

### 1174. Complexes of $\beta$ -Diketones with Group IV Tetrachlorides.

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The reactions of several  $\beta$ -diketones with the Group IV tetrachlorides have been studied. Three classes of derivative have been isolated: (a) non-electrolytes of the type  $[M(\text{diketone})_2\text{Cl}_2]^0$  which are formed by titanium, zirconium, germanium, and tin; (b) cationic derivatives,  $[M(\text{diketone})_3]X$ , with silicon, titanium, zirconium, hafnium, and germanium; (c) seven-co-ordinate complexes,  $[M(\text{diketone})_3\text{Cl}]^0$ , for zirconium and hafnium. The physical evidence in support of these formulations is presented and discussed.

An interesting rearrangement of the type  $M\text{Cl}_4 + \text{Fe}(\text{diketone})_3 \rightarrow [M(\text{diketone})_3][\text{FeCl}_4]$  occurs when certain of the Group IV tetrahalides react with a tris- $\beta$ -diketoneiron(III) complex in solution. For metals where the trisdiketone cation is not known the non-electrolytes  $[M(\text{diketone})_2\text{Cl}_2]^0$  or  $[M(\text{diketone})_3\text{Cl}]^0$  are produced in this reaction.

THE reaction between titanium(IV) chloride and acetylacetonone (acacH) was first studied by Dilthey<sup>1</sup> who obtained a compound to which the structure  $[\text{Ti}(\text{acac})_3]_2^{2+}[\text{TiCl}_6]^{2-}$  was assigned. This assignment was based on the similarity between the reactions of this titanium(IV) complex with certain metal halides<sup>1</sup> and those of a corresponding silicon compound  $[\text{Si}(\text{acac})_3]^+[\text{HCl}_2]^-$  with the same halides.<sup>2</sup> Thus, both of these derivatives when treated in solution with iron(III) chloride (glacial acetic acid or chloroform), platinum(IV) chloride (chloroform), and gold(III) chloride (glacial acetic acid or chloroform) gave products which were formulated as  $[M(\text{acac})_3][\text{FeCl}_4]^-$ ,  $[M(\text{acac})_3]_2^{2+}[\text{PtCl}_6]^{2-}$ , and  $[M(\text{acac})_3][\text{AuCl}_4]^-$ , respectively. However, the structure originally suggested for compound  $[\text{Ti}(\text{acac})_3]_2[\text{TiCl}_6]$  by Dilthey was not supported by the work of others, who claimed that it was the monomeric non-electrolyte  $[\text{Ti}(\text{acac})_2\text{Cl}_2]^0$ .<sup>3,4</sup> Mehrotra *et al.*<sup>3</sup> studied the reaction between  $[\text{Ti}(\text{acac})_2\text{Cl}_2]^0$  and iron(III) chloride and proposed that the product of this reaction was a 1:1 addition complex between  $[\text{Fe}(\text{acac})_3]^0$  and titanium(IV) chloride, *i.e.*,  $\text{Fe}(\text{acac})_3, \text{TiCl}_4$ ; this was claimed to be identical with the product obtained by Dilthey on reaction of iron(III) chloride with  $[\text{Ti}(\text{acac})_2\text{Cl}_2]^0$ . This conclusion was based mainly on preparative evidence, the same compound being obtained by the two reactions, and the structure was based on the low conductivity of the complex in nitrobenzene.

Recently Fackler *et al.*<sup>5</sup> have shown from a study of the ultraviolet spectrum of this derivative that the original Dilthey formulation  $[\text{Ti}(\text{acac})_3][\text{FeCl}_4]^-$  is correct, and, in contrast to the results of Mehrotra *et al.*, the conductivity indicated a 1:1 electrolyte in

<sup>1</sup> W. Dilthey, *Ber.*, 1904, **37**, 588.

<sup>2</sup> W. Dilthey, *Ber.*, 1903, **36**, 923.

<sup>3</sup> K. C. Pande and R. C. Mehrotra, *Chem. and Ind.*, 1958, 1198.

<sup>4</sup> D. M. Puri and R. C. Mehrotra, *J. Less-Common Metals*, 1961, **3**, 247, 253; 1963, **5**, 2.

<sup>5</sup> R. J. Woodruff, J. L. Marini, and J. P. Fackler, *Inorg. Chem.*, 1964, **3**, 687.

nitrobenzene, nitromethane, and acetonitrile solutions. Finally, Mössbauer studies on the solid derivative also suggested the presence of the  $[\text{FeCl}_4]^-$  species.

In this investigation we have prepared several other derivatives from  $[\text{Ti}(\text{acac})_2\text{Cl}_2]^0$  to confirm that the  $[\text{Ti}(\text{acac})_3]^+$  ion is formed. In all cases the observed physical properties support the Dilthey structure for these complexes (Table 1). Further confirmation of the

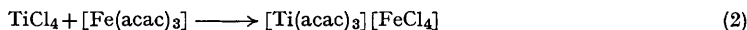
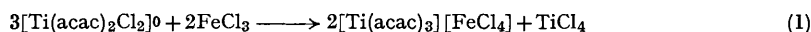
TABLE 1.

