

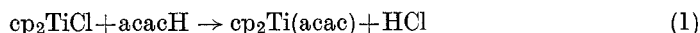
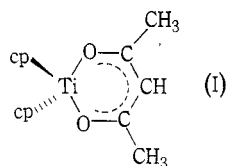
ACETYLACETONATOBIS(CYCLOPENTADIENYL)TITANIUM(III)

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Previous work in these laboratories has shown that bis(cyclopentadienyl)-titanium(III) complexes with bidentate chelate compounds can be formed readily with both four-¹ and five²-membered chelate rings. An obvious extension to this work is the synthesis of β -diketonate derivatives of titanium(III) in which the chelated rings will be six-membered.

When a fourfold excess of acetylacetone was added to a vigorously stirred solution of cp_2TiCl ($\text{cp} = \pi$ -cyclopentadienyl) in air-free water, a deep blue air-sensitive precipitate was obtained, identified from the data given below as (I), i.e. $\text{cp}_2\text{Ti}(\text{acac})$, formed as in equation (1).



Pentane-2,4-dionatobis(cyclopentadienyl)titanium(III) (I) is monomeric and the magnetic moment is independent of temperature with one unpaired electron per titanium atom (Table 1).

TABLE 1
MAGNETIC PROPERTIES OF $\text{cp}_2\text{Ti}(\text{acac})$
Ligand correction 152×10^{-6} CGS units

T ($^{\circ}\text{K}$)	$10^6 \chi'_M$	μ_{eff} (B.M.)	T ($^{\circ}\text{K}$)	$10^6 \chi'_M$	μ_{eff} (B.M.)
287	1316	1.74	196	1960	1.76
263	1415	1.73	166	2288	1.75
234.5	1632	1.76	136	2671	1.71
202.5	1862	1.74			

The yield of (I) is about 50%. The rest of the titanium is found in the red aqueous filtrate from which the titanium(IV) compounds $[\text{cp}_2\text{Ti}(\text{acac})]\text{ClO}_4$ and $[\text{cp}_2\text{Ti}(\text{acac})]\text{BF}_4$ can be precipitated by addition of ClO_4^- or BF_4^- under air-free conditions. These complexes are identical in every respect with those obtained from acetylacetone and $\text{cp}_2\text{Ti}(\text{ClO}_4)_2$ (or cp_2TiCl_2) in water, and which were recently characterized by Doyle and Tobias.³

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¹ Coutts, R. S. P., and Wailes, P. C., *Aust. J. Chem.*, 1967, **20**, 1579; 1968, **21**, 373; 1968, **21**, 1181; Coutts, R. S. P., Wailes, P. C., and Kingston, J., *Chem. Commun.*, 1968, 1170.

² Coutts, R. S. P., and Wailes, P. C., *Aust. J. Chem.*, 1968, **21**, 2199.

³ Doyle, G., and Tobias, R. S., *Inorg. Chem.*, 1967, **6**, 1111.

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This oxidation to titanium(IV) could be brought about by protonation of titanium(III) species by the hydrochloric acid produced in the initial reaction. Alternatively, oxidation by an electron-transfer process involving chloride (similar to the oxidation of ferrocene to ferricenium ion; for a discussion see⁴) could occur.

Experimental

General

All manipulations were carried out in a nitrogen-filled glove-box or in a stream of purified argon.

Reaction of Acetylacetone with cp_2TiCl

The cp_2TiCl_2 (10 g) was stirred overnight in air-free water (150 ml) with excess granulated zinc (10 g). The solution was filtered in a stream of argon to remove unchanged zinc and a small amount of blue insoluble $\text{Ti}(\text{OH})_3$ which is always formed. The deep blue filtrate* was vigorously stirred with acetylacetone (18 ml, added in small portions) for 2 hr, giving a deep blue precipitate (5.9 g) of $\text{cp}_2\text{Ti}(\text{acac})$ which was removed by filtration and washed several times with air-free water. The product had m.p. 71° (dec.) (evacuated capillary) and sublimed readily at $100^\circ/10^{-3}$ mm (Found:† C, 64.5; H, 6.2; Ti (sulphate ash), 17.4; mol. wt. 278.‡ Calc. for $\text{C}_{15}\text{H}_{17}\text{O}_2\text{Ti}$: C, 65.0; H, 6.2; Ti, 17.3%; mol. wt. 277).

Spectral Data

The spectrum of $\text{cp}_2\text{Ti}(\text{acac})$ was measured between 250 and 25000 cm^{-1} in KBr disk (to 4000 cm^{-1}) and tetrahydrofuran solution.

Infrared.—The main bands due to the acetylacetonato ligand are at 1583 cm^{-1} (C=C str), 1512 cm^{-1} (C=O str), and 1380 cm^{-1} (C=O str), and clearly indicate that the ligand is bidentate. The cyclopentadienyl groups absorb at 3090 cm^{-1} (C—H str), 1430 cm^{-1} (C=C str), 1015 cm^{-1} (C—H deform), and 785 cm^{-1} (C—H deform).

Visible spectrum.—This was run on a Cary 14 spectrophotometer; bands due to $d-d$ transitions were observed at 10260 sh , 13040 sh , 14560 (ϵ 61), and 17240 cm^{-1} (ϵ 43). This is very similar to the spectra of other bis(cyclopentadienyl)titanium(III) compounds prepared and examined in these laboratories.^{1,2} The only effect of the acetylacetonato ligand is to raise the frequency of the highest-energy $d-d$ transition from $13000\text{--}14000$ to 14560 cm^{-1} .

Magnetic Susceptibility

Susceptibility was measured by the Gouy method in a sealed tube over the temperature range $136\text{--}287^\circ\text{K}$. The moment is independent of temperature and close to the spin-only value for a d^1 system.

* In organic solvents (tetrahydrofuran, methanol, etc.) cp_2TiCl_2 is reduced by zinc to (II),⁵ but in water the ion $\text{cp}_2\text{Ti}^{III+}$ is present and can be precipitated by those anions which do not have insoluble zinc derivatives.

† Analyses for C and H were carried out by the Australian Microanalytical Service, Melbourne, on small pellets sealed in aluminium capsules of the type used in calorimetry.

‡ Ebulliometric in benzene.

§ Assignment by Nakamoto;⁵ others assign this band to C=O and the 1512 cm^{-1} band to C=C. See ref.⁶ for a discussion of these bands.

⁴ Rosenblum, M., "Chemistry of the Iron Group Metallocenes." Part I. (Interscience: New York 1965.)

⁵ Vonk, C. G., personal communication to Martin, H. A., and Jellinek, F., in *J. organomet. Chem.*, 1967, 8, 115; Salzmann, J. J., *Helv. chim. Acta*, 1968, 51(3), 526.

⁶ Nakamoto, K., "Infrared Spectra of Inorganic and Co-ordination Compounds." p. 216. (John Wiley: New York 1963.)

