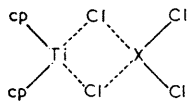
Electron Paramagnetic Resonance Hyperfine Pattern of Gallium-69 and -71 in a New Titanium–Gallium Complex

By G. HENRICI-OLIVÉ and S. OLIVÉ

(*Monsanto Research S.A., Eggbuhlstrasse* 36, CH-8050 *Zürich, Switzerland*)

THE Ti^{III}–B and Ti^{III}–Al complexes (I) and (II) have been investigated. We have prepared a Ti^{III}–Ga complex and have studied its e.p.r. spectrum in toluene.



Cp = π-cyclopentadienyl
(I) X = B
(II) X = Al
(III) X = Ga

The spectrum is reasonably resolved at $-20°$ and shows clearly the interaction of the unpaired electron of the Ti^{III} atom with the ^{69}Ga (I 3/2; μ 2·01) and the ^{71}Ga (I 3/2; μ 2·55) nuclei, giving rise to two superimposed signals of four equivalent lines each (see Figure a and b). Lines are somewhat broadened at $+20°$ (see Figure 1c), and also below $-20°$. The slight asymmetry of the spectrum is probably due to field-dependent linewidth effects which, however, could not be evaluated quantitatively at the present resolution. The complexes have a g-value of 1·974. The isotropic HFS-constants [$a(^{69}Ga)$ 91 MHz, $a(^{71}Ga)$ 116 MHz] are in satisfactory agreement with the magnetic moments as determined by n.m.r.:[2] the intensities of the two quadruplets are proportional to the natural abundances of the two isotopes (^{69}Ga 60%, ^{71}Ga 40%). On both sides of the main spectrum appear the weak ^{47}Ti–^{49}Ti satellites. Figure d represents the outer, well resolved, lines at increased signal level. Although the satellite hyperfine pattern must be very crowded in the central part, the position of the extreme high-field and low-field lines allow an estimate of the isotropic coupling constant of the two magnetic Ti isotopes (^{47}Ti I 7/2, ^{49}Ti I 5/2). The two extreme lines belong to $m_I(^{49}Ti) = \pm 7/2$ and $m_I(^{71}Ga) = \pm 3/2$. Thus their total distance ΔH of 575 MHz is composed of, $\Delta H = 7 \times a(^{49}Ti) + 3 \times a(^{71}Ga)$. From this follows for the splitting constant, which is supposed to be the same for both titanium isotopes, $a(^{47}Ti$–$^{49}Ti) \simeq 32$ MHz.

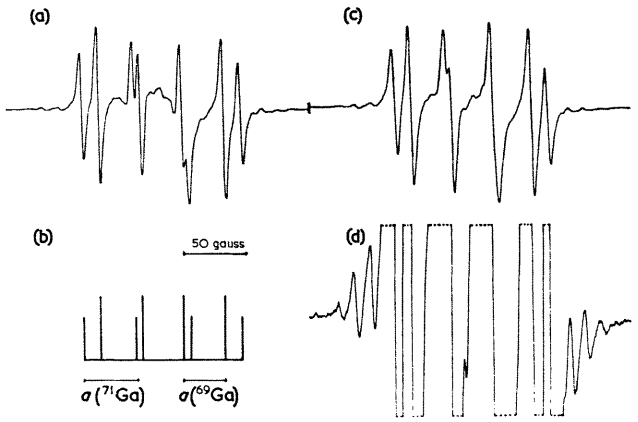


FIGURE. *E.p.r. signal of the complex* $Cp_2TiCl_2GaCl_2^{III}$: (a) *at* $-20°$; (b) *block diagram for the* ^{69}Ga *and* ^{71}Ga *hyperfine quadruplets*; (c) *at* $+20°$; (d) ^{47}Ti–^{49}Ti *satellites at increased signal level.*

The very similar g-value and Ti splitting-constant, as compared with those of complexes (I) and (II),[1] and the completely analogous preparation, suggest that the observed e.p.r. spectrum may be attributed to complex (III). The relatively high value of the unpaired spin-density at the Ga nuclei indicates that $GaCl_3$ is the strongest Lewis acid (electron acceptor) of the Group III trichlorides.

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[1] G. Henrici-Olivé and S. Olivé, *Angew. Chem.*, 1968, **80**, 796.
[2] NMR Tables, Varian Associates.