Complex	M. p.	$\Lambda_M$ ( $10^{-3}\text{M}$ -soln. in $\text{PhNO}_2$ ) (mhos mole $^{-1}$ )	Mol. wt. in nitrobenzene		
			Exptl.	Concn. (g./l.)	Calc. for monomer
$[\text{Ti}(\text{acac})_2\text{Cl}_2]^0$ .....	190—193°	1.2	293	10.4	317
$[\text{Ti}(\text{acac})_3]^+[\text{FeCl}_4]^-$ .....	170—172	24.8	251	1.4	543*
$[\text{Ti}(\text{acac})_3]^+[\text{FeCl}_4]^-$ .....	170—172	27.0	262	2.3	543†
$[\text{Ti}(\text{acac})_3]^+[\text{SbCl}_6]^-$ .....	153—155	82.4‡	364	3.3	680
$[\text{Ti}(\text{acac})_3]^+[\text{AuCl}_4]^-$ ...		85.0‡	337	4.6	684

1:1 electrolyte: in nitrobenzene ( $10^{-3}\text{M}$ -soln.) 20—30 mhos mole $^{-1}$ ; in nitromethane ( $10^{-3}\text{M}$ -soln.) 70—100 mhos mole $^{-1}$ .

\* Prepared as in ref. 1. † Prepared as in ref. 3. ‡ In nitromethane solution.

formation of  $[\text{Ti}(\text{acac})_3]^+[\text{FeCl}_4]^-$  was afforded by conductometric titrations, the following equations being verified by discontinuities in the conductance curves at the molar ratios 3:2 and 1:1 (Figs. 1 and 2).



It is interesting to note that the acetylacetonate residue can be transferred from iron to titanium in the above reaction (eqn. 2). This is the first example of  $\beta$ -diketone transfer

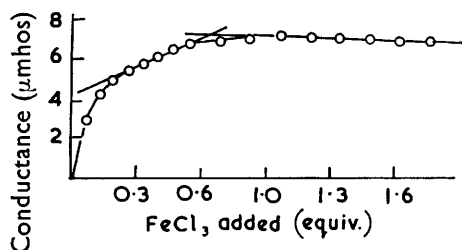


FIG. 1. Conductometric titration of  $[\text{Ti}(\text{acac})_2\text{Cl}_2]^0$  against iron(III) chloride in glacial acetic acid solution.

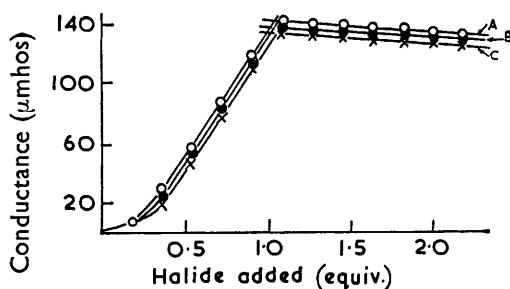


FIG. 2. Conductometric titrations in nitrobenzene solution of:

- A,  $[\text{Fe}(\text{acac})_3]^0$  against  $\text{TiCl}_4$ ;
- B,  $[\text{Hf}(\text{bzcz})_3\text{Cl}]^0$  against  $\text{FeCl}_3$ ;
- C,  $[\text{Zr}(\text{bzcz})_3\text{Cl}]^0$  against  $\text{FeCl}_3$ .

involving  $[\text{Fe}(\text{acac})_3]^0$ , although this type of reaction can be used as a method of preparation of  $\beta$ -diketone complexes with the copper(II) and thallium(I) derivatives as starting materials.<sup>6</sup>

The structures proposed for dichlorobisacetylacetonatotitanium(IV) and trisacetylacetonatotitanium(IV) tetrachloroferrate(III) are supported by the formation of compounds of

<sup>6</sup> W. E. Fernelius and B. E. Bryant, *Inorg. Synth.*, 1958, **5**, 105.

a similar type when benzoylacetone (bzacH) and dibenzoylmethane (bzbzH) are used as ligands (Table 2). The reaction of these ligands with titanium(IV) chloride in glacial acetic acid gives  $[\text{Ti}(\text{bzac})_2\text{Cl}_2]^0$  and  $[\text{Ti}(\text{bzbz})_2\text{Cl}_2]^0$ , respectively. The cationic derivatives  $[\text{Ti}(\text{bzac})_3][\text{FeCl}_4]$  and  $[\text{Ti}(\text{bzbz})_3][\text{FeCl}_4]$  can be prepared from treatment of the dichloro-compounds in solution with iron(III) chloride or from the corresponding iron(III) chelate and titanium(IV) chloride (Table 2).

TABLE 2.

Compound	M. p.	$\Lambda_M$ ( $10^{-3}\text{M}$ -soln. in $\text{CH}_3\text{NO}_2$ ) (mhos mole $^{-1}$ )	Mol. wt. in $\text{PhNO}_2$ (cryoscopic)		
			Exptl.	Concn. (g./l.)	Calc. for monomer
$[\text{Ti}(\text{bzac})_2\text{Cl}_2]^0$ .....	—	2.20	395	6.71	441
$[\text{Ti}(\text{bzac})_3][\text{FeCl}_4]$ .....	—	71.2	365	5.75	729
$[\text{Ti}(\text{bzbz})_2\text{Cl}_2]^0$ .....	—	1.4	580	10.04	565
$[\text{Ti}(\text{bzbz})_3][\text{FeCl}_4]$ .....	—	83.4	473	7.46	915
$[\text{Zr}(\text{bzac})_3\text{Cl}]^0$ .....	122—124°	3.66	633	16.9	610
$[\text{Zr}(\text{bzbz})_3\text{Cl}]^0$ .....	256—258	4.85	801	6.26	796
$[\text{Zr}(\text{bzbz})_3][\text{FeCl}_4]$ .....	170	65.0	514	7.81	959
$[\text{Zr}(\text{bzbz})_3][\text{AuCl}_4]$ .....	—	28.9*	527	6.63	1100
$[\text{Hf}(\text{bzac})_3\text{Cl}]^0$ .....	125—128	1.18	647	4.86	698
$[\text{Hf}(\text{bzbz})_3\text{Cl}]^0$ .....	258—260	9.7	828	6.25	884
$[\text{Hf}(\text{bzbz})_3][\text{FeCl}_4]$ .....	—	63.4	412	5.85	1046

\* In nitrobenzene solution.

