511. β-*Diketone Complexes of Titanium*

By M. Cox, J. Lewis, and R. S. Nyholm

A series of titanium(III) complexes, $[Ti(diketone)_3]^0$, has been prepared, using as ligands the β-diketones acetylacetone, benzoylacetone, dibenzoylmethane, trifluorothenoylacetone, and 3-cyanoacetylacetone. All the complexes are intensely coloured with magnetic moments in the range 1·56—1·67 B.M. They are readily oxidised in air to give titanium(IV) derivatives, $[TiO(diketone)_2]^0$, which have also been studied. The physical properties indicate that these oxidation products possess a Ti=O linkage; molecular-weight data, conductivity studies, and infrared spectra agree with the monomeric formulation.

THE physical properties, such as spectra and magnetism, of metal complexes having a d^1-configuration have not been studied very much primarily owing to the relative scarcity of compounds of this type. Indeed, in the first transition series, only titanium(III) and vanadium(IV) give d^1-octahedral complexes. For vanadium(IV), the presence of the vanadyl group (VO^+) in most of these complexes appears to dominate their magnetism and spectra. The corresponding complexes of titanium(III) have received little attention, primarily owing to the ease of oxidation; it was therefore decided to study the reactions of β-diketones with tervalent titanium in order to obtain derivatives of the type $[Ti(diketone)_3]^0$. The electron spin resonance spectrum of trisacetylacetonatotitanium(III), $[Ti(acac)_3]^0$, had been studied [1] and the compound had been prepared from pure titanium(III) chloride.[2] The deep blue complex was easily oxidised by atmospheric oxygen to a titanium(IV) derivative with the empirical formula $[TiO(acac)_2]$.[2] As the trisacetylacetonate is comprised of three symmetrical chelate rings it might be expected that distortion from the highest symmetry, D_3, would be small. However, the electron spin resonance,[1] visible spectrum,[3,4] and magnetic measurements [5] indicate that strong trigonal distortion occurs in the complex.

The oxidation product, $[TiO(acac)_2]_n$, is of interest because of the possibility that it contains the titanyl group Ti=O. The corresponding vanadium(IV) derivative, $[VO(acac)_2]^0$, has a monomeric square-pyramidal structure with the vanadium atom slightly above the plane of two acetylacetonate rings, the oxygen atom being at the apex of the pyramid.[6] The titanium compound can be formulated as a monomer containing a Ti=O link, a dimer with two oxygen bridges, or a polymer containing –Ti–O–Ti–O– chains. Evidence for

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[4] T. W. Piper and R. L. Carlin, *Inorg. Chem.*, 1963, **2**, 260.
[5] B. N. Figgis, J. Lewis, and F. E. Mabbs, *J.*, **1963**, 2473.
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the last structure has been provided by the *X*-ray analysis of the titanyl compounds $TiOF_2$ [7] and $TiOSO_4$,[8] and it is believed that most simple titanyl compounds have this structure. However, a titanyl phthalocyanine (Pc) derivative, TiOPc, has been prepared; [9] this is isomorphous with the corresponding vanadium(IV) compound, and its infrared spectrum has a sharp band at *ca.* 970 cm.$^{-1}$ which is consistent with the presence of an M=O group,[10] whereas other titanyl compounds [11] show broad bands in the range 800—900 cm.$^{-1}$. This absorption at lower frequencies may be associated with the lower bond order of the –Ti–O–Ti–O– system. Some evidence for the dimeric structure with oxygen bridges can be obtained from the physical properties of another compound with the empirical formula $[TiO(acac)_2]^0$. This derivative has been prepared by hydrolysis of the alkoxy-compound $[Ti(acac)_2(OR)_2]$; [12] it is dimeric in benzene solution and hence probably contains the oxygen-bridge structure, although other workers observed a monomeric molecular weight, also in benzene solution.[13] We have shown that the oxidation product of $[Ti(diketone)_3]$ is monomeric and a non-electrolyte, and hence the titanyl structure with a Ti=O link is most likely.

RESULTS AND DISCUSSION

A number of derivatives of titanium(III) with substituted β-diketones have been prepared (Table 1). All have the general formula $[Ti(diketone)_3]^0$ and are monomeric non-electrolytes in nitrobenzene and nitromethane solutions. Atmospheric oxidation to the titanium(IV) complex occurs readily in solution but in the solid state the derivatives of the less volatile ligands, *e.g.*, trifluorothenoylacetone and dibenzoylmethane are more stable

The magnetic susceptibilities of the compounds were measured by the Gouy method, using sealed glass tubes to prevent oxidation during the measurement. The paramagnetic susceptibility results indicate the presence of one unpaired electron, magnetic moments being between 1·56—1·67 B.M. The titanium(III) derivatives of acetylacetone and benzoylacetone have been studied over a temperature range; [5] the results are difficult to correlate with current theories involving allowance for axial distortion of the ligand field, and electron delocalisation. A magnetic moment of 1·68 B.M. for the acetylacetonate was obtained at room temperature by Verkade (cf. ref. 4).

