# Studies on Cyclo-octatetraene Compounds of Titanium by Electron Spin Resonance and Electronic Absorption Spectroscopy

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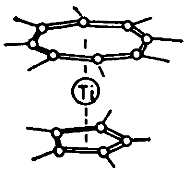
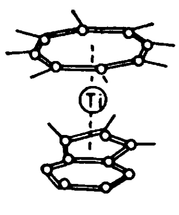
The compounds η-cyclopentadienyl- and η-indenyl-(η-cyclo-octatetraene)titanium have been studied by e.s.r. spectroscopy at room and low temperatures. Titanium hyperfine and proton superhyperfine coupling parameters are accurately determined. Electronic-absorption spectra in the u.v.–visible and near-i.r. regions have also been recorded, and a coherent molecular-orbital diagram for both compounds is proposed. These results show that the proton hyperfine-interaction constant of the unpaired electron with the $C_8H_8$ ring is almost twice that with the other (five-membered) ring, and that the charge borne by the metal atom is close to unity.

THE mixed sandwich compounds of titanium having the formula [Ti(cot)L] [cot = η-$C_8H_8$, L = cp = η-$C_5H_5$ (1) or η$^5$-$C_9H_7$ (2)] are among the very few early transition-metal compounds having an authentic sandwich structure. Their synthesis has already been described[1-3] and *X*-ray studies on (1) have shown[4] that the metal atom lies closer to the cot than to the cp ring plane (Ti–cot 1.414, Ti–cp 2.09 Å). Another interesting feature of these compounds is that they are paramagnetic, having a 17-electron configuration, so that their study by e.s.r. spectroscopy is of particular importance since it allows one to gain insight into the extent of electron delocalization on each of the π-bonded rings and consequently to speculate on the reactivity of the rings as potential sites towards aromatic substitution. E.s.r. studies have actually been undertaken[5,6] but they were rather fragmentary and incomplete. Thus, (*a*) the e.s.r. spectrum of (1) was[5] apparently not recorded on a pure sample, judging from the presence of an unassigned intense signal adjoining the main signal, and (*b*) the superhyperfine interaction in compound (2) was not resolved[6] either at room or liquid-nitrogen temperature. Also no hyperfine structure was identified either for (1) or for (2) and [(*c*)] the data on the principal *g* tensor values for compound (1) revealed a discrepancy.[6]



(1)



(2)

For these reasons we undertook a detailed reinvestigation of the e.s.r. spectra and present in this paper a full analysis of the spin-Hamiltonian parameters; these data, together with those deduced from electronic-absorption spectra of both compounds, are used to determine the magnitude of the charge distributions both on the metal and on each of the π-bonded rings.

## EXPERIMENTAL

The compounds described were prepared according to known procedures.[1-3] All manipulations were conducted under argon using rigorously dried solvents. E.s.r. spectra were recorded on a JEOL ME 3X *X*-band spectrometer equipped with a BNM-12 Bruker n.m.r. gaussmeter for field calibration and a tunable resonant cavity for microwave frequency measurements. Electronic-absorption spectra were recorded for toluene solutions on a Cary 14 spectrometer.

## RESULTS

*E.S.R. Spectra.—Compound* (1). The e.s.r. spectrum at room temperature in toluene [or tetrahydrofuran (thf)] exhibits a single wide band (20 G) centred at $g = 1.981$.† Cooling to $-30$ °C reveals both the isotropic hyperfine and the proton superhyperfine components (Figure 1). This is attributed to the slowing down of the reorientation frequency of the rings with respect to the magnetic field. Further cooling is accompanied by progressive sharpening of the lines until the freezing point is reached, and for temperatures $< -130$ °C the anisotropic spectrum of the frozen solution depicted in Figure 2 is obtained. This spectrum is characteristic of an $S = \frac{1}{2}$ ion in a ligand field of axial symmetry.[7]

*Compound* (2). In contrast to compound (1), the e.s.r. spectrum displays at room temperature both hyperfine and superhyperfine structures which are clearly resolved at $-80$ °C (Figure 1). In methyltetrahydrofuran or quickly frozen toluene solution at $-130$ °C an anisotropic spectrum very similar to the frozen solution spectrum of (1) is obtained. However, by slow cooling of the toluene solution to $-130$ °C a distorted spectrum is obtained, the line shape of which undergoes considerable changes with sample orientation with respect to the magnetic field, indicating the presence of orientated crystallites in the bulk. This spectrum was not suitable for the measurements of the parallel and perpendicular components of the *g* tensor because of the lack of a random distribution of molecular orientations.