TABLE 3.

Compound	M. p.	$\Lambda_M$ ( $10^{-3}\text{M}$ -soln. in $\text{CH}_3\text{NO}_2$ ) (mhos mole $^{-1}$ )	Mol. wt. in $\text{PhNO}_2$ (cryoscopic)		
			Exptl.	Concn. (g./l.)	Calc. for monomer
$[\text{Si}(\text{acac})_3]^+[\text{HCl}_2]^-$ .....	85—87°	27.1†	138§	2.65	397
$[\text{Si}(\text{acac})_3]^+[\text{FeCl}_4]^-*$ .....	189—190	94.7	235	4.03	523
$[\text{Si}(\text{acac})_3]^+[\text{FeCl}_4]^-†$ .....	189—190	89.3	267	4.60	523
$[\text{Si}(\text{acac})_3]^+[\text{AuCl}_4]^-$ .....	—	81.6	370	5.23	664
$[\text{Si}(\text{acac})_3]^+[\text{SbCl}_6]^-$ .....	170—172	87.3	304	3.90	660
$[\text{Ge}(\text{acac})_2\text{Cl}_2]^0$ .....	236—240	9.2	326	4.43	341
$[\text{Ge}(\text{acac})_3]^+[\text{FeCl}_4]^-*$ .....	184—185	84.3	294	5.00	568
$[\text{Ge}(\text{acac})_3]^+[\text{FeCl}_4]^-†$ .....	184—185	81.1	277	5.09	568
$[\text{Ge}(\text{acac})_3]^+[\text{SbCl}_6]^-$ .....	161—163	80.5	346	4.99	704
$[\text{Sn}(\text{acac})_2\text{Cl}_2]^0$ .....	201—203	2.5	306	4.14	388
$[\text{Sn}(\text{acac})_2\text{Cl}_2]^0†$ .....	201—203	7.8	341	5.76	388
$[\text{Zr}(\text{acac})_2\text{Cl}_2]^0$ .....	236	1.5	387	3.27	360
$[\text{Zr}(\text{acac})_3\text{Cl}]^0$ .....	134	1.7	405	4.46	424
$[\text{Zr}(\text{acac})_3\text{Cl}]^0†$ .....	134—136	2.2	—	—	—
$[\text{Hf}(\text{acac})_3\text{Cl}]^0$ .....	154—156	0.6	534	8.45	511
$[\text{Hf}(\text{acac})_3\text{Cl}]^0†$ .....	154—157	0.4	—	—	—

\* Prepared using  $\text{FeCl}_3$ . † Prepared from  $\text{Fe}(\text{acac})_3$ . ‡ In nitrobenzene solution. § Owing to slight hydrolysis during the measurement this value is lower than expected.

As an extension of this investigation the reactions between  $[\text{Fe}(\text{acac})_3]^0$  and other Group IVA and IVB tetrachlorides were studied, and wherever possible the products of the reactions were compared with known derivatives. The results are given in Table 3. For silicon and germanium, rearrangement of the acetylacetone residues to give the complex  $[\text{M}(\text{acac})_3]^+[\text{FeCl}_4]^-$  was observed. This type of cation is well known in the case of silicon<sup>2</sup> but the reaction between  $[\text{Ge}(\text{acac})_2\text{Cl}_2]^0$  and iron(III) chloride had not been studied previously, although a compound  $[\text{Ge}(\text{acac})_3]^+[\text{CuCl}_2]^-$  had been prepared.<sup>7</sup> The reaction between  $[\text{Ge}(\text{acac})_2\text{Cl}_2]^0$  and iron(III) chloride occurs readily, and other derivatives of the  $[\text{Ge}(\text{acac})_3]^+$  ion can be obtained in a similar manner.

The compound obtained when tin(IV) chloride was treated with acetylacetone is

<sup>7</sup> G. T. Morgan and H. D. K. Drew, *J.*, 1924, **125**, 1261.

$[\text{Sn}(\text{acac})_2\text{Cl}_2]^0$ .<sup>8</sup> This has now been shown to be a monomeric non-electrolyte, and a dipole moment of 8.8 D suggests that the two chlorine atoms are in the *cis*-octahedral positions. In marked contrast to the behaviour of the silicon and germanium compounds, treatment of this derivative in solution with iron(III) chloride or antimony(V) chloride gave only the starting materials. When a solution of  $[\text{Fe}(\text{acac})_3]^0$  was treated with tin(IV) chloride, the products were  $[\text{Sn}(\text{acac})_2\text{Cl}_2]^0$  and iron(III) chloride. The reason for the difference in behaviour of the Group IV elements is not apparent and poses an interesting question.

