying the annealing system at high powers, such that the organic radical features were strongly saturated. This species changed

TABLE 2

E.s.r. parameters for radicals formed from $[Ti(cp)Cl_3]$

	g values				*A* values/G				
Medium	*x*	*y*	*z*	av.	*x*	*y*	*z*	iso.	$2B$
mthf [a]	*ca.* 1.962	*ca.* 1.962	1.945	1.956	*ca.* (+) 6	*ca.* (+) 5	(+) 24	*ca.* +12	*ca.* +12
mthf [b,c]	1.950	1.985	1.995	1.977	(+) 22	(+) 13	(+) *ca.* 4	(+) 13	(−) 9.0
CD_3OD [c]	1.944	1.983	1.995	1.974	(+) 22	(+) 14	≤5		

[a] At 77 K. [b] At 77 K after annealing. [c] Compare data for $[Ti(cp)Cl_2]$ formed by photolysis in thf: $g_{av.} = 1.976$, $A_{iso.} \approx 12$ G (ref. 14).

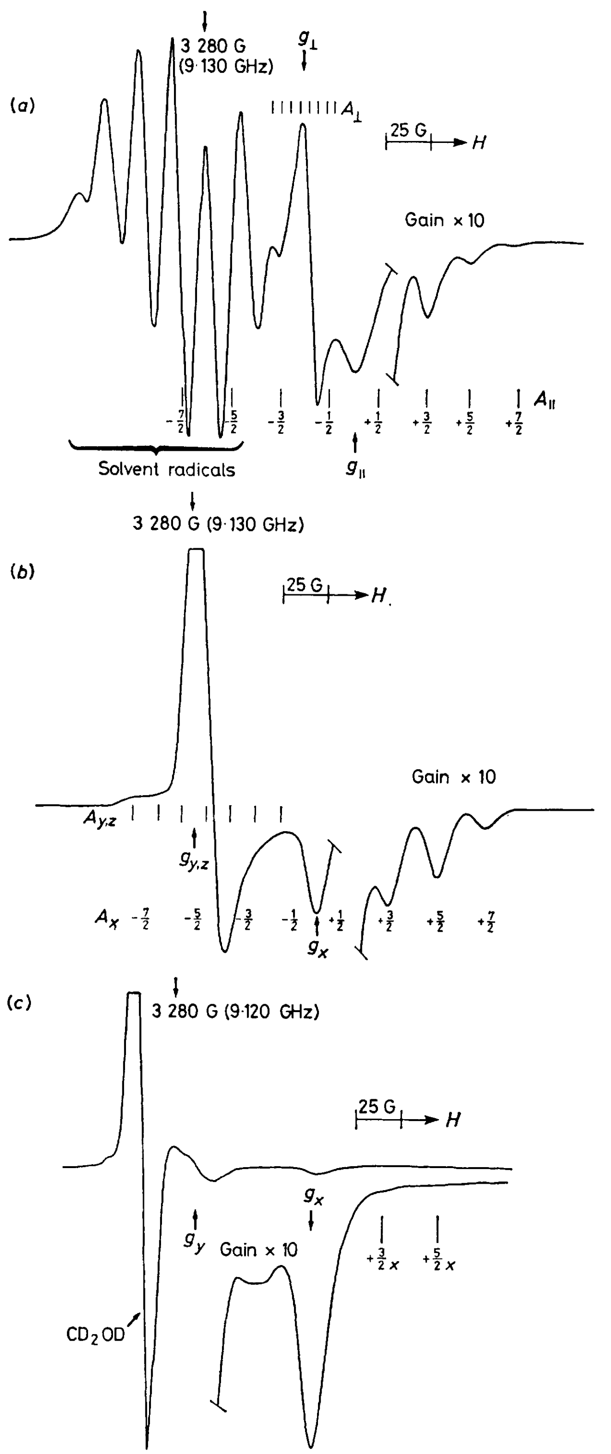
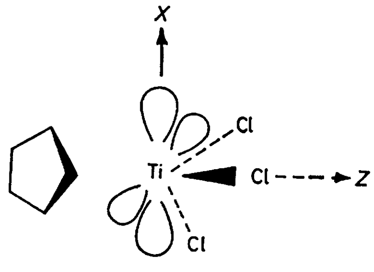


FIGURE 3 First-derivative X-band e.s.r. spectra for [Ti(cp)Cl$_3$] after exposure to ^{60}Co γ-rays at 77 K, (*a*) in methyltetrahydrofuran before annealing (the narrow low-field lines are due to solvent radicals), (*b*) as (*a*), after annealing to remove solvent radicals, and (*c*) in CD$_3$OD

irreversibly into a second titanium(III) centre, whose spectrum is shown in Figure 3(*b*). Results for these two species are given in Table 2. Solutions in [^{2}H$_4$]methanol, again prepared at low temperatures to minimize solvolysis, gave features for the second species only. This strongly suggests that the primary species in mthf is the parent anion, [Ti(cp)Cl$_3$]$^-$, the secondary species being [Ti(cp)Cl$_2$], formed by loss of Cl$^-$. As before, loss of Cl$^-$ is strongly promoted by methanol.

