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Mixed Ligand Diketonate Complexes of Tervalent Titanium

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Reaction of $TiCl_3\cdot 3thf$ (thf = tetrahydrofuran) with β-diketones gives the complexes dichloro-β-diketonatobis(tetrahydrofuranato)titanium(III). The spectroscopic and magnetic properties of the complexes have been investigated. Their e.p.r. spectra indicate structures with cis-*chlorines and* cis-*thf ligands.*

Introduction

According to current views on Ziegler–Natta catalysis [1] an active catalyst requires a weakly held ligand or vacant coordination site *cis*- to the metal–alkyl bond. Catalytic activity is dependent on the relative strengths of the metal–monomer and metal–alkyl bonds which in turn will be determined by the nature and oxidation state of the metal and by the nature of any ancillary ligands. As the first part of an effort to produce Ziegler–Natta catalysts based on tervalent titanium in which the properties of the ancillary ligands could be varied in a systematic way we have prepared and investigated the physicochemical properties of some Ti(III)–diketonate complexes.

Two classes of Ti(III)–diketonate complex have been reported previously: $Ti(dik)_3$ (dik = acac [2–7], bzacac [3], dbm [3, 4], trifluorotheonylacetone [3], CN-acac [3], and F_6-acac [8]) and $TiCl_n(acac)_{3-n}$ (n = 1, 2) [9]. The complexes reported here are representatives of a new class: $TiCl_2(dik)(thf)_2$*.

Experimental

All operations were carried out in an atmosphere of dry oxygen-free nitrogen. Tetrahydrofuran (thf) was dried over sodium and distilled directly into reaction vessels. $TiCl_3\cdot 3thf$ was prepared according to the literature method [10]. Acetylacetone (acacH), benzoylacetone (bzacacH) and dibenzoylmethane (dbm) were commercial materials and were used without further purification.

Reactions of $TiCl_3\cdot 3thf$ with β-diketones

(a) With acacH. A solution of acacH (0.6 cm^3, 6.0 mmol) in thf (10 cm^3) was added to a stirred solution of $TiCl_3\cdot 3thf$ (2.22 g, 6.0 mmol) in thf (80 cm^3) at room temperature. A very dark red solid precipitated almost immediately. The mixture was stirred for a further 10 min. and its volume then reduced to *ca.* 20 cm^3. Filtration yielded a microcrystalline solid which was washed with n-hexane and dried *in vacuo* to give maroon *dichloroacetylacetonatobis(tetrahydrofuran)titanium(III)*, (I) (79%).

The bzacac and dbm complexes (Table I) were prepared in an exactly analogous manner.

TABLE I. Analytical, Magnetic Moment and E.p.r. Data.

Complex	Yield/%	Colour	Analyses[a]				μ_{eff}/μ_B	g-values[b]			
			C %	H %	Cl %	Ti %		g_1	g_2	g_3	g_{iso}
I Ti(acac)$Cl_2\cdot$2thf	79	Maroon	43.1 (43.8)	6.6 (6.5)	19.6 (19.8)	13.2 (13.6)	1.74	1.990 1.992	1.944 1.947	1.876 1.882	1.943
II Ti(bzacac)$Cl_2\cdot$2.5thf	68	Very Dark Green	52.2 (52.3)	6.3 (6.4)	15.3 (15.6)	10.4 (10.2)	1.72	1.989 1.990	1.946 1.939	1.888 1.903	1.945
III Ti(dbm)$Cl_2\cdot$2thf	70	Dark Blue	56.8 (56.5)	5.8 (5.8)	14.6 (14.8)	9.9 (9.8)	1.74	1.989 1.991	1.944 1.939	1.913 1.916	1.946

[a]Calculated values in parentheses. [b]Values for 298K and 123K respectively, solid state.

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*Whilst this paper was in preparation a brief note appeared which mentioned the preparation of $TiCl_2(dik)(thf)_2$ (dik = dipivolylmethane). L. E. Manzer, *J. Am. Chem. Soc., 99,* 277 (1977).

TABLE II. I.r. Spectra: ^{a}Band Maxima (cm^{-1}) and Assignments.

dik = acac	bzacac	dbm	Band Assignments
1595 w	1585 w, sh	1590 w	νC---C)
	1580	1582 w	
1523 vs, br	1536 s	1517 s, sh	ν(C---O)
	1524 s	1506	
1032	1030 sh (1065 m)	1034 w, sh	ν_{asym}(C–O–C)
1018	1022	1020 m	
860 s	863 s (917 w)	856 s, br	ν_{sym}(C–O–C)
836 s	846 m		
	790 s	780 m, sh	aromatic π(C–H)
	713 vs	775 s	
		716 vs	
	685 m	687 s	
542 m	545 m	546 w	π (ring) (chelate)
446 s	430 m	458 w	
356 vs	360 vs, br	345 s	ν(Ti–O) (chelate)
334 vs		329 s	ν(Ti–Cl)
304 vs	303 s, br	302 s	

^{a}In Nujol mulls.

