Contribution from the Department of Chemistry,
Sir George Williams Campus, Concordia University, Montreal, Quebec, H3G-1M8, Canada

Five-Coordinate Titanium(IV) Complexes. Infrared Spectral Studies on X_3Ti(diketonato) and XY_2Ti(diketonato) Complexes and the Crystal and Molecular Structure of Di-μ-chloro-tetrachlorobis(2,4-pentanedionato)dititanium(IV)

N. SERPONE,* P. H. BIRD, A. SOMOGYVARI, and D. G. BICKLEY

Received March 8, 1977 AIC70179B

A series of apparent five-coordinate titanium(IV) complexes of the type X_3Ti(dik) and XY_2Ti(dik) [where X = Y and $X \neq Y$; X = Y = F, Cl, or Br; dik = 2,4-pentanedionate anion (acac), benzoylacetonate anion (bzac), diisobutyrylmethanate anion (dibm), and dipivaloylmethanate anion (dpm)] have been prepared by reacting TiX_4 with Hdik or with $Ti(dik)_2X_2$ in equimolar amounts. Those species containing bromine appear to be less stable to decomposition and to be more moisture sensitive. Solid state (Nujol) infrared spectra for Cl_3Ti(acac) and FCl_2Ti(acac) are reported and compared with those of the parent six-coordinate $Ti(acac)_2X_2$ (X = F, Cl) complexes. Absence of the terminal Ti–F stretching frequency in the spectrum of FCl_2Ti(acac) indicates at least a dimeric structure for this species. The low solubility of the above species in various organic solvents precluded solution infrared spectra. The structure of di-μ-chloro-tetrachlorobis(2,4-pentanedionato)dititanium(IV), $[Cl_3Ti(acac)]_2$, has been determined by x-ray single-crystal diffraction methods using Mo Kα radiation (0.71069 Å). The unit cell data are space group $P2_1/n$ (No. 14), $Z = 2$, $a = 8.381$ (5) Å, $b = 10.734$ (5) Å, $c = 10.517$ (6) Å, $\alpha = 90.00°$, $\beta = 93.92$ (3)°, $\gamma = 90.00°$, and $V = 994.573$ Å^3. Diffractometer data were collected using a coupled θ–2θ scan technique and final unweighted and weighted R values after anisotropic full-matrix refinement of all nonhydrogen atoms and isotropic full-matrix refinement of all hydrogen atoms (with rigid body constraints on methyl hydrogens) were 0.031 and 0.029, respectively. The structure is centrosymmetric as required by symmetry and consists of a cyclic dimer with the two titanium(IV) atoms linked by two chlorine bridges. The geometry at titanium is a distorted octahedron with bond angles between adjacent donor atoms in the range 81.77 (4)–97.43 (5)°, and bond angles between the three titanium–donor atom trans bonds in the range 166.50 (9)–173.17 (5)°. The titanium–chlorine bridge distances are 2.418 (1) and 2.569 (1) Å; the two titanium–terminal chlorine bond lengths are 2.214 (1) and 2.250 (1) Å. The O–O "bite" distance of 2.582 (4) Å in $[Cl_3Ti(acac)]_2$ is considerably shorter than those reported in other acetylacetonate complexes (e.g., $Zr(acac)_4$, 2.67 Å). This is rationalized in terms of a greater effective nuclear charge at titanium induced by the electronegative chlorines, and supports the notion of significant pπ–dπ type bonding in the Ti(acac) planar heterochelated ring.

Introduction

A coordination number of five appears to be quite rare for titanium(IV) complexes.[1] It does occur in $[TiCl_2(OR)_2]_2$ complexes, where R = phenyl[2] and ethyl,[3] and has recently been observed in the $[TiCl_2NSiMe_3]_n$ polymer.[4,5] The square-pyramidal $[TiOCl_4]^{2-}$ anion is the only known monomeric five-coordinate titanium(IV) complex in the solid state.[6] In contrast, the propensity of apparently five-coordinate titanium(IV) complexes to achieve octahedral geometry by forming dimers with bridging ligands is well known.[1]