With the elements zirconium and hafnium, expansion of the co-ordination number to 8 can occur, and compounds of the type  $[\text{M}(\text{acac})_4]^0$  are easily obtained. However, by careful choice of reaction conditions it is possible to replace the chlorine atoms of zirconium(IV) chloride in stages to give  $[\text{Zr}(\text{acac})\text{Cl}_3]$ ,<sup>9</sup>  $[\text{Zr}(\text{acac})_2\text{Cl}_2]$ ,<sup>10</sup> and  $[\text{Zr}(\text{acac})_3\text{Cl}]$ .<sup>10</sup> The last of these is a monomeric non-electrolyte in nitrobenzene solution and thus contains a seven-co-ordinate zirconium atom, as the infrared spectrum implies that all the oxygens of the acetylacetonate residues are co-ordinated. As in the case of the tin derivative it has proved impossible to obtain the  $[\text{Zr}(\text{acac})_3]^+$  ion by treatment of this complex or  $[\text{Zr}(\text{acac})_2\text{Cl}_2]^0$  with a metal halide, and reaction between zirconium(IV) chloride and  $[\text{Fe}(\text{acac})_3]^0$  gave the monochloro-acetylacetonate  $[\text{Zr}(\text{acac})_3\text{Cl}]^0$ . Similar results were obtained when benzoylacetone was used as ligand, the seven-co-ordinate complex  $[\text{Zr}(\text{bzac})_3\text{Cl}]^0$  being formed by reaction of zirconium(IV) chloride with benzoylacetone in boiling benzene, and also from the reaction of zirconium(IV) chloride with trisbenzoylacetoneiron(III). However, it is interesting that, although the corresponding dibenzoylmethane zirconium(IV) derivative  $[\text{Zr}(\text{bzbz})_3\text{Cl}]^0$  is a non-electrolyte in solution, treatment of this compound with iron(III) chloride does give a cationic complex  $[\text{Zr}(\text{bzbz})_3][\text{FeCl}_4]$ .<sup>10</sup> This ionic compound can also be obtained from the iron(III) chelate and zirconium(IV) chloride (Table 2). In agreement with the above, in a conductometric study of the reaction between these seven-co-ordinate zirconium chelates and iron(III) chloride in nitrobenzene solution, only in the case of the dibenzoylmethane derivative was any discontinuity in the conductance curve observed, and this was at the required ratio for formation of  $[\text{Zr}(\text{bzbz})_3][\text{FeCl}_4]$  (Fig. 2).

The only hafnium derivative of acetylacetonate reported<sup>11</sup> is the fully chelated derivative  $[\text{Hf}(\text{acac})_4]^0$ . As the chemical properties of zirconium and hafnium are so similar it was expected that there would exist a range of chloro-substituted compounds like those of zirconium. The dichloro-compound  $[\text{Hf}(\text{acac})_2\text{Cl}_2]^0$  was much less stable than the corresponding zirconium complex and was obtained as an impure product by reaction of hafnium(IV) chloride with acetylacetonate in light petroleum at  $-10^\circ$ . The monochloro-derivative  $[\text{Hf}(\text{acac})_3\text{Cl}]^0$  was prepared readily and is isomorphous with the zirconium compound.

The complexes  $[\text{Hf}(\text{bzac})_3\text{Cl}]^0$  and  $[\text{Hf}(\text{bzbz})_3\text{Cl}]^0$  were also prepared, and these were similar in properties to the corresponding zirconium compounds. Thus, while no evidence could be obtained for formation of either  $[\text{Hf}(\text{acac})_3]^+$  or  $[\text{Hf}(\text{bzac})_3]^+$ , the dibenzoylmethane derivative did give the  $[\text{Hf}(\text{bzbz})_3]^+$  ion on treatment with iron(III) chloride (Table 2; Fig. 2). All the hafnium compounds prepared were isomorphous with the corresponding  $\beta$ -diketone complexes of zirconium.

It appears that, in the reaction between  $[\text{Fe}(\text{acac})_3]^0$  and a Group IV tetrachloride, transfer of the acetylacetonate residues occurs, to give an acetylacetonate derivative of the Group IV element. If the tri-chelated cation  $[\text{M}(\text{acac})_3]^+$  is known, then this species is obtained, thus, in the case of titanium, the complex  $[\text{Ti}(\text{acac})_3][\text{FeCl}_4]$  is obtained, otherwise some other chloro-substituted derivative results. This rearrangement seems to be a general property of iron(III)- $\beta$ -diketone complexes, similar reactions occurring with the benzoylacetone and dibenzoylmethane derivatives and the Group IV transition-element tetrachlorides (Table 2).

<sup>8</sup> G. T. Morgan and H. D. K. Drew., *J.*, 1924, **125**, 375.

<sup>9</sup> G. Jantsch, *J. prakt. Chem.*, 1927, **115**, 7.

<sup>10</sup> G. T. Morgan and A. R. Bowen, *J.*, 1924, **125**, 1252.

<sup>11</sup> C. von Hevesy and M. Lögstrup, *Ber.*, 1926, **59**, 1891.

## EXPERIMENTAL

All organic reagents were purified and dried by procedures given by Weissburger.<sup>12</sup> Before use traces of water were removed from solvents by distilling from suitable drying agents under dry nitrogen.

*Dichlorobisacetylacetonatotitanium(IV)*.—This, prepared by the method of Dilthey,<sup>1</sup> had m. p. 190—193° (Found: C, 37.3; H, 4.4; Cl, 22.3; Ti, 15.6. Calc. for C<sub>10</sub>H<sub>14</sub>Cl<sub>2</sub>O<sub>4</sub>Ti: C, 37.9; H, 4.3; Cl, 22.4; Ti, 15.1%).

*Trisacetylacetonatotitanium(IV) Tetrachloroferrate(III)*.—(a) Prepared by the method of Dilthey,<sup>1</sup> this had m. p. 170—172° (Found: C, 33.3; H, 4.0; Cl, 25.3; Fe, 10.4; Ti, 8.7; Calc. for C<sub>15</sub>H<sub>21</sub>Cl<sub>4</sub>FeO<sub>6</sub>Ti: C, 33.2; H, 3.9; Cl, 26.1; Fe, 10.3; Ti, 8.8%).