*Solid state.* The powder spectra of pure (1) and (2) are different from the frozen solutions, although they are also characteristic of axially symmetric $d^1$ ions (Figure 3).

The fluid solution spectra of both compounds (1) and (2) at low temperature can be interpreted in terms of a $Ti^{3+}$

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† Throughout this paper: 1 G = $10^{-4}$ T; 1 eV ≈ $1.60 \times 10^{-19}$ J.

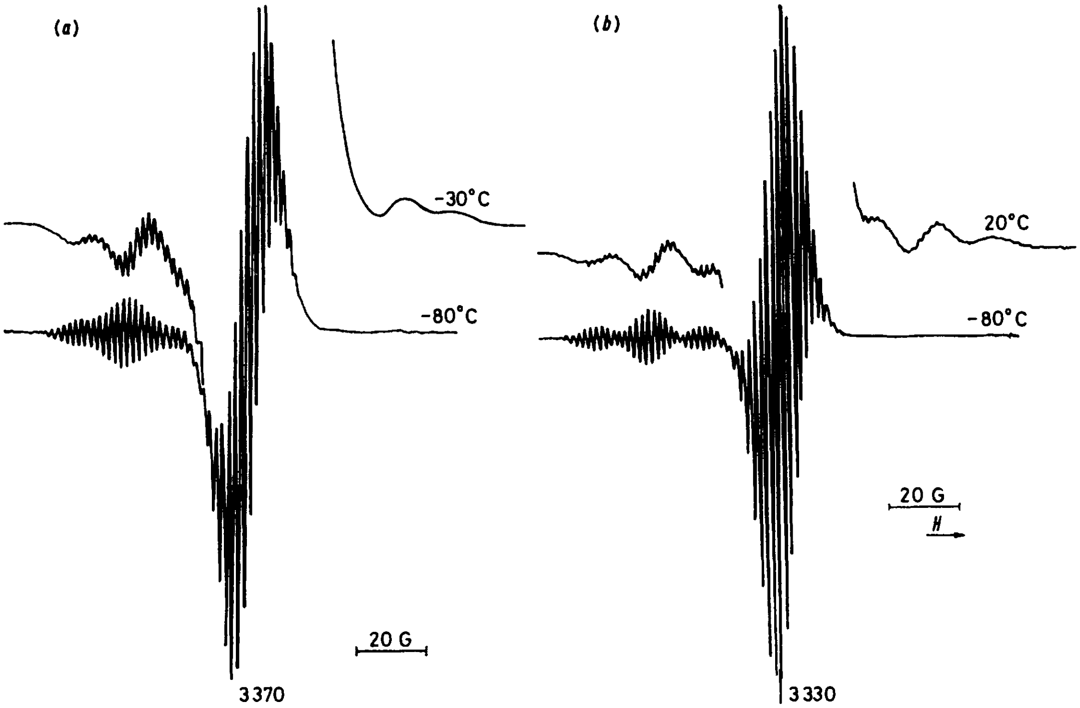

FIGURE 1 E.s.r. spectra in toluene ($10^{-3}$ mol dm$^{-3}$) of (*a*) compound (1) and (*b*) compound (2). Modulation 0.2, power 4 mW