Interest has developed in recent years concerning the nature of this apparent five-coordination in titanium(IV) complexes of the type $Ti(dik)X_3$ (where dik is a diketonate ligand and X is halogen or alkoxy group). Mehrotra and co-workers[7–10] observed that $TiCl_4$ and acetylacetone ($C_5H_8O_2$; Hacac) react in a 1:1 mole ratio to yield a complex having the Cl_3Ti(acac) stoichiometry. They also noted that the $(OR)_3Ti$(dik) complexes underwent the disproportionation reaction

$$2(OR)_3Ti(dik) \rightleftharpoons Ti(dik)_2(OR)_2 + Ti(OR)_4$$

In cases of bulky R groups, molecular weights were close to the monomeric formulation; less bulky R groups resulted in molecular weights significantly above those required for a monomer.

Thompson and co-workers[11] have also reported the X_3Ti(3-CH_3-acac) (X = Cl, Br) complexes and found them to be monomeric nonelectrolytes in nitrobenzene; unfortunately, complicated temperature-dependent NMR spectra in nitrobenzene precluded the assignment of stereochemistry. In contrast, Holloway and Sentek,[12] on the basis of NMR evidence, have postulated that these apparently five-coordinate X_3Ti(dik) species are in fact weakly associated compounds of the well-known four- and six-coordinate TiX_4 and $Ti(dik)_2X_2$ complexes, respectively. Subsequent studies on the Cl_3Ti(bzac) (bzac = anion of benzoylacetone) species were interpreted by Thompson and co-workers[13] in terms of a five-coordinate structure participating in the equilibrium reaction above. More recently, Alyea and Merrell[14] have presented evidence for five-coordinate titanium(IV) complexes of the type $(OR)_3Ti$(chel), in which chel is a uninegative, bidentate ligand with an ethane backbone (e.g., $OCH_2CH_2N(CH_3)_2$).

We, earlier, reported our preliminary crystallographic studies on the $Cl_3Ti(C_5H_7O_2)$ complex.[15] The present work reports the full crystal and molecular structural data on this apparent five-coordinate titanium(IV) complex and some infrared spectral studies we have carried out on this and analogous complexes.

Experimental Section

Materials. Dichloromethane, benzene, and hexane were dried by continuous reflux over calcium hydride chips and distilled therefrom whenever needed. Titanium tetrachloride and acetylacetone (Fisher Certified Reagents), titanium tetrabromide and tetrafluoride (Alfa Inorganics), benzoylacetone (Hbzac, Aldrich), and Eastman Kodak Chemical diisobutyrylmethane (Hdibm) and dipivaloylmethane (Hdpm) were used as received without further purification.

Syntheses. Generally, either one of the two methods described below was used to prepare these X_3Ti(dik) and mixed XY_2Ti(dik) complexes of apparent five-coordinate geometry.

Method A for X_3Ti(dik). A dichloromethane (or benzene) solution of the diketone was added dropwise to a dichloromethane (or benzene) solution of the titanium tetrahalide in a 1:1 molar ratio under continuous stirring in an inert atmosphere of nitrogen. The mixture was stirred and continually purged with a stream of dry N_2 until no more evolution of HCl (or HBr) was noticeable. Upon cooling, crystals of the desired product were obtained, filtered, and dried in vacuo for ca. 10–12 h. Where no crystallization occurred on cooling, the solution was concentrated to approximately one-half its initial volume and hexane added slowly until turbidity appeared. Cooling in a freezer (ca. 0 °C) brought about crystallization.

Method B. Dihalobis(diketonato)titanium(IV), $Ti(dik)_2X_2$, and titanium tetrahalides were mixed in a 1:1 molar ratio in dichloromethane (or benzene) solution and stirred for ca. 2 h in an inert atmosphere of nitrogen. Crystallization and collection of the product were effected as in method A. The six-coordinate $Ti(dik)_2X_2$

Table I. Summary of "$XY_2Ti(dik)$" Complexes Prepared

dik	X	Y	Comments
acac	F	Cl	Stable[a]
acac	F	Br	Unstable
acac	Cl	F	Reaction occurs, intractable oil
acac	Cl	Cl	Stable
acac	Br	Br	Unstable
acac	Cl	Br	Unstable
acac	Br	Cl	Unstable
dibm	F	Cl	Stable
dibm	Cl	Cl	Stable
dpm	F	Cl	Stable
dpm	Cl	Cl	Stable
dpm	Br	Br	Unstable
bzac	F	Cl	Stable
bzac	Cl	Cl	Stable

[a] With respect to decomposition by atmospheric moisture. Those depicted as "stable" may be handled in the atmosphere for only very short periods.