(b) Titanium tetrachloride (1 mol.) was added dropwise to a solution of trisacetylacetonatoiron(III) (1 mol.) in glacial acetic acid. The resulting orange-red crystalline precipitate was recrystallised from glacial acetic acid, m. p. 170—172° (Found: C, 32.5; H, 4.4; Cl, 25.8; Fe, 10.1; Ti, 8.7%); ultraviolet and infrared absorption spectra and X-ray powder photograph the same as those of the sample from (a).

*Trisacetylacetonatotitanium(IV) Hexachloroantimonate(V)*.—Addition of antimony pentachloride (1 mol.) to a solution of dichlorobisacetylacetonatotitanium(IV) (1 mol.) in glacial acetic acid gave a pale yellow compound which crystallised from glacial acetic acid as needles, m. p. 153—155° (Found: C, 26.5; H, 3.1; Sb, 17.8; Ti, 7.1. C<sub>15</sub>H<sub>21</sub>Cl<sub>6</sub>O<sub>6</sub>SbTi requires C, 26.5; H, 3.1; Sb, 17.9; Ti, 7.1%).

*Trisacetylacetonatotitanium(IV) Tetrachloroaurate(III)*.—This was prepared by the method of Dilthey<sup>1</sup> (Found: C, 26.7; H, 3.3; Au, 29.1; Ti, 7.0. Calc. for C<sub>15</sub>H<sub>21</sub>AuCl<sub>4</sub>O<sub>6</sub>Ti: C, 26.4; H, 3.1; Au, 28.8; Ti, 7.0%).

*Trisacetylacetonatotitanium(IV) Hexachloroplatinate(IV)*.—This was obtained as a red precipitate by the method of Dilthey<sup>1</sup> (Found: C, 30.9; H, 3.8; Cl, 19.4; Pt, 17.8; Ti, 8.4. Calc. for C<sub>30</sub>H<sub>42</sub>Cl<sub>6</sub>O<sub>12</sub>PtTi<sub>2</sub>: C, 32.8; H, 3.8; Cl, 19.4; Pt, 17.8; Ti, 8.7%). It was not soluble in any solvents suitable for measurement of conductivity or molecular weight.

*Trisacetylacetonatosilicon(IV) Hydrogen Dichloride*.—This was prepared by the method of Dilthey.<sup>2</sup> The cream compound was easily hydrolysed, so all operations were carried out in a dry-box; it had m. p. 85—87° (Found: C, 45.2; H, 5.3; Cl, 17.7. Calc. for C<sub>15</sub>H<sub>22</sub>Cl<sub>2</sub>O<sub>6</sub>Si: C, 45.4; H, 5.4; Cl, 17.8%).

*Trisacetylacetonatosilicon(IV) Tetrachloroferrate(III)*.—(a) Prepared by the method of Dilthey,<sup>2</sup> this had m. p. 189—190° (Found: C, 34.3; H, 4.2; Cl, 26.7; Fe, 10.5. Calc. for C<sub>15</sub>H<sub>21</sub>Cl<sub>4</sub>FeO<sub>6</sub>Si: C, 34.5; H, 4.0; Cl, 27.1; Fe, 10.7%).

(b) Silicon tetrachloride (1 mol.) was added dropwise to a solution of trisacetylacetonatoiron(III) (1 mol.) in glacial acetic acid. The yellow precipitate was crystallised from glacial acetic acid as yellow needles, m. p. 189—190° (Found: C, 34.4; H, 4.0; Cl, 27.3; Fe, 10.6%), identical with the compound prepared as in (a).

*Trisacetylacetonatosilicon(IV) Hexachloroantimonate(V)*.—This was prepared by a similar method to that for the titanium derivative and obtained as cream needles by recrystallisation from chloroform-ether, m. p. 170—172° (Found: C, 27.6; H, 3.5; Cl, 29.6; Sb, 18.3. C<sub>15</sub>H<sub>21</sub>Cl<sub>6</sub>O<sub>6</sub>SbSi requires C, 27.3; H, 3.2; Cl, 32.2; Sb, 18.4%).

*Trisacetylacetonatosilicon(IV) Tetrachloroaurate(III)*.—This, prepared according to the method of Dilthey,<sup>2</sup> crystallised from chloroform-ether as yellow needles (Found: C, 27.1; H, 3.4; Au, 29.9; Cl, 21.3. Calc. for C<sub>15</sub>H<sub>21</sub>AuCl<sub>4</sub>O<sub>6</sub>Si: C, 27.1; H, 3.2; Au, 29.7; Cl, 21.4%).

*Dichlorobisacetylacetonatogermanium(IV)*.—This was prepared, as colourless crystals, by the method of Morgan and Drew,<sup>7</sup> m. p. 236—240° (Found: C, 35.2; H, 4.2; Cl, 20.9. Calc. for C<sub>10</sub>H<sub>14</sub>Cl<sub>2</sub>GeO<sub>4</sub>: C, 35.2; H, 4.2; Cl, 20.8%).

*Trisacetylacetonatogermanium(IV) Tetrachloroferrate(III)*.—(a) Iron(III) chloride (1 mol.) in glacial acetic acid solution was added to a hot solution of dichlorobisacetylacetonatogermanium(IV) (1.5 mol.) in the same solvent; on cooling, a yellow precipitate was formed. The product crystallised as yellow needles from glacial acetic acid, m. p. 184—185° (Found: C, 31.9; H, 3.8; Cl, 25.1; Fe, 9.7. C<sub>15</sub>H<sub>21</sub>Cl<sub>4</sub>FeGeO<sub>6</sub> requires C, 31.7; H, 3.7; Cl, 24.9; Fe, 9.8%).