($d^1$) ion exhibiting an intense central line ($I = 0$) flanked by satellites due to interaction of the unpaired electron with $^{47}$Ti ($I = \frac{5}{2}$, natural abundance 7.75%) and $^{49}$Ti ($I = \frac{7}{2}$, natural abundance 5.51%) isotopes of nearly equivalent $\mu_N/I$ ratio.[7] The central and satellite lines are further split because of superhyperfine interaction with π-bonded ring protons; this splitting is clearly revealed at moderately low temperatures because of the slowing down of the ring motion. The remarkable appearance of a partially resolved structure in compound (2) and the complete absence of resolution in the spectrum of (1) at room temperature is obviously attributable to the slower molecular tumbling of the indenyl fragment compared to cyclopentadienyl. In both compounds a high-field line-broadening effect is clearly observed and is believed to arise from modulation of the $g$ and $A$ hyperfine tensors due to molecular tumbling; this effect has been widely studied in copper and vanadium compounds.[8] We note that the sharp resonance at $g = 2$ observed by Thomas and Hayes [5] for the cyclopentadienyl compound was completely absent in all the preparations we examined.

*Isotropic Hyperfine Constants.*—In the light of the above observations, the assignments of the Ti hyperfine isotropic constants is straightforward (Table 1). The problem of the superfine proton-interaction constants, however, is not as easy to resolve due to the presence of two non-equivalent π-bonded rings, and therefore two different superhyperfine constants are expected. In order to determine them accurately, a computer simulation for compound (1) was undertaken on the basis of the parameters postulated by Thomas and Hayes,[5] namely $a_{\text{cp}} = 3.24$ G and $a_{\text{cot}} = 1.62$ G, which yielded a calculated spectrum in complete disagreement with the experimental one. In contrast, an exact replica of the experimental spectrum was obtained with the values $a_{\text{cp}} = 1.62$ and $a_{\text{cot}} = 3.24$ G. Simulation of the spectrum of the indenyl compound was also performed (Figure 4) and found to give slightly different superhyperfine constants (Table 1). The spectrum of the frozen solution of compound (1) (Figure 2) in toluene or Me-thf reveals the anisotropies of both the $g$ and $A$ tensors, and the $g_{\parallel}$ and $g_{\perp}$ values obtained (Table 1) are very close to those

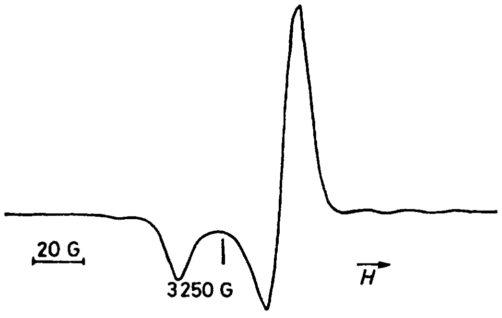

FIGURE 2 E.s.r. spectrum at −130 °C of (1) in toluene

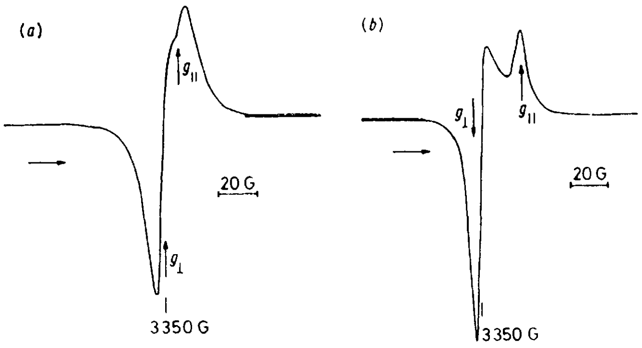

FIGURE 3 E.s.r. powder spectra of (*a*) compound (2) and (*b*) compound (1)

TABLE 1

E.s.r. parameters

| Compound | $g_{av.}$ | $g_{\parallel}$ | $g_{\perp}$ | $\langle A \rangle$ | $A_{\parallel}$ [a] | $A_{\parallel}$ | $a_H$ (ligands) |
|---|---|---|---|---|---|---|---|
| [Ti(cot)($\eta$-$C_5H_5$)] solution [b] | 1.981 3 | 2.000 8 | 1.972 3 | 14.6 | 3.4 | 20.2 | $a_H$(cp) 1.62 |
| powder | 1.981 | 1.972 2 | 1.985 4 | | | | |
| [Ti(cot)($\eta^5$-$C_9H_7$)] solution [b] | 1.980 4 | 1.999 | 1.971 | 15.5 | 6.5 | 20.0 | $a_H$($C_9H_7$) 1.64<br>$a_H$(cot) 3.15 |
| powder | 1.980 | 1.974 | 1.983 | | | | |