Table II. Summary of Crystal Data and Intensity Collection for $[Cl_3Ti(acac)]_2$

A. Crystal Parameters at 18 °C with λ(Mo Kα) 0.710 69 Å

a	8.381 (5) Å	Mol wt	506.74 (for $[Cl_3Ti(acac)]_2$; $Z = 2$)
b	10.734 (5) Å		
c	10.517 (6) Å	ρ_{calcd}	1.692 g cm^{-3}
α	90.00°	ρ_{exptl}	1.78 g cm^{-3}
β	93.92 (3)°	μ	16.4 cm^{-1}
γ	90.00°	Crystal dimension	0.2 × 0.2 × 0.2 mm
V	944.573 $Å^3$	Estd transmission factors	$t_{min} = 72\%$; $t_{max} = 80\%$
Space group	$P2_1/n$ (No. 14)		

B. Measurement of Intensity Data

Radiation	Mo Kα	
Monochromator	Graphite; $2\theta_{002} = 12.1°$	
Crystal to detector dist	25 mm	
Detector	Scintillation detector and pulse height analyzer set for 100% of Mo Kα peak	
Attenuators	Ni foil used for intensities $>10^4$ Hz	
Takeoff angle	3.0°	
Detector aperture	4 × 4 mm square	
Scan type	Coupled θ-2θ, 1° min^{-1}	
Scan length	$\Delta(2\theta)$ = (base width + 0.692 tan θ) starting (base width/2) below the Mo $K\alpha_1$ peak	
Rotation axis	*a*	
Reflections measd	±*h*, +*k*, ±*l*	
Max and min 2θ	45.0°, 4.0°	
Scan base width	1.3°	
Std reflection	002	
Variation of standards	±3%	
No. of reflections collected	1301	
No. of reflections with $I > 3\sigma(I)$	1092	
Weighted *R*	0.029	includes hydrogen atoms
Unweighted *R*	0.031	

complexes were prepared by standard procedures.[16,17]

Table I summarizes the various products prepared and comments on the stability toward hydrolysis by atmospheric moisture. The purity of these products was verified by infrared spectroscopy (absence of OH and free carbonyl stretching frequencies at 3300 cm^{-1} and above 1600 cm^{-1}, respectively) and nuclear magnetic resonance spectroscopy (absence of free diketone proton resonances) and by melting point determinations.[18]

Infrared Spectra. Solid-state infrared spectra were recorded on both Perkin-Elmer 457 and 225 grating infrared spectrophotometers as Nujol mulls between KBr windows. The samples were prepared in a glovebag under anhydrous conditions.

Space Group and Unit Cell Parameter Determination. A suitable crystal of the apparent five-coordinate $Cl_3Ti(acac)$ complex was chosen and sealed in a capillary in a glovebag under nitrogen to avoid atmospheric moisture hydrolysis.

Weissenberg and precession photographs taken with Mo Kα radiation were used to determine the space group (Table II) and to check the crystal for defects other than a normal mosaic structure. Accurate cell dimensions were obtained on a fully automated Picker FACS-1 diffractometer. Values of 2θ, ω, χ, and ϕ obtained for 12 Bragg reflections centered at both positive and negative 2θ values, and appropriately averaged, were used in the least-squares refinement of the unit cell parameters and the crystal orientation matrix. The programs employed for this procedure were those supplied by the Picker Nuclear Co.

Data Collection and Reduction. Unique intensity data were collected on the diffractometer to $2\theta = 45°$, which included all reasonably strong reflections. The background was estimated from a measured curve. Instrument stability was monitored by measuring the intensity of a standard reflection after every 30 cycles and by determining the intensity of the reciprocal axis reflections with both positive and negative indices before and after data collection.

