Electron Spin Resonance Spectra of some Germanium, Tin, and Lead Complexes of Bis(cyclopentadienyl)titanium(III)

By J. G. KENWORTHY and J. MYATT*

(*Imperial Chemical Industries Limited, Petrochemical & Polymer Laboratory, P.O. Box 11, The Heath, Runcorn, Cheshire*)

Summary E.s.r. evidence is presented for the formation of germanium, tin, and lead derivatives of bis(cyclopentadienyl)titanium(III).

THE formation in solution of titanium(III) derivatives of the type $[(\pi\text{-}C_5H_5)_2Ti(MPh_2)_2]^-$, where M = nitrogen, phosphorus, or arsenic, has been reported earlier.[1,2] The observation of a strong interaction with sodium and lithium cations[1,3] confirmed that these species were anions, and a comparison of the intensities of the satellite lines with the major lines showed that the unpaired electron interacted with only one titanium nucleus. Hence, the above monomeric structure was preferred to a dimeric bridged structure containing two titanium atoms.

We now report the formation of similar germanium, tin, and lead complexes which have been examined in solution by e.s.r. The preparations of the related non-bridged compounds $(\pi\text{-}C_5H_5)_2TiSnPh_3$, $(\pi\text{-}C_5H_5)_2TiGePh_3$, and the Ti^{IV} complex $(\pi\text{-}C_5H_5)_2Ti(SnPh_3)_2$ have been described,[4] but no e.s.r. examination of the Ti^{III} complexes was undertaken.

Addition of titanocene dichloride to an excess of $Ph_3Ge^-K^+$ in 1,2-dimethoxyethane under vacuum conditions, gave immediately the e.s.r. spectrum shown in the Figure (a). The strong central line in the spectrum results from molecules containing only the non-magnetic isotopes of titanium and germanium. The satellite lines consist of a ten-line pattern arising from coupling to one ^{73}Ge nucleus ($I = 3/2$; abundance = 7·6%),[5] and eight lines, broadened at high field, due to the ^{47}Ti ($I = 5/2$; 7·75%), and ^{49}Ti ($I = 7/2$; 5·51%) contributions.

The presence of two germanium atoms per molecule is evident from the same spectrum at increased sensitivity. This is shown in the Figure (b). The arrows mark part of a nineteen line spectrum of intensity ratio 1 : 2 : 3 : 4 · · · · · ; 4 : 3 : 2 : 1, due to two equivalent ^{73}Ge nuclei, and the remaining weak satellite lines are attributed to molecules containing one ^{73}Ge and a ^{47}Ti or ^{49}Ti atom. Again, the titanium lines are broadened at high field.

The tin and lead complexes were prepared in a similar manner by the addition of titanocene dichloride to solutions of $Ph_3Sn^-K^+$ and $Ph_3Pb^-K^+$ respectively. The spectra of both of these complexes contain the large unsplit central line and the characteristic titanium isotope pattern. The tin complex has, in addition to this, two doublet splittings which arise from coupling to the tin isotopes ^{117}Sn ($I = 1/2$; 7·67%), and ^{119}Sn ($I = 1/2$; 8·68%). At higher sensitivity further weak lines can be seen, which confirm the presence of two tin atoms per molecule, from molecules containing two of the magnetic isotopes of tin.

TABLE

Probable structure of complex	Titanium coupling (MHz)	Apparent ligand coupling (MHz)	True g-value measured from unsplit centre line
$[(\pi\text{-}C_5H_5)_2Ti(GePh_3)_2]^-$ ..	25·0	21·4	1·988
$[(\pi\text{-}C_5H_5)_2Ti(SnPh_3)_2]^-$ ..	21·9	^{117}Sn = 408·5 ^{119}Sn = 424·2	1·980
$(\pi\text{-}C_5H_5)_2TiPbPh_3$	17·1	539·6	1·973

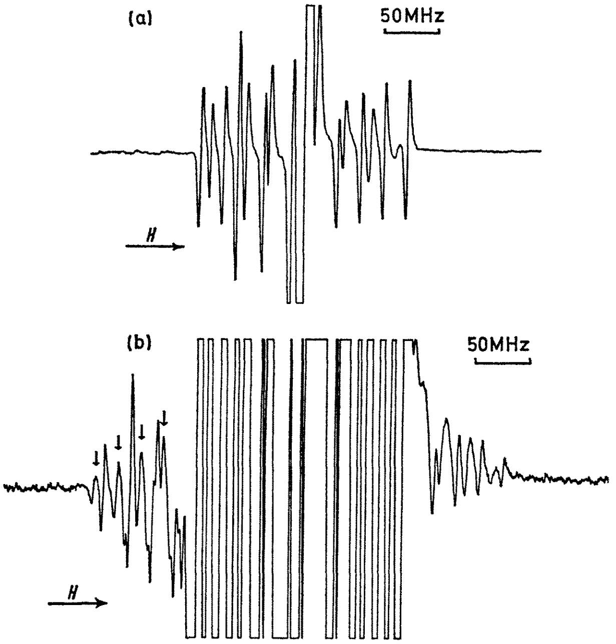

FIGURE. (a) *E.s.r. spectrum attributed to the complex* $[(\pi\text{-}C_5H_5)_2Ti(GePh_3)_2]^-$. (b) *The same spectrum at increased sensitivity.*

The spectrum from the lead compound has, about the central line, a less intense doublet splitting due to interaction with one ^{207}Pb nucleus ($I = 1/2$; 21·1%). If two equivalent lead atoms had been present in the complex, additional lines would have been detected with an intensity approximately one tenth of the observed doublet from a single ^{207}Pb nucleus. Since no additional lines were seen, when working at a sensitivity calculated to be greater than that required for their detection, the complex formed contains only one lead atom. Further shaking of the reactants destroyed the signal and did not produce a paramagnetic di-lead derivative.

Using the arguments outlined in the introduction, and presented more fully in an earlier report,[2] we formulate the Group IVB complexes described here as $[(\pi\text{-}C_5H_5)_2Ti(GePh_3)_2]^-$, $[(\pi\text{-}C_5H_5)_2Ti(SnPh_3)_2]^-$, and $(\pi\text{-}C_5H_5)_2TiPbPh_3$ respectively (see Table).

The satellite lines in the spectra of the tin and lead complexes are found to be asymmetrically placed about the central line. This is because the hyperfine splitting is sufficiently large to invalidate the high-field approximation in the Breit–Rabi formula. Corrections to the measured coupling constants were calculated[6] but found to be only of the same order as the experimental errors. The true g-values were measured directly from the unsplit central line.

In a recent publication[2] we reported that bis(cyclopentadienyl)titanium(III) compounds of the type described here have g-values which are proportional to the titanium isotropic coupling constants. We find, however, in the present series of Group IVB derivatives, that a decrease in titanium coupling constant on going from the germanium to the lead complex is accompanied by a decrease in g-value.

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