(b) Germanium(IV) chloride (1 mol.) was added to a solution of trisacetylacetonatoiron(III) in glacial acetic acid, and the resultant yellow precipitate recrystallised from glacial acetic acid, m. p. 184—185° (Found: C, 31.8; H, 3.9; Cl, 24.7; Fe, 9.7%).

<sup>12</sup> A. Weissburger, "Technique of Organic Chemistry," vol. 7, Organic Solvents, Interscience, New York and London, 2nd edn., 1955.

*Trisacetylacetonatogermanium(IV) Hexachloroantimonate(V)*.—This was obtained as a white precipitate by the addition of diethyl ether to a mixture of antimony(V) chloride (1 mol.) and dichlorobisacetylacetonatogermanium(IV) (1 mol.) in chloroform. It crystallised as white *needles* from chloroform–ether, m. p. 161–163° (Found: C, 25.4; H, 3.2; Cl, 30.0; Sb, 17.2.  $C_{15}H_{21}Cl_6GeO_6Sb$  requires C, 25.6; H, 3.0; Cl, 30.2; Sb, 17.3%).

*Dichlorobisacetylacetonatotin(IV)*.—This was obtained as colourless prisms by the method of Morgan and Drew,<sup>8</sup> m. p. 201–203° (Found: C, 30.9; H, 3.8; Cl, 18.3; Sn, 30.3. Calc. for  $C_{10}H_{14}Cl_2O_4Sn$ : C, 31.0; H, 3.6; Cl, 18.3; Sn, 30.5%).

Tin(IV) chloride (3 mol.) was added to a solution of trisacetylacetonatoiron(III) (2 mol.) in glacial acetic acid, and the mixture refluxed for 1 hr. On cooling, a red-brown compound was deposited which contained both tin and iron. However, after four recrystallisations from chloroform–ether a colourless compound was obtained which contained no iron, m. p. 200–203° (Found: C, 30.7; H, 3.8; Cl, 18.1; Sn, 30.8%). The physical properties of this complex were identical with those of dichlorobisacetylacetonatotin(IV) prepared according to Morgan and Drew.<sup>8</sup>

#### Determination of dipole moment in benzene solution.

$10^3 w$	$\Delta\epsilon/w$	$-\Delta V/w$	$\Delta n/w$
37.43	17.01	0.5834	0.0454
53.70	15.35	0.5880	0.0441
69.64	14.45	0.5728	0.0475

Hence  $\tau P = 1709$  c.c.  $\epsilon P = 71.2$  c.c. Whence  $\mu = 8.8$  D.

The dipole moment of dichlorobisacetylacetonatotin(IV) was determined from measurements on a series of benzene solutions of decreasing concentration of the complex. Results are given in the Table.

*Dichlorobisacetylacetonatozirconium(IV)*.—This was obtained as colourless prisms by the method of Jantsch,<sup>9</sup> m. p. 233–235° (Found: C, 33.5; H, 4.9; Cl, 19.7. Calc. for  $C_{10}H_{14}Cl_2O_4Zr$ : C, 33.3; H, 3.9; Cl, 19.6%).

*Chlorotrisacetylacetonatozirconium(IV) Monohydrate*.—Zirconium(IV) chloride (1 mol.) was refluxed for several hours in a benzene solution of acetylacetone (3 mol.). After filtration to remove any undissolved tetrachloride and zirconium dioxide formed by hydrolysis, the filtrate was refluxed until colourless crystals of the complex appeared. Cooling gave the monohydrate as colourless *crystals* which could be recrystallised from benzene solution, m. p. 132–134° after losing water at 100° (Found: C, 40.9; H, 5.2; Cl, 7.9.  $C_{15}H_{23}ClO_7Zr$  requires C, 40.7; H, 5.2; Cl, 8.0%. Loss of weight at 100°/0.1 mm., 3.9%. Calc. for  $1H_2O$ : 4.1%).

The infrared spectrum in hexachlorobutadiene mull showed the presence of water (a broad band at 3570–3050  $cm^{-1}$  which was not present for the anhydrous compound).

*Chlorotrisacetylacetonatozirconium(IV)*.—This could be prepared by vacuum-drying the monohydrate or, better, by recrystallisation from acetylacetone, m. p. 132–134° (Found: C, 42.4; H, 5.0; Cl, 8.3; Calc. for  $C_{15}H_{21}ClO_6Zr$ : C, 42.5; H, 5.0; Cl, 8.4%).

This compound was also prepared by refluxing a mixture of zirconium(IV) chloride (2 mol.) and trisacetylacetonatoiron(III) (3 mol.) in dry diethyl ether. After 1 hr. a heavy yellow oil had been formed, and after separation this oil was extracted with hot dry diethyl ether in a liquid–liquid extraction apparatus. The oil gradually solidified as the impurity, iron(III) chloride, was removed by the ether. The resulting colourless solid was chlorotrisacetylacetonatozirconium(IV), m. p. 132–136° (Found: C, 42.6; H, 5.4; Cl, 8.3%).