A locally written program, which determines an overall isotropic thermal parameter and an approximate scale factor, was employed to perform data reduction. Reflection intensities, *I*, and standard deviations, $\sigma(I)$, were computed as $I = [N - Bt_s/t_b]$ and $\sigma(I) = [N + B(t_s/t_b)^2 + (0.02N)^2]^{1/2}$, where *N* and *B* are the total counts accumulated during the scan period, t_s, and the total background counting time, t_b, respectively. Data for which $I < 3\sigma(I)$ were rejected; the remaining intensities were corrected for Lorentz and polarization effects. The expression used to effect the correction is $(Lp)^{-1} = \sin 2\theta_s(\cos^2 2\theta_m + 1)/(\cos^2 2\theta_m + \cos^2 2\theta_s)$, where $2\theta_m$ and $2\theta_s$ are the diffraction angles at the monochromator and the sample crystal, respectively. No corrections were made for absorption.

Structure Solution and Refinement. The Concordia University CDC 6400 computer was used for all computations.[19] The structure was solved from conventional Patterson syntheses based on "sharpened data" which revealed the titanium atom position. Structure factor calculations followed by Fourier syntheses revealed the remaining nonhydrogen atom positions. After five cycles of isotropic refinement, a difference Fourier synthesis showed the usual peaks attributable to anisotropic motion of the atoms included in the model, and also peaks at positions expected for all hydrogen atoms, albeit very diffuse in the case of the methyl groups. The refined positions of the carbon atoms of the methyl groups and those of the carbonyl carbons were used together with the clearest hydrogen peaks of each methyl group to define idealized positions for all three methyl hydrogens of each group. Thus, the hydrogen atoms were positioned 1.6 Å apart at the corners of an equilateral triangle and placed symmetrically 0.98 Å from their carbon atom. The two sets of hydrogen atoms were then included in the least-squares refinement as rigid groups, each with single group isotropic thermal parameters. The C3 hydrogen was also allowed to refine isotropically. Refinement converged with $R = 0.031$ and $R_w = 0.029$. No parameter shifted by more than 0.2 of its standard deviation in the final cycle of refinement. The discrepancy indices referred to above are $R = [\sum(||F_o| - |F_c||)/\sum|F_o|]$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, where $w = [\sigma(F_o)]^{-2}$. The error in an observation of unit weight (the "goodness of fit"), defined by $[\sum w(|F_o| - |F_c|)^2/(n - m)]^{1/2}$, where *n* and *m* are the numbers of observations and parameters varied, respectively, reduced to 1.25 after three cycles. Scattering factors for neutral atoms were taken from the compilation of Ibers.[20] Anomalous dispersion corrections were not applied.

The final positional and thermal parameters of the nonhydrogen atoms are summarized in Table III while those of the hydrogen atoms are collected in Table IV. Structure factor amplitudes are presented in Table V.[21]

Results and Discussion

Preparation of the apparent five-coordinate titanium(IV) species, $XY_2Ti(dik)$, via direct reaction of the octahedral $Ti(dik)_2X_2$ complex with TiY_4 in an equimolar ratio proved to be the simplest and most convenient synthetic route, according to the reaction

$$Ti(dik)_2X_2 + TiY_4 \rightleftharpoons 2XY_2Ti(dik) \text{ or } [XY_2Ti(dik)]_2$$

$$X = Y, X \neq Y$$

Table I summarizes the reactions attempted; some of these products[8,13,18] and $X_3Ti(C_6H_9O_2)$,[11] X = Cl, Br, and $C_6H_9O_2$ = 3-methyl-2,4-pentanedionate anion, have been reported previously. In the case of $X_3Ti(C_6H_9O_2)$ and $Cl_3Ti(bzac)$

Table III. Final Positional and Thermal Parameters[a] for the Nonhydrogen Atoms with Estimated Standard Deviations