The structure of [Ti(cp)Cl$_3$]$^-$ clearly differs from that of [Ti(cp)$_2$Cl$_2$]$^-$, since the g tensor is nearly axial, and there are no g values close to 2.0023 (Table 2). We suggest that, in this case, a $d_{x^2-y^2}{}^1$ ground state is favoured, (II).



(II)

Coupling to the d_{xy} orbital is responsible for the large shift for $g_\parallel$ and coupling to the equivalent d_{xz} and d_{yz} levels gives rise to the shift for $g_\perp$. The hyperfine coupling is typical for a $d_{x^2-y^2}{}^1$ system. The $2B$ value of $+12$ corresponds to nearly unit spin density in the $d_{x^2-y^2}$ orbital: other sign combinations give even larger values. It is possible that our estimate of $A_\perp$ (+6 G) is in error since it is based only on the inflections shown in Figure 3(*a*). However, these were always present. The marked fall in the intensities of the parallel titanium components on going to high field shows that $A_\perp$ must be small. If our values are correct, it seems that ligand delocalization is much less for the $d_{x^2-y^2}{}^1$ than for the $d_{z^2}{}^1$ configuration.

Data assigned to the complex [Ti(cp)Cl$_2$] tie in quite well with values quoted for this complex, formed by photolysis in thf solution [14] (see Table 2). This link suggests that A_z has the same sign as A_x and A_y, as indicated in Table 2. If this is correct the orbital population is again quite low (*ca.* 74%). We therefore suggest that this complex has a $d_{z^2}{}^1$ configuration.

Results for pure [Ti(cp)Cl$_3$] were complex and, in our view, uninterpretable. Finally, we report a result for irradiated TiCl$_4$. No spectra assignable to a well defined titanium(III) complex were obtained from solutions in mthf, but in this instance, spectra for the pure compound after irradiation were quite well defined. At 77 K a highly complex spectrum was obtained which contained two sets of features. One set remained after annealing (Figure 4), whilst the other set resembled the spectrum for Cl$_2^-$. Only the parallel features for the latter were well defined. These gave $A_\parallel(^{35}\text{Cl}) = 73$ G, $A_\parallel(^{37}\text{Cl}) = 61$ G, and $g_\parallel = 2.002$. If, as we first supposed, these were due to Cl$_2^-$ anions the value of $A_\parallel$ is too small (normally *ca.* 100 G) unless the radicals are librating extensively. However, libration would cause the measured $g_\parallel$ value to increase from the free-spin value towards the isotropic value of *ca.* 2.03. Since this shift

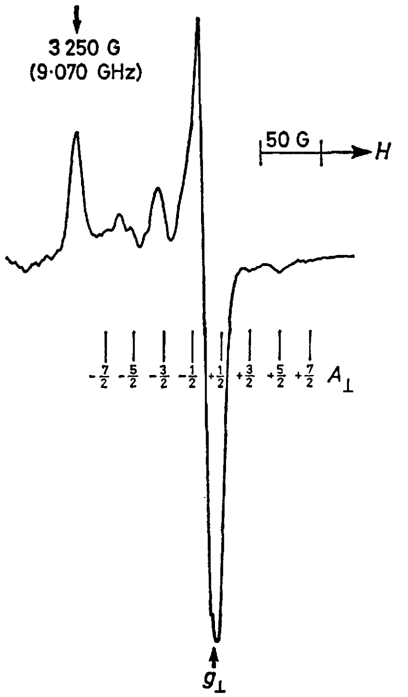


FIGURE 4 First-derivative X-band e.s.r. spectrum for $TiCl_4$ after exposure to ^{60}Co γ-rays at 77 K and annealing to *ca.* 100 K to remove features assigned to $[TiCl_4]^+$

has not occurred, we rule out Cl_2^-, and suggest instead that the species is $[TiCl_4]^+$, the ' hole ' being localized on two of the four ligands. In T_d symmetry the orbital concerned is t_1 and is spread over all four ligands. A distortion of some form must occur, and our results suggest that this is a bending motion that moves two ligands together, the unpaired electron being largely confined to these ligands.

The other species, also formed in poor yield in tetramethylsilane solution at 77 K, is surely the anion, $TiCl_4^-$. This must also distort, and could give either a $d_{z^2}^1$ or a $d_{x^2-y^2}^1$ ground state. The results, taken from Figure 4, show that the $d_{z^2}^1$ configuration is probably preferred. Thus, $g_{\parallel} = 2.000$ and $g_{\perp} = 1.934$, $A_{\parallel}$ is small, and $A_{\perp} = 22 \pm 1$ G.

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