Hyperfine constants are given in G; $A$ values are relative to $^{47,49}$Ti. [a] Calculated. [b] In toluene, $10^{-3}$ mol dm$^{-3}$.

previously reported.[5] Compound (2) yields similar $g$ values and for both compounds $g_{\parallel}$ is close to the free-electron value, which indicates a $d_{z^2}$ ground state.[9] The discrepancy between these values for (1) and those reported [6] ($g_{\parallel}$ 1.974, $g_{\perp}$ 1.988) is most probably due to the crystalline-like behaviour of the frozen solution obtained when cooling to liquid-nitrogen temperature (see above).

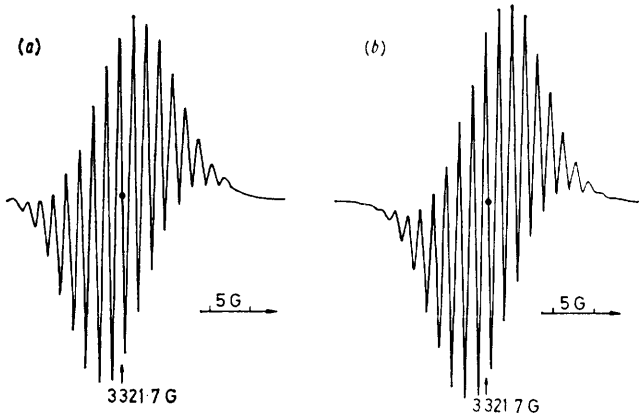

FIGURE 4 E.s.r. spectrum of the central line ($I = 0$) of compound (2): (a) measured, (b) simulated

The spectrum of the frozen solution also reveals perpendicular components of the hyperfine structure, thus allowing direct determination of the $A_{\perp}$ values, and from which $A_{\parallel}$ can be calculated using the relationship $\langle A \rangle = 1/3\,(A_{\parallel} + 2A_{\perp})$. However, the respective relative signs of $A$ can be determined from the trend in band broadening of the high-field hyperfine lines. The condition for this broadening is known to be:[10] $\langle A \rangle(\langle A \rangle - A_{\perp}) \times (g_{\parallel} - g_{\perp}) < 0$. With the experimental $g$ values, this condition can only be fulfilled if $\langle A \rangle$ and $A_{\perp}$ are of the same sign. Using the experimental values of $A_{\parallel}$ and $A_{\perp}$, one obtains the absolute value of $A_{\parallel}$ and it follows that $\langle A \rangle$, $A_{\parallel}$, and $A_{\perp}$ are all of the same sign. Finally, careful recording of the low-field hyperfine satellites at −130 °C for (1) at high gain revealed the perpendicular superhyperfine structure with a line separation of 1.55 G, a value very close to the 1.62 G found for the fluid solution.

The powder spectra of both (1) and (2) show unusual behaviour in that the $g$-tensor parameters are the reverse of those found in the rigid glass, so that $g_{\parallel} < g_{\perp}$; this is due presumably to metal–metal interactions. In fact, measurement of the nearest-neighbour Ti–Ti distance from $X$-ray data for compound (1) indicates a value of 6.6 Å, which shows that the two metal centres are reasonably close to allow of magnetic interaction,[11, 12] thus leading to a shift in the observed $g$ values.