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ti	0.015 037 (79)	0.158 716 (65)	−0.075 155 (78)	0.00841 (11)	0.00528 (7)	0.00958 (7)	0.00058 (7)	0.00040 (8)	−0.00001 (7)
Cl1	0.234 28 (12)	0.201 11 (10)	0.052 97 (12)	0.0095 (2)	0.0065 (1)	0.0114 (1)	−0.0007 (1)	−0.0016 (1)	−0.0010 (1)
Cl2	0.104 94 (13)	0.229 68 (11)	−0.254 60 (12)	0.0152 (2)	0.0100 (1)	0.0098 (1)	0.0018 (1)	0.0029 (1)	0.0030 (1)
Cl3	0.097 06 (11)	−0.052 18 (9)	−0.118 51 (10)	0.0104 (2)	0.0052 (1)	0.0079 (1)	0.0012 (1)	0.0023 (1)	−0.0008 (1)
O1	−0.093 34 (28)	0.304 81 (23)	−0.030 32 (27)	0.0090 (4)	0.0051 (3)	0.0108 (4)	0.0014 (3)	0.0006 (3)	−0.0008 (3)
O2	−0.194 75 (28)	0.109 63 (24)	−0.154 63 (26)	0.0077 (4)	0.0070 (3)	0.0090 (4)	0.0009 (3)	−0.0003 (3)	−0.0007 (3)
C1	−0.264 63 (53)	0.475 22 (43)	0.000 05 (50)	0.0147 (9)	0.0062 (5)	0.0143 (7)	0.0031 (5)	0.0035 (6)	0.0001 (5)
C2	−0.240 43 (48)	0.345 57 (38)	−0.044 99 (41)	0.0107 (7)	0.0061 (4)	0.0081 (5)	0.0011 (5)	0.0022 (5)	0.0010 (4)
C3	−0.359 37 (52)	0.271 70 (44)	−0.097 14 (46)	0.0082 (7)	0.0093 (6)	0.0111 (6)	0.0032 (5)	0.0007 (6)	−0.0009 (5)
C4	−0.334 91 (45)	0.155 74 (39)	−0.150 70 (39)	0.0101 (7)	0.0079 (5)	0.0060 (5)	0.0000 (5)	0.0009 (4)	0.0010 (4)
C5	−0.470 32 (54)	0.079 92 (46)	−0.208 44 (52)	0.0100 (7)	0.0111 (6)	0.0128 (7)	−0.0005 (6)	−0.0018 (6)	−0.0018 (6)

[a] Anisotropic thermal parameters are applied as $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

Table IV. Hydrogen Atom Positional and Isotropic Thermal Parameters

Atom	x	y	z	B, Å^2
H31	−0.4501 (47)	0.3007 (40)	−0.1068 (41)	1.7 (1.1)
H11	−0.1625 (37)	0.5245 (45)	−0.0036 (43)	4.9 (1.0)
H12	−0.3395 (45)	0.5190 (48)	−0.0559 (37)	4.9 (1.0)
H13	−0.2984 (52)	0.4701 (46)	0.0837 (37)	4.9 (1.0)
H51	−0.4947 (73)	0.1164 (47)	−0.2824 (50)	7.4 (1.0)
H52	−0.4510 (61)	−0.0115 (40)	−0.2166 (54)	7.4 (1.0)
H53	−0.5693 (62)	0.0838 (48)	−0.1490 (45)	7.4 (1.0)

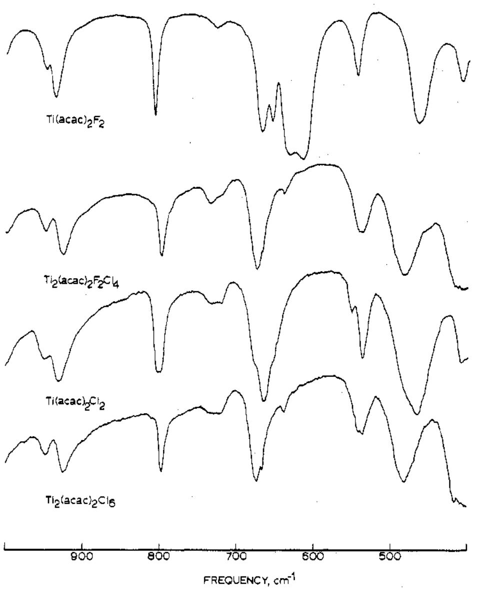

Figure 1. Infrared spectra for solid $Ti(acac)_2F_2$, $[FCl_2Ti(acac)]_2$, $Ti(acac)_2Cl_2$, and $[Cl_3Ti(acac)]_2$ in Nujol in the frequency range 1000–400 cm^{-1}.