*Dichlorobisacetylacetonatohafnium(IV)*.—This could not be obtained by a method similar to that used for the zirconium analogue. Refluxing hafnium(IV) chloride (1 mol.) with acetylacetone (2 mol.) in dry diethyl ether gave the chlorotrisacetylacetonate on cooling. An impure sample of the dichloro-derivative was prepared by suspending finely powdered hafnium(IV) chloride (1 mol.) in dry light petroleum (b. p. 60–80°) at  $-10^\circ$  and slowly adding a solution of acetylacetone (2 mol.) in the same solvent also at  $-10^\circ$ . After allowing the mixture to stand for 1 hr. at this temperature the unreacted hafnium(IV) chloride was filtered off and the filtrate slowly warmed to room temperature. Hydrogen chloride was evolved and colourless crystals appeared. These were removed by filtration and dried *in vacuo*. The *compound* is very easily hydrolysed and reproducible analyses could not be obtained (Found: Cl, 14.7; 13.2.  $C_{10}H_{14}Cl_2O_4Hf$  requires Cl 15.9%).

*Chlorotrisacetylacetonatohafnium(IV)*.—Hafnium(IV) chloride (1 mol.) was refluxed with acetylacetone (3 mol.) in benzene solution with evolution of hydrogen chloride. After several hours the



unreacted hafnium chloride was removed and the filtrate refluxed until crystals appeared. After cooling the solution the colourless crystals were removed and dried *in vacuo*. The complex could be recrystallised from either benzene or acetylacetone, m. p. 154—156° (Found: C, 34.7; H, 4.4; Cl, 7.0.  $C_{15}H_{21}ClO_6Hf$  requires C, 35.2; H, 4.1; Cl, 6.9%). No evidence of the formation of a hydrate was obtained with this compound, unlike the zirconium analogue.

The same complex could also be prepared by refluxing hafnium(IV) chloride (2 mol.) with trisacetylacetonatoiron(III) (3 mol.) in dry diethyl ether. The yellow oil which appeared was treated in a similar way to the zirconium compound and the colourless crystals so obtained were identified by their physical properties as chlorotrisacetylacetonatohafnium(IV), m. p. 154—156° (Found: C, 35.0; H, 4.2; Cl, 7.0%).

*Dichlorobisbenzoylacetonatotitanium(IV)*.—Titanium tetrachloride (1 mol.) was added dropwise to a solution of benzoylacetone (2 mol.) in glacial acetic acid solution. The mixture was refluxed for 10 min. and, after cooling, the red precipitate was collected, washed with glacial acetic acid and dried *in vacuo*. The complex crystallised from glacial acetic acid (Found: C, 54.8; H, 4.2; Cl, 15.8; Ti, 10.7.  $C_{20}H_{18}Cl_2O_4Ti$  requires C, 54.4; H, 4.1; Cl, 16.1; Ti, 10.8%).

*Trisbenzoylacetonatotitanium(IV) Tetrachloroferrate(III)*.—(a) A solution of iron(III) chloride (2 mol.) in glacial acetic acid was added to a solution of dichlorobisbenzoylacetonatotitanium(IV) (2 mol.) in the same solvent. After concentration *in vacuo* the red-brown solid was collected and recrystallised from glacial acetic acid (Found: C, 49.1; H, 3.5; Cl, 19.6; Ti, 6.7.  $C_{30}H_{27}Cl_4FeO_6Ti$  requires C, 49.4; H, 3.7; Cl, 19.4; Ti, 6.6%).

(b) To a solution of trisbenzoylacetonatoiron(III) (1 mol.) in dry carbon tetrachloride was added, dropwise, titanium(IV) chloride (1 mol.). A red oil was formed which, on standing, solidified to give a red-brown precipitate which was collected and recrystallised from glacial acetic acid. It was isomorphous with the product from the previous preparation (Found: C, 50.4; H, 4.2; Cl, 19.2; Ti, 6.5%).

*Dichlorobisbenzoylmethanatotitanium(IV)*.—This compound was prepared by a method similar to that for the benzoylacetonatotitanium derivative (Found: C, 63.3; H, 3.8; Cl, 12.5; Ti, 8.3.  $C_{30}H_{22}Cl_2O_4Ti$  requires C, 63.7; H, 3.9; Cl, 12.6; Ti, 8.5%).

*Trisdibenzoylmethanatotitanium(IV) Tetrachloroferrate(III)*.—This compound was also prepared by two methods similar to those for the benzoylacetonatotitanium derivative.

(a) From dichlorobisbenzoylmethanatotitanium(IV) and iron(III) chloride (Found: C, 59.2; H, 4.0; Cl, 15.9; Ti, 5.1.  $C_{45}H_{33}Cl_4FeO_6Ti$  requires C, 59.0; H, 3.7; Cl, 15.4; Ti, 5.3%).

(b) From trisdibenzoylmethanatoiron(III) and titanium(IV) chloride (Found: C, 59.4; H, 4.2; Cl, 15.3; Ti, 5.1%).

*Chlorotrisbenzoylacetonatozirconium(IV)*.—This, prepared by a method similar to that for chlorotrisacetylacetonatozirconium(IV), had m. p. 122—124° (Found: C, 59.8; H, 4.3; Cl, 5.6. Calc. for  $C_{30}H_{27}ClO_6Zr$ : C, 59.1; H, 4.4; Cl, 5.8%).

The reaction between trisbenzoylacetonatoiron(III) and zirconium(IV) chloride in diethyl ether gave a yellow oil which after continuous extraction with diethyl ether gave a colourless solid, m. p. 122° (Found: C, 59.0; H, 4.0; Cl, 5.9%), identical with the previous sample of chlorotrisbenzoylacetonatozirconium(IV).