*Absorption Spectra and Assignments.*—Absorption spectra of compounds (1) and (2) are shown in Figure 5 and Table 2. Absorptions at 13 980 and 11 360 cm$^{-1}$ are observed for compound (1) and at 14 250, 12 050, and 10 150 cm$^{-1}$ for (2). The e.s.r. parameters provide a basis for the assignments of these bands since it was found from $g_{\parallel}$ values for both (1) and (2) that the ground state is $d_{z^2}$ of essentially metallic character. It can be assumed, therefore, that the transition common to both compounds (13 980 and 14 250 cm$^{-1}$) involves the ground-state $d_{z^2}$ level and the metal + cot level since the latter contains a contribution from the ligand cot common to both compounds. To the second band at 11 360 cm$^{-1}$ of (1) corresponds two bands at 12 050 and 10 150 cm$^{-1}$ of (2). We assign these bands to transitions between the ground level and a level involving metal + cp in (1) and metal + indenyl in (2), the splitting in (2) being due to lowering of symmetry due to the indenyl ligand.

TABLE 2

Electronic-absorption bands (cm$^{-1}$) and assignments

| Compound | Absorption | Assignment |
|---|---|---|
| [Ti(cot)($\eta$-$C_5H_5$)] | 13 980 | $A_1 \leftarrow {}^1E_2$ |
| | 11 360 | ${}^3E_1 \leftarrow A_1$ |
| [Ti(cot)($\eta^5$-$C_9H_7$)] | 21 700 | $A_1 \leftarrow {}^2E_1$ |
| | 23 260 | $A_1 \leftarrow {}^2E_1$ |
| | 14 250 | $A_1 \leftarrow {}^1E_2$ |
| | 10 150<br>12 050 | ${}^3E_1 \leftarrow A_1$ |

Two molecular-orbital diagrams have been proposed in the literature for [Ti(cot)(cp)], one based on photoelectron spectroscopic measurements [1] and the other on INDO–SCF–MO calculations by Warren and his co-workers.[13]

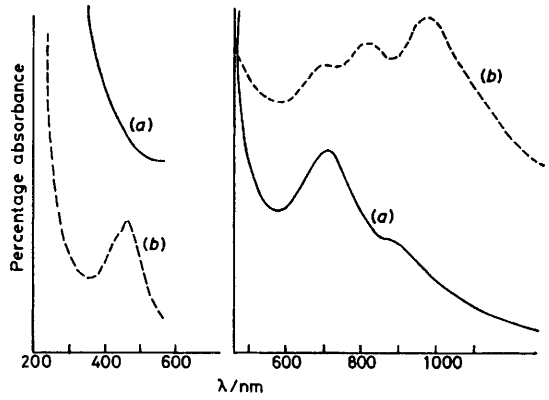

FIGURE 5 Electronic-absorption spectra in toluene ($10^{-3}$ mol dm$^{-3}$) of (a) compound (1) and (b) compound (2)

Both diagrams agree on a $d_{z^2}$ ground state, but differ on the energy level of the first excited state which is postulated to be $e_1$ (metal + cp) in the first case and $e_2$ (metal + cot) in the second (Figure 6). On the basis of the above experimental evidence, we find the second (Warren's) diagram to be inappropriate for the following reasons. (a) According to Warren's diagram [Figure 6(*a*)] the low-energy transition is expected to involve $a_1$ and either $1e_2$ or $2e_2$ orbitals, both of which are constructed from cot orbitals, which is in contradiction to what has been deduced from the experimental absorption spectrum. (*b*) The calculation of spin transfer to hydrogen leads to hyperfine-interaction constants [$A_H$(cot) = 1.03 G and $A_H$(cp) = 2.27 G] which are in the reverse order to those found experimentally (see above).

In contrast, the first diagram [Figure 6(*a*)] satisfactorily accounts for the observed spectrum in that the first excited state in (1) is assigned to $3e_1$ (metal + cp) level. This degenerate level is expected to be split in the indenyl compound because of lowering of symmetry [Figure 6(*b*)]. The experimental absorption spectrum shows this to be indeed the case. Moreover, the photoelectron spectrum of (1) gives ionization potentials for $a_1$ and $1e_2$ of 7.62 and 5.67 eV respectively, which corresponds to an energy separation of 1.95 eV or 15 700 cm$^{-1}$, in fairly close agreement to the absorption observed at 13 980 and 14 250 cm$^{-1}$ for compounds (1) and (2) respectively. Finally, the photoelectron spectrum gives an energy separation of 2.96 eV or 23 874 cm$^{-1}$ between the $2e_1$ and $a_1$ levels, which corresponds to the absorption band at 21 700 cm$^{-1}$ with a shoulder at 23 260 cm$^{-1}$ for compound (2). This absorption seems to be shifted to higher energies with compound (1) and masked by important overlap with the highly intense charge-transfer (c.t.) band in this region of the spectrum.