TABLE 1

Physical properties of complexes of titanium(III) with β-diketones

Complex	Colour	Λ_M * (mhos mole^{-1})	Molecular wt. Found (g./l.)	Molecular wt. Reqd.	μ_{eff} (B.M.) at 293° K
$Ti(acac)_3$	Blue	0·04	365(16·0)	345	1·56
$Ti(CNacac)_3$	Purple	2·8	396(10·35)	384	—
$Ti(bzac)_3$	Green	0·5	517(18·75)	531	1·67
$Ti(bzbz)_3$	Green	4·2	699(5·44)	718	1·66
$Ti(TTA)_3$	Green	0·7	791(7·14)	753	1·66

* 10^{-3}M-Solution in $MeNO_2$; 1 : 1-electrolyte in $MeNO_2$ 10^{-3}M soln., 70—100 mhos mole^{-1}.

acac = Acetylacetone; CNacac = 3-cyanoacetylacetone; bzac = benzoylacetone; bzbz = dibenzoylmethane; TTA = trifluorothenoylacetone.

The visible spectra were measured in benzene solution. Care was taken to prevent oxidation, by using degassed solvent and performing all operations in an atmosphere of purified nitrogen. The spectrum of an octahedrally co-ordinated titanium(III) ion consists of a single asymmetric band at 18,000—20,000 cm.$^{-1}$ of intensity 10—50 l. mole^{-1} cm.$^{-1}$,[14]

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TABLE 2

Absorption spectra of tris-β-diketonetitanium(III) compounds

Complex	Bands (cm.$^{-1}$)	Intensity (l. mole^{-1} cm.$^{-1}$)	Complex	Bands (cm.$^{-1}$)	Intensity (l. mole^{-1} cm.$^{-1}$)
$Ti(acac)_3$	15,150sh	870	$Ti(bzac)_3$.........	12,800	800
	16,500	1120		14,080	880
	17,860sh	930		15,870sh	670
	20,830sh	430			
	25,250sh	750	$Ti(TTA)_3$	12,060	2600
				13,510	2380
$Ti(CNacac)_3$ ...	16,130sh	810		15,290sh	1320
	17,300	1000		20,410	1590
	18,520sh	910		21,600	1560
	20,830sh	670			

sh = shoulder.

which arises from distortion of a regular octahedral field and can be attributed to two overlapping *d–d* bands which are *ca.* 1000—3000 cm.$^{-1}$ apart. The tris-β-diketonetitanium(III) compounds are all deeply coloured in the solid state, and in solution their absorption spectra consist of intense bands in the region 12,000—25,000 cm.$^{-1}$ (Table 2) with extinction coefficients about 1000 l. mole^{-1} cm.$^{-1}$, which is large for the *d–d* transitions expected to occur in this region. Nevertheless, in the case of the trisacetylacetonate the major component of the band system has been assigned to a *d–d* transition which is modified by considerable mixing of the metal and ligand systems through low-lying π-orbitals.[4] The shoulders which occur on this band are attributed to vibrational fine structure.[3,4]

All these β-diketone derivatives are easily oxidised in air to diamagnetic titanium(IV) compounds, with release of a ligand molecule. The molecular structure of these compounds is interesting because of the three possible structures, namely, a monomeric titanyl with a Ti=O link, a dimer with oxygen bridges, or a polymer with –Ti–O–Ti–O– chains. The physical properties of these derivatives, prepared by oxidation of the corresponding titanium(III) compounds, are summarised in Table 3. In nitromethane solution the compounds are non-electrolytes, and they are monomeric in freezing nitrobenzene.