Table VI. Infrared Frequencies for Solid $Ti(acac)_2X_2$ and $[X_3Ti(acac)]_2$ Complexes in Nujol[a]

Ti-$(acac)_2F_2$[b]	$[FCl_2Ti(acac)]_2$	Ti-$(acac)_2Cl_2$[b]	$[Cl_3Ti(acac)]_2$[c]	Possible mode[d]
947 m	948 m	948 m	947 m	$\nu(C{-}CH_3)$
935 ms	926 ms	930 ms	924 ms	
806 ms	799 ms	802 ms	798 ms	$\pi(C{-}H)$
		678 sh		
669 s	676 s	666 s	675 s	$\nu(Ti{-}O)$
	641 w	652 sh	668 sh	
			640 w	
634 vs				$\nu(Ti{-}F)_{ter}$
615 vs				$\nu(Ti{-}F)_{ter}$
556 m				
546 m	541 m, br	553 m	544 m	
			539 m	
466 s, br	485 s, br	472 s, br	483 s, br	$\nu(Ti{-}O)$
(412 m)		411 m	420 s	
	ca. 400 s[e]		399 s	$\nu(Ti{-}Cl)_{ter}$
		(389 sh)		$\nu(Ti{-}Cl)$
		(378 s)		$\nu(Ti{-}Cl)$
(356 m)		(372 s)		
(311 w)		(317 m)	322	$\nu(Ti{-}O)$
			276	$\nu(Ti{-}Cl)_{br}$
(256 w)		(265 w)		
			246	$\nu(Ti{-}Cl)_{br}$
		(222 w)		
			199	
			165	

[a] Key: sh, shoulder; s, strong; v, very; br, broad; m, medium; w, weak. [b] Band positions agree with those reported by Lowry.[22] Values in parentheses are taken from ref 22. [c] Values below 420 cm^{-1} were taken on a Beckman IR-11 infrared spectrophotometer (we thank Professor D. W. Thompson for these measurements). [d] According to ref 22 and 23. [e] Values below 400 cm^{-1} have not been determined.

complexes, infrared, molecular weight, and conductance data support the nonionic and monomeric five-coordinate nature and oxygen chelation by the bidentate $C_6H_9O_2$ and bzac ligands. Further, for $X_3Ti(dpm)$ where X = Cl or Br, conductivity and molecular weight data[18] also indicate that these are nonionic and monomeric in nitrobenzene solutions.

In general, products containing bromine were observed to be less stable to decomposition and more moisture sensitive than their chloro or mixed halo (F, Cl) analogues; poor quality solid-state infrared spectra were obtained. A reaction occurred between $Cl_2Ti(acac)_2$ and TiF_4 but no solid product could be isolated; only intractable oils formed.

In this study, we have focused our attention principally on the $FCl_2Ti(dik)$, dik = acac, bzac, dibm, and dpm, and $Cl_3Ti(acac)$ complexes.

Infrared Spectra. The parent $Ti(dik)_2F_2$ complexes exhibit an intense, broad absorption centered at ca. 620 cm^{-1} assigned to a terminal Ti–F stretching frequency.[22,23] On reaction with $TiCl_4$ to form the "five-coordinate" species, the $\nu(Ti{-}F)$ band in the parent complex should shift to higher frequency[24] upon going from six- to five-coordination. Where the Ti–F moiety forms a bridging unit in a dimeric structure such as $[FCl_2Ti(dik)]_2$, the $\nu(Ti{-}F)_{ter}$ band should be replaced by a $\nu(Ti{-}F)_{br}$ band at lower frequency.