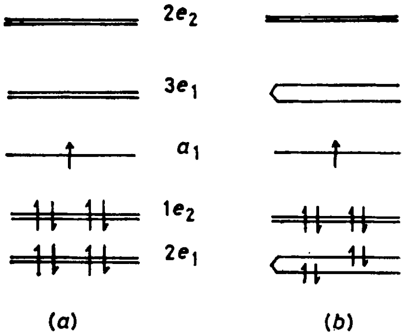

FIGURE 6 Molecular-orbital digram of (*a*) compound (1) according to ref. 13*a* and (*b*) compound (2) as proposed in this work. Warren's diagram is the same as (*a*) except that the levels $3e_1$ and $2e_2$ are reversed

*Interpretation of E.S.R. Parameters*.—It has been shown that the ground state is mainly of $d_{z^2}$ character; in axial symmetry and to a first-order approximation, this leads to the *g* values [9] in equations (1) and (2), where λ is the spin–orbit coupling constant of the Ti ion in the compound.

$$g_{\parallel} = 2.002\,3 \qquad (1)$$

$$g_{\perp} = 2.002\,3 - \frac{6\lambda}{E(d_{z^2}) - E(d_{xz},d_{yz})} \qquad (2)$$

λ can be determined, using equation (2) and the known *E* values from Table 2, as 56.8 cm$^{-1}$ for compound (1).

For the indenyl compound, degeneracy of the *e* level is removed as evidenced by the u.v. spectrum (Table 2), and would normally give rise to a splitting of the $g_{\perp}$ component into $g_x$ and $g_y$. However, the experimental spectrum allows one to determine the mean *g* value only, so that λ was calculated using the expression $g_{\perp} = \frac{1}{2}(g_x + g_y)$ and was found to be 57.5 cm$^{-1}$. From this value, $g_x$ and $g_y$ are found to be 1.967 3 and 1.973 7 respectively and therefore too close to permit an observable separation with the *X*-band spectrometer.

The Ti hyperfine coupling constants allow one to calculate the dipolar constant *P* and the Fermi-contact term $A_{\text{iso.}}$. If we write the $a_1$ ground-state wavefunction as in (3), where L = ligand, equations (4)—(6) can be derived for the $^{47,49}$Ti hyperfine coupling constants,[14] where $P = 2.002\,3 g_N\beta_e\beta_N\langle r^{-3}\rangle$, $\beta_e,\beta_N$ are the electronic and nuclear Bohr magnetons, $g_N$ is the nuclear *g* factor, and $A_{\text{iso.}}$ is the Fermi-contact parameter.

$$|a_1\rangle = \alpha_1(|d_{z^2}\rangle,|4s\rangle) + \alpha_2|\phi_L\rangle \qquad (3)$$

$$A_{\parallel} = A_{\text{iso.}} + P[\tfrac{4}{7}\alpha_1^2 - \tfrac{1}{7}(g_{\perp} - 2.002\,3)] \qquad (4)$$

$$A_{\perp} = A_{\text{iso.}} + P[-\tfrac{2}{7}\alpha_1^2 + \tfrac{15}{14}(g_{\perp} - 2.002\,3)] \qquad (5)$$

$$\langle A\rangle = \tfrac{1}{3}(A_{\parallel} + 2A_{\perp}) = A_{\text{iso.}} + \frac{2P}{3}(g_{\perp} - 2.002\,3) \qquad (6)$$