U.v. and visible diffuse-reflectance (against magnesium oxide), solution**, and i.r. spectra were recorded with Optica C4DR, Unicam SP 700, and Perkin–Elmer 621 spectrophotometers, respectively. Magnetic susceptibilities were measured on powdered samples by the Faraday method with Hg[Co(NCS)$_4$] as calibrant. E.p.r. spectra were recorded on a Varian E-9 spectrometer operating in the dual-cavity mode (frequency = 9.3 GHz). Conductivities were measured with a Cambridge Instruments conductivity bridge. Titanium was determined colorimetrically using hydrogen peroxide. Carbon, hydrogen, nitrogen and chlorine were determined by standard microanalytical techniques.

Results and Discussion

TiCl$_3$ dissolved in thf to give a light-blue solution containing TiCl$_3$·3thf. The addition of a β-diketone to this solution results in the rapid precipitation of an intensely coloured solid. Elemental analyses of the solid reaction products I–III (Table I) support their formulation as TiCl$_2$(dik)2thf·nthf (dik = acac, dbm, n = 0; dik = bzacac, n = 0.5). The dry complexes are air-sensitive surviving for only a few minutes in moist air. They are moderately soluble in thf, chloroform, acetone and ethanol but only sparingly soluble or insoluble in non-polar solvents. Their solutions begin to change colour to orange or orange–yellow within seconds on exposure to air. Stability to air diminishes along the series: dik = bzacac > acac > dbm. This sensitivity to oxidation and/or hydrolysis prevented the determination of molecular weights. The complexes are non-electrolytes in thf; this suggests that they may be regarded as six-coordinate species derived by replacement of one chlorine and one thf from TiCl$_3$·3thf, a suggestion which is supported by spectroscopic evidence (*vide infra*).

I.r. Spectra

Principal i.r. absorptions and their assignments are listed in Table II. The absence from the spectra of the complexes of a weak band at *ca.* 3550 cm^{-1} and a strong broad band at *ca.* 1600 cm^{-1} attributable respectively to ν(OH) and ν(C=O) of the enol forms of the β-diketones [12], and the general band pattern is characteristic of chelated β-diketonates [13].

Bands associated with ν(C–O–C) of coordinated thf [14] appear as two sets of doublets at *ca.* 835–865 cm^{-1} and 1020–1030 cm^{-1} except for the dbm complex where the lower frequency doublet structure is not resolved. Additional bands assigned to uncoordinated thf are present in the spectrum of the bzacac complex. This accords with the elemental analysis of this complex (Table I).

The positions of Ti–X(X=Cl, Br, I) absorption bands have been shown to depend on the oxidation state of the metal and on the geometry of the Ti–X species [15]. TiCl$_3$·3thf has strong bands at 353 and 326 cm^{-1} with a shoulder at 292 cm^{-1}. Three bands appear in this region in the spectra of the acac and dbm complexes. A maximum of two are expected for TiCl$_2$(dik)2thf assuming site symmetry effects to be

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**An apparatus similar to that designed by Clark [11] was used to prepare solutions for electronic spectroscopy.

absent. We assign the lower frequency pair tentatively to ν(Ti–Cl) and the highest frequency band to ν(M–O) of the metal–diketonate system. The latter assignment is supported by the occurrence of a ν(M–O) band at 355 cm^{-1} in the spectrum of Cr(acac)$_3$ [13].

Electronic Spectra

The intensities of the bands in the electronic spectra of the complexes (Table III) lie towards the lower end of the range usually associated with charge transfer transitions. M.O. calculations on M^{III}(acac)$_3$ complexes [6] place the metal d-orbital energies between those of the uppermost π- and lowest π^*-orbitals of the acac$^-$ ligand. Thus the possibilities for charge transfer are $\pi \rightarrow t_{2g}$, $\pi \rightarrow e_g$, $t_{2g} \rightarrow \pi^*$ and $e_g \rightarrow \pi^*$ (in O_h symmetry) [14]. In pseudo-tetrahedral symmetry such as that proposed [9] for acacTiCl$_2$ the same transitions can occur but their relative energies would be different. Three of these transitions are possible sources of visible absorption for the d^1 Ti(III) ion. The similar optical electronegativities of [16] acac$^-$ (2.7) and Cl$^-$ (3.0) suggest that the relative positions of the metal and acac-ligand orbitals are not likely to be altered by the partial replacement of acac$^-$ by Cl$^-$. This contention is supported by the similarities between the electronic spectra of Ti(acac)$_3$, Ti(acac)$_2$Cl, Ti(acac)Cl$_2$ and Ti(acac)Cl$_2$·2thf (Table III). Lengthening the conjugation path in the ligand by successive substitution of methyl by phenyl groups would be expected to diminish the π–π^* energy gap and thus to diminish the energies of the charge transfer transitions. There is a marked drop in the energies of the electronic absorption bands on going from Ti(acac)Cl$_2$·2thf to the bzacac analogue and a much smaller drop between this and the dbm complex.

Magnetic Susceptibilities and E.p.r. Spectra

In accordance with their formulation as Ti(III) complexes, compounds I–III exhibit magnetic moments close to the spin-only value for a d^1 ion (Table I).