The preparation of the complex $[TiO(acac)_2]_2$ by hydrolysis of the titanium(IV) compound $[Ti(acac)_2(OR)_2]$ [12] was repeated, and the physical properties are included in Table 3. In benzene solution it behaved as a dimer as previously described [12] but in nitrobenzene a monomeric value was obtained, presumably owing to breaking of the oxygen bridges in the more polar solvent. Because of the possibility of this depolymerisation in solution, the solid-state infrared spectra of these complexes were measured. It has been shown in a number of cases [10] that M=O bonds give rise to a band at *ca.* 1000 cm.$^{-1}$. The infrared spectrum of $[TiO(acac)_2]$ in Nujol has a band of medium intensity at 1087 cm.$^{-1}$ which is not observed for $[Ti(acac)_3]$. This band is also absent in the dimer $[TiO(acac)_2]_2$, but in the spectrum of this compound another band, strong and broad, appears at 829 cm.$^{-1}$ and probably arises from the Ti–O–Ti bond. Similar strong broad bands have been observed [11]

TABLE 3

Physical properties of oxotitanium(IV) complexes

Complex	Λ_M* (mhos mole^{-1})	Molecular weight Found (g./l. in $PhNO_2$)	Calc. for monomer
$[TiO(acac)_2]$	3·7	282(3·14)	262
		298 † (3·42)	—
$[TiO(CNacac)_2]$	1·60	263(2·86)	288
$[TiO(bzac)_2]$	0·8	384(3·96)	386
$[TiO(bzbz)_2]$	0·04	482(5·18)	512
$[TiO(TTA)_2]$	0·04	498(2·96)	536
$[TiO(acac)_2]_2$ ‡	0·38	272(4·72)	262
		526 † (4·74)	—

* 10^{-3}M-Solution in $MeNO_2$. † In benzene solution. ‡ Prepared as in ref. 12.

in the infrared spectra of $TiOSO_4$ (820 and 920 cm.$^{-1}$) and $K_2TiO(oxalate)_2$ (800 and 900 cm.$^{-1}$).

Unfortunately, the infrared spectra of the remaining β-diketone derivatives are too complex in the 900—1100 cm.$^{-1}$ region for the observation of any Ti=O stretching frequency, but no new strong broad bands appear between 800 and 900 cm.$^{-1}$ on oxidation, which could be attributed to a –Ti–O–Ti– polymeric structure. Therefore, the structure of these oxy-β-diketonetitanium(IV) complexes, prepared by oxidation of the titanium(III) chelates, is still doubtful, but all the above evidence seems to indicate a monomeric structure with a Ti=O link.

EXPERIMENTAL

Solvents were carefully degassed before use by freezing and remelting several times *in vacuo*. Nitrogen (British Oxygen Co. " white-spot ") was further purified by passing over activated copper wire at 300°, bubbling through chromium(II) sulphate solution, and drying with magnesium perchlorate.

Tris-β-diketonetitanium(III) *Complexes*.—These compounds were all prepared by the same method given below, all operations being carried out in a nitrogen atmosphere.

A solution of titanium(III) sulphate was prepared by the zinc amalgam reduction of a freshly precipitated titanium(IV) oxide hydrate, and to it was added an excess of the ligand in aqueous sodium carbonate solution. The deeply coloured mixture was warmed gently for several minutes, and the solid complex was extracted with benzene, leaving a pale purple aqueous layer. The benzene layer was removed and dried over anhydrous sodium carbonate, the sodium carbonate was filtered off and washed with benzene, and the combined filtrate and washings were concentrated in a vacuum. When all the solvent had been removed the bath temperature was raised to sublime off the excess ligand, leaving behind the titanium(III) complex, which was ground up under nitrogen, purified by resublimation, and stored in ampoules under a vacuum.

The ligands used, except 3-cyanoacetylacetone, were commercial samples redistilled or sublimed before use. 3-Cyanoacetylacetone was prepared by the action of cyanogen chloride on acetylacetone in sodium hydroxide solution at 0°. The free ligand was obtained from the sodium salt by the addition of concentrated hydrochloric acid and recrystallised from light petroleum (Found: C, 57·6; H, 6·0; N, 11·9. Calc. for $C_6H_7NO_2$: C, 57·6; H, 5·6; N, 11·2%).

Trisacetylacetonatotitanium(III) [Found: Ti(III), 13·8. $C_{15}H_{21}O_6Ti$ requires Ti(III) 13·9%]. This compound was oxidised too rapidly for accurate determination of carbon and hydrogen.

Tribenzoylacetonatotitanium(III) [Found: C, 67·0; H, 5·3; Ti(III), 9·0. $C_{30}H_{27}O_6Ti$ requires C, 67·7; H, 4·6; Ti(III), 9·0%].

Trisdibenzoylmethanatotitanium(III) [Found: C, 75·6; H, 5·3; Ti(III), 6·6. $C_{43}H_{33}O_6Ti$ requires C, 67·7; H, 4·6; Ti(III), 6·7%].