McGarvey [14] has shown that, for $^{47,49}$Ti, *P* is negative, so that from (5) and (6) we obtain (7). Thus, $\langle A\rangle - A_{\perp}$ is negative and with our experimental values the only possibility for this to be so is that $\langle A\rangle$, $A_{\perp}$, and $A_{\parallel}$ are all positive. Knowing the absolute signs of $\langle A\rangle$ and $A_{\perp}$ and assuming that the ground state is largely of metallic character, $\alpha_1$ can be taken as equal to 1 so that (7) gives $P = -18.8$ and $-15.1$ G for (1) and (2) respectively. Substituting in either (4) or (5) one obtains $A_{\text{iso.}} = 14.2$ and 15.2 G for (1) and (2) respectively.

$$\langle A\rangle - A_{\perp} = P[\tfrac{2}{7}\alpha_1^2 - \tfrac{17}{42}(g_{\perp} - 2.002\,3)] \qquad (7)$$

Superhyperfine interaction with the ring protons can result from two mechanisms: [15] direct overlap between the metal orbital and the ring-proton orbitals (σ mechanism which delocalizes unpaired spin density on to the ring protons), and dipolar coupling (pseudo-contact mechanism and a π mechanism which involves atomic exchange polarization). The expressions (8)—(10) can be written for the superhyperfine splitting,[16] where $\alpha_H$ is the hydrogen 1*s* orbital coefficient in the molecular orbital, $|\psi_0(s)|^2$ is the probability of finding the electron in a unit volume at the hydrogen nucleus, and $a_c$ is the superhyperfine contact-interaction parameter for the complex studied. $\alpha_H^2$ can be evaluated by taking the ratio of the observed isotropic superhyperfine proton interaction to that calculated for an electron in a 1*s* hydrogen orbital, taken to be 508 G,[9] which gives $(\alpha_H)$(cp) = 0.056, $(\alpha_H)$(cot) = 0.08 for (1) and $(\alpha_H)(C_9H_7)$ = 0.057, $(\alpha_H)$(cot) = 0.079 for (2). This result is in agreement with values found for metallocenes [17,18] such as [V(η-$C_7H_7$)(η-$C_5H_5$)] and [Cr(η-$C_6H_6$)$_2$]$^+$.

$$\langle a\rangle_H = a_c = (8\pi/3)g_N\beta_N|\psi_0(s)|^2(\alpha)_H{}^2 \qquad (8)$$

$$(a_{\parallel})_H = a_c + 2a_{\text{dip}} \qquad (9)$$

$$(a_{\perp})_H = a_c - a_{\text{dip}} \qquad (10)$$

## DISCUSSION

From the results presented above, information can be deduced about the effective charge and molecular-orbital (m.o.) coefficients of the ground and the first excited states in both compounds (1) and (2). First, it should be noted that the spin–orbit coupling constant λ is rather low for both compounds [57 cm$^{-1}$ for (1) and 57.5 cm$^{-1}$ for (2)] compared to the value of 155 cm$^{-1}$ for

$Ti^{3+}$ ion.[19] $\lambda$ may be expressed as in (11), where $k^2$ is the orbital-reduction factor[9] ($k^2 = \alpha_1{}^2\beta_1{}^2$) and $\alpha_1,\beta_1$ are

$$\lambda(\text{complex}) = k^2\lambda(\text{free ion}) \qquad (11)$$

the atomic orbital coefficients of $3d_{z^2}$ and $3d_{xz,yz}$ in the $a_1$ and $3e_1$ molecular orbitals respectively.

It is apparent from the m.o. diagram (Figure 6) that these molecular orbitals are mainly of metal character. In view of the slight reduction in the value of $\lambda$(complex) arising from the $k^2$ coefficient, it follows that $\lambda$(free ion) in our compounds is close to the value of 71 $cm^{-1}$ given by Dunn[19] for Ti with zero charge and in fair agreement with photoelectron spectroscopic measurements[20] on [Ti(cot)(cp)] which give a charge of 0.4.