Polycrystalline samples of compounds I–III gave clearly defined three line spectra at room temperature (Table I). Line widths varied from *ca.* 12 gauss for the acac complex to *ca.* 50 gauss for the dbm complex. Titanium hyperfine coupling was just discernible on the central *g*-feature in the 123K spectrum of the acac complex. Three well-separated *g*-features are characteristic of five coordinate Ti(III) complexes or of six coordinate complexes with less than axial symmetry [17, 18]. The ranges of *g*-values spanned by complexes I–III are similar to those of the six coordinate complexes TiCl$_3$·LL$^1{}_2$ TiCl$_3$(C$_4$H$_8$O$_2$)$_2$(MeCN), TiCl$_3$(C$_4$H$_8$O$_2$)(C$_4$H$_8$O) and Et$_4$N[TiCl$_4$2L] (L = MeCN, C$_4$H$_8$O$_2$ or C$_4$H$_8$O) for which *cis*-structures have been proposed [18]. Only broad single *g*-features were observed for solid TiCl$_2$-

TABLE III. Electronic Absorption and Diffuse Reflectance Spectra of Ti^{III} Diketonate Complexes.[a]

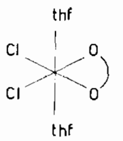
Ti(acac)$_3$^{b} [9]	Ti(acac)$_2$Cl^{b,c} [9]		Ti(acac)Cl$_2$^{b,c} [9]		Ti(acac)Cl$_2$·2thf^{d,e}		Ti(bzac)Cl$_2$·2.5thf^{d,c}		Ti(dbm)Cl$_2$·2thf^{d,e}	
(37.4)										
(35.7)										
(34.5)										
32.4										
25.6 [690]^f	26.6		25.6			(25.8)				(25.6)
					24.0	(25.4) [400]		23.2 [693]	23.6	
(21.3)	(24.6)		(21.8)	21.9 [472]	21.4	21.6 [473]	21.4	20.4 [322]	20.0	21.8 [763]
			(20.4)							20.6 [630]
(18.2)	(18.5)	(18.8) [417]	18.8	18.7 [519]	(18.7)	(19.2) [380]				
			17.6			18.4 [454]				
16.8 [1510]	16.6	17.4 [430]	16.9		(17.4)		(16.5)	17.0 [670]		
							15.8	15.7 [745]	(15.8)	(15.8) [650]
						13.0 [*ca.* 330]	(14.7)	15.0 [700]	(14.7)	14.4 [620]

[a] Band positions in kK, figures in parentheses indicate shoulders. [b] In CHCl$_3$. [c] In KCl discs. [d] In thf. [e] In MgCO$_3$ discs. [f] Molar extinction coefficients.

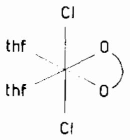
(acac) and TiCl(acac)$_2$ [9] the former is thought to have a pseudo-tetrahedral structure and the latter to be a dimer with chlorine bridges.

Fluid solution spectra of compounds I–III in thf exhibited isotropic *g*-features with *g*-values close to 2 (Table I). *g*-Values of this order are usually associated with quenching of the electron's orbital angular momentum by distortions from octahedral symmetry and are consistent with the proposed *cis*-chlorine, *cis*-thf structure for the complexes. Only for TiCl$_2$-(acac)2thf was it possible to resolve hyperfine splitting due to coupling of the unpaired electron spin with the titanium nuclei ^{47}Ti (I = 5/2, 7.7%) and ^{49}Ti-(I = 7/2, 5.5%). The value of 15 gauss for A$_{iso}$(Ti) is typical for Ti(III) complexes and indicates essentially complete localization of the single d-electron on the titanium atom. Strong *g*-anisotropy was evident in the spectra of frozen solutions, as with the solids. Individual titanium hyperfine splittings were not resolved.

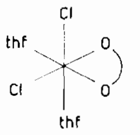
Neutral complexes of the type Ti(dik)Cl$_2$·2thf where dik is a symmetrical diketonate may exist as the *trans* isomers A or B, or as the *cis* isomer C.



A



B



C

Isomers A and B have axial symmetry and would therefore be expected to give rise to a two line e.p.r. spectrum corresponding to g$_\parallel$ and g$_\perp$. *Cis* isomer C on the other hand has three unique axes and is expected to produce a three line spectrum. The lower symmetry of isomer C is also in accord with the appearance of a well-defined e.p.r. spectrum at room temperature. *Cis* structure C is proposed for the acac and dbm complexes in the solid state, the similarities between the solution and solid-state diffuse reflectance electronic spectra suggest that the solid state structure is retained in solution. The unsymmetrical bzacac complex should give a three line e.p.r. spectrum in either the *cis* or the *trans* isomeric form. However the *cis* structure is preferred on the basis of the similarities in the electronic spectra of all three complexes. A cis D$_3$ structure has been established for TiCl$_3$·3thf, thus it appears from the evidence presented here that one *cis* chlorine–thf pair has been replaced by the dik ligand to give the *cis* structure C.

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