*Chlorotrisdibenzoylmethanatozirconium(IV)*.—This, also prepared by a method similar to that for chlorotrisacetylacetonatozirconium(IV), had m. p. 256—258° (Found: C, 67.8; H, 4.6; Cl, 4.2. Calc. for  $C_{45}H_{33}ClO_6Zr$ : C, 67.9; H, 4.2; Cl, 4.5%).

*Trisdibenzoylmethanatozirconium(IV) Tetrachloroferrate(III)*.—(a) From chlorotrisdibenzoylmethanatozirconium(IV) (1 mol.) and iron(III) chloride (1 mol.) in chloroform solution. The yellow complex was crystallised from chloroform—light petroleum. The product contained some chloroform of crystallisation which was easily removed by heating at 80° until no further loss of weight occurred, m. p. 170° (Found: C, 57.9; H, 4.0; Cl, 14.7. Calc. for  $C_{45}H_{33}Cl_4FeO_6Zr$ : C, 56.5; H, 3.5; Cl, 14.8%).

(b) The same complex was also formed by the reaction between trisdibenzoylmethanatoiron(III) and zirconium(IV) chloride in diethyl ether solution, m. p. 170° (Found: C, 57.3; H, 3.9; Cl, 14.8%).

*Trisdibenzoylmethanatozirconium(IV) Tetrachloroaurate(III)*.—Chlorotrisdibenzoylmethanatozirconium(IV) (1 mol.) was refluxed with gold(III) chloride (1 mol.) in chloroform. After filtration, the filtrate was concentrated and light petroleum added, to precipitate an oil which solidified on standing to a yellow solid (Found: C, 48.7; H, 3.1; Cl, 12.7. Calc. for  $C_{45}H_{33}AuCl_4O_6Zr$ : C, 49.0; H, 3.0; Cl, 12.8%).

*Chlorotrisbenzoylacetonatohafnium(IV)*.—The pale yellow complex was obtained by a method

similar to that for chlorotrisbenzoylacetonatozirconium(IV), m. p. 125—128° (Found: C, 51.5; H, 4.0; Cl, 4.9; Hf, 25.3.  $C_{30}H_{27}ClHfO_6$  requires C, 51.6; H, 3.9; Cl, 5.1; Hf, 25.6%). It was isomorphous with the corresponding zirconium derivative.

The reaction between trisbenzoylacetonatoiron(III) (1 mol.) and hafnium(IV) chloride (1 mol.) in dry diethyl ether gave an oil, and after continuous extraction of this oil with ether a pale yellow solid was obtained. This product was identical with the previous sample, m. p. 125—126° (Found: C, 51.7; H, 4.0; Cl, 5.3; Hf, 25.9%).

*Chlorotrisdibenzoylmethanatohafnium(IV)*.—This compound was prepared by a procedure similar to that for the corresponding zirconium derivative, m. p. 258—260° (Found: C, 61.4; H, 3.3; Cl, 3.9.  $C_{45}H_{33}ClHfO_6$  requires C, 61.2; H, 3.8; Cl, 4.0%).

*Trisdibenzoylmethanatohafnium(IV) Tetrachloroferrate(III)*.—Chlorotrisdibenzoylmethanatohafnium(IV) (1 mol.) was refluxed with iron(III) chloride (1 mol.) in chloroform. Light petroleum was added to the cold solution and a yellow oil obtained. After removal of the supernatant liquor the oil was redissolved in chloroform and reprecipitated as yellow crystals by the addition of light petroleum (Found: C, 51.4; H, 3.9; Cl, 13.6.  $C_{45}H_{33}Cl_4FeHfO_6$  requires C, 51.6; H, 3.2; Cl, 13.5%).

The same compound was obtained by refluxing hafnium(IV) chloride (1 mol.) with trisdibenzoylmethanatoiron(III) in ether solution and, after filtration, concentrating the filtrate until crystals appeared (Found: C, 51.9; H, 3.0; Cl, 13.6%).

*Infrared Spectra*.—These were measured on a Grubb-Parsons double-beam grating instrument Type GS2A, using Nujol or hexachlorobutadiene mulls.

*Determination of Dipole Moment*.—Dielectric constants ( $\epsilon$ ) were measured with a resonance bridge using a Muirhead precision air condenser as a reference and a glass cell with gold-fired surfaces for the solution under investigation. The refractive indices of these solutions ( $n$ ) were determined with a Pulfrich refractometer using sodium illumination, and specific volumes ( $v$ ) measured with a U-shaped pycnometer. The dipole moments were calculated by the method of Everard, Hill, and Sutton<sup>13</sup> but the atomic polarisation,  ${}_A P$ , was assumed to be 50%  ${}_E P$ , the value obtained for other metal acetylacetonates.<sup>14</sup>

*Conductivity*.—This was measured with a normal dip-type cell with bright platinum electrodes. For conductometric titrations the same electrode system was placed in a cell fitted with a burette and magnetic stirrer. The cell was totally enclosed so that a dry atmosphere could be maintained during the titration.

*Molecular Weights*.—These were determined cryoscopically in nitrobenzene solution using a Beckman thermometer in an enclosed system fitted with vertical magnetic stirring.

*Analyses*.—Carbon and hydrogen were determined by normal micro-methods, and chlorine by potentiometric titration with silver nitrate using silver and calomel electrodes. Titanium was determined by the reduction with liquid zinc amalgam of a sulphuric acid solution of the complex after first removing any oxidisable material by the addition of potassium permanganate. The reduction was carried out in an inert atmosphere and the tervalent titanium thus produced titrated with standard ceric sulphate using ferroin as indicator. Other elements were determined by standard methods.

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<sup>14</sup> I. E. Coop and L. E. Sutton, *J.*, 1938, 1269.