Another independent value of the charge can be deduced from the experimental $P$ values compared with those calculated by McGarvey[14] for Ti ions in various oxidation states. Plotting $P$ as a function of the charge on Ti and interpolating for the experimental values leads to an effective positive charge of 1.0 and 0.3 for (1) and (2) respectively, both of which fall within the range of values found above. The difference between the two values (0.4 and 1) for (1) as determined by photoelectron and e.s.r. spectroscopy respectively falls within the experimental errors; it may also be due to lack of precision on $\langle r^{-3}\rangle$ values used in the calculations of the theoretical $P$ values. However, in spite of this uncertainty in the absolute charge of (1), what is significant is the difference in magnitude between the charges for (1) and (2); their determination as presented above is in our view not inconsistent since both values are deduced from the same experimental $P$ parameters. The smaller the charge, the smaller is the spin–orbit constant for the free ion. It follows that $k^2$ is higher for (2) than for (1) and the assumption that $\alpha_1 = 1$ leads to the result that the metal-orbital contribution to the $3e_1$ state is higher for (2) than (1). This can be explained by the fact that the $e_1$ ($\pi$) m.o. of the indenyl ligand is lower in energy compared to that of the cp ring and therefore less prone to mix with the metal orbitals.

For compounds of $Ti^{3+}$ where the unpaired electron is mainly in the $d_{z^2}$ orbital there is also a small contribution of the 4$s$ orbital to the ground state. The extent of admixture of the 4$s$ orbital can be deduced from the experimental value of the Fermi-contact parameter using expression (12),[21] where $\alpha_1{}^2\chi$ and $\alpha_1{}^2(1-\chi)$ are the

$$A_{\text{iso.}} = \alpha_1{}^2\chi A_{\text{iso.}}(3d) + \alpha_1{}^2(1-\chi)A_{\text{iso.}}(4s) \qquad (12)$$

Ti 3$d$ and 4$s$ spin densities respectively, $A_{\text{iso.}}(3d)$ is the Fermi-contact term for the unpaired electron in the 3$d$ orbital (which depends on the charge on Ti[9]), and $A_{\text{iso.}}(4s)$ is the Fermi-contact term corresponding to the 4$s$ orbital. Taking $A_{\text{iso.}}(3d) = 16.3$ G for (1) and 17.6 G for (2) and $A_{\text{iso.}}(4s) = -175.7$ G,[22] it follows from (12), with $\alpha_1{}^2 = 1$, that $\chi_{d_{z^2}} = 0.988$ and 0.987 and $(1-\chi)_{4s} = 0.012$ and 0.013 for compounds (1) and (2). These values are in agreement with those found for other sandwich compounds such as $[Cr(\eta\text{-}C_6H_6)_2]^+$ and $[V(\eta\text{-}C_5H_5)_2]$.[18, 23]

Analysis of the proton superhyperfine coupling constants of (1) and (2) has shown that $a$(cp) = 1.62 G for (1) and $a(C_9H_7)$ = 1.64 G for (2), values close to those found for the cp ring protons in [V(cp)(cht)] (cht = cycloheptatrienylium) where $a$(cp) = 1.8 G.[17] However, the coupling with the cot rings [3.24 and 3.15 G for (1) and (2) respectively] is approximately twice the value for the $C_5$ ring protons; likewise, it was found that for [V(cp)(cht)], $a_H$(cht) = 4.5 G so that the higher coupling constants are obtained in both cases with the larger rings. This may be explained by the increased overlap of the metal orbitals with the $C_7$ or $C_8$ ring orbitals due to the shorter metal–ring distances.[4, 24]

Two conclusions may be drawn from the above study. First, the $C_8$ ring bears more electron density in compounds (1) and (2) than the $C_5$ ring and therefore is more negatively charged. Experimental results on the relative ease of attack of LiBu on the $C_5$ ring in (1)[20] tend to be more consistent with the notion that such metallation reactions are nucleophilic (attack of LiBu on the ring bearing the more positive charge) rather than electrophilic substitutions.[20,25] Secondly, the metal is more positively charged in the cyclopentadienyl (1) than in the indenyl (2) compound. Reasons for this may be sought in the electron-withdrawing effect of the $C_6$ ring in (2) which leaves a lower residual negative charge on the $\eta$-$C_5$ ring of the indenyl ligand. Studies on the fluorenyl analogue are underway to investigate whether this trend is actually followed.

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