Tristrifluorothenoylacetonatotitanium(III) [Found: C, 42·8; H, 2·4; F, 22·2; S, 12·5; Ti(III), 6·1. $C_{27}H_{18}F_9O_6S_3Ti$ requires C, 43·0; H, 2·4; F, 22·7; S, 12·8; Ti(III), 6·3%].

Tris-3-cyanoacetylacetonatotitanium(III) [Found: C, 47·5; H, 4·5; N, 10·4; Ti(III), 12·4. $C_{18}H_{18}N_3O_6Ti$ requires C, 46·8; H, 4·7; N, 10·9; Ti(III), 12·5%].

Oxotitanium(IV) *Derivatives*.—All the above titanium(III) compounds were readily oxidised in air. To prepare the oxotitanium(IV) compounds the corresponding titanium(III) complex was exposed to the atmosphere and the free ligand was removed from the resulting yellow solid by washing with light petroleum (b. p. 60—80°) or by recrystallisation of the titanium(IV) compound from benzene.

Oxobisacetylacetonatotitanium(IV) (Found: C, 45·3; H, 5·6; Ti, 18·4. $C_{10}H_{14}O_5Ti$ requires C, 45·8; H, 5·4; Ti, 18·3%).

Oxobisbenzoylacetonatotitanium(IV) (Found: C, 61·6; H, 4·7; Ti, 12·4. $C_{20}H_{18}O_5Ti$ requires C, 61·6; H, 4·7; Ti, 12·4%).

Oxobisdibenzoylmethanatotitanium(IV) (Found: C, 69·3; H, 4·8; Ti, 9·6. $C_{30}H_{42}O_5Ti$ requires C, 70·3; H, 4·7; Ti, 9·3%).

Oxobistrifluorothenoylacetonatotitanium(IV) (Found: C, 39·8; H, 1·8; F, 19·5; S, 12·0; Ti, 8·8. $C_{18}H_{12}F_6O_5S_2Ti$ requires C, 40·4; H, 2·6; F, 21·2; S, 12·0; Ti, 8·9%).

Oxobis-3-cyanoacetylacetonatotitanium(IV) (Found: C, 40·5; H, 4·0; N, 9·5; Ti, 16·7. $C_{12}H_{12}N_2O_5Ti$ requires C, 41·7; H, 4·2; N, 9·7; Ti, 16·6%).

µ-Dioxo-di[bisacetylacetonatotitanium(IV)]. This compound was prepared by the method of Yamamoto and Kambara[12] from the hydrolysis of dipropoxybisacetylacetonatotitanium(IV) (Found: C, 45·3; H, 5·5; Ti, 18·2. Calc. for $C_{20}H_{28}O_{10}Ti_2$: C, 45·8; H, 5·4; Ti, 18·3%).

Infrared Spectra.—These were measured on a Grubb–Parsons double-beam grating spectrometer type GS2A using Nujol mulls prepared in an atmosphere of carbon dioxide.[14]

Visible Spectra.—For the titanium(III) compounds these were measured on benzene solutions prepared in the absence of air using an apparatus similar to that described previously.[15]

Magnetic Susceptibility.—It was difficult to obtain uniform packing of the compounds in glass tubes for measurement by the Gouy method. The best method was to grind the powdered compound with a glass ball in an ampoule to which was sealed the magnetic susceptibility tube. Small quantities of the finely powdered material were introduced into the tube and firmly packed by tapping. This procedure was continued until sufficient compound had been introduced into the tube. The tube was then sealed off and tapped again until no further contraction of sample length occurred. After the magnetic susceptibility had been measured the sealed tip of the tube was removed and the compound reanalysed for titanium(III) content to ensure that oxidation had not taken place. Finally, the diamagnetic correction of the empty tube was measured.

Conductivity.—This was measured using a cell described previously.[14]

Molecular Weight.—This was determined cryoscopically using a totally enclosed system for the preparation of solutions in degassed nitrobenzene. The depression of the freezing point was measured by a Beckman type thermometer in a cell with vertical magnetic stirring.

Analysis.—The titanium(III) content of the complexes was determined by dissolving the solid in acidified standard iron(III) alum solution and titrating the excess iron(III) with standard titanium(III) sulphate solution using potassium thiocyanate as indicator. This procedure was carried out under a blanket of carbon dioxide to prevent atmospheric oxidation.

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DEPARTMENT OF CHEMISTRY, UNIVERSITY COLLEGE,
GOWER STREET, LONDON W.C.1.

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