Infrared spectra for the $Ti(acac)_2F_2$, "$FCl_2Ti(acac)$", $Ti(acac)_2Cl_2$, and "$Cl_3Ti(acac)$" complexes in the 1000–400-cm^{-1} region are illustrated in Figure 1; band positions and possible vibrational modes are listed in Table VI. The spectrum of $Ti(acac)_2F_2$ reveals two $\nu(Ti{-}F)_{ter}$ bands at 634 and 615 cm^{-1} in agreement with those reported earlier.[22] These bands are absent from the spectra of the "$FCl_2Ti(acac)$", $Ti(acac)_2Cl_2$, and "$Cl_3Ti(acac)$" complexes. No additional band(s) appears in the higher frequency region of the "$FCl_2Ti(acac)$" spectrum that might be correlated with a vibration of the parent Ti-$(acac)_2F_2$ complex, as would be expected from the formation of a five-coordinate complex. Thus, the Ti–F stretching frequency has been shifted to a lower frequency and must result from the formation of a dimeric unit with bridging fluorine groups. No earlier reports of values of $\nu(Ti{-}F)_{br}$ in titanium(IV) complexes are available.

Monocyclopentadienyltitanium(III) halides, $(\eta^5\text{-}C_5H_5)TiX_2$, are at least dimeric and probably polymeric in the solid state.[25] The X = F complex has recently been reported;[26] a strong band at 470 cm^{-1} was assigned to the bridging Ti–F stretching mode. It appears that $\nu(\text{Ti–F})_{\text{br}}$ should increase[24] with an increase in oxidation state, and therefore it would not be inconceivable to find $\nu(\text{Ti–F})_{\text{br}}$ in the $[FCl_2Ti(acac)]_2$ complex at ca. 500 cm^{-1}.

Solid-state structures of the $Ti_2Cl_9^-$ and $Ti_2Cl_{10}^{2-}$ anions have been reported;[27] differences between $(\text{Ti–Cl})_{\text{br}}$ and $(\text{Ti–Cl})_{\text{ter}}$ bond distances are 0.28 and 0.20–0.24 Å, respectively. From the assignment of $\nu(\text{Ti–Cl})_{\text{ter}}$ and $\nu(\text{Ti–Cl})_{\text{br}}$ for the $Ti_2Cl_9^-$ anion[28] the ratio $\nu(\text{Ti–Cl})_{\text{br}}/\nu(\text{Ti–Cl})_{\text{ter}}$ falls in the range 0.55–0.74. As the $Ti_2Cl_{10}^{2-}$ anion, which bears greater structural resemblance to the $[FCl_2Ti(acac)]_2$ complex, has a slightly smaller difference in Ti–Cl bond lengths, the above ratio is expected to be slightly larger in this dianion. Consequently, extension of this range (0.55–0.74) to the $[FCl_2Ti(acac)]_2$ dimer, assuming similar ratios involving Ti–F bonds, predicts $\nu(\text{Ti–F})_{\text{br}}$ to occur in the 340–460-cm^{-1} region. Unfortunately, bands ascribable to terminal Ti–Cl stretching modes occur around 400 cm^{-1} for the $[FCl_2Ti(acac)]_2$ complex and therefore preclude assignment of the $\nu(\text{Ti–F})_{\text{br}}$ mode. However, as noted earlier, absence of $\nu(\text{Ti–F})_{\text{ter}}$ is strong evidence for a dimeric species involving fluorine bridges in $[FCl_2Ti(acac)]_2$.

Analogous observations were made on the same series of "$FCl_2Ti(dik)$" complexes in which dik is bzac, dibm, and dpm. Unfortunately, the presence of the phenyl groups, when dik is bzac, and the apparent overlap of ligand (or ν(Ti–O)) vibrations with ν(Ti–F) of the $Ti(dik)_2F_2$ parent complexes, when dik is dibm and dpm, preclude unequivocal implications about the nature of these species in the solid state.

In the case of the $[Cl_3Ti(acac)]_2$ species, the presence of bands at 276 and 246 cm^{-1}, not present in the spectrum of the parent $Ti(acac)_2Cl_2$ complex, suggests these two bands to be attributable to $\nu(\text{Ti–Cl})_{\text{br}}$ modes. This is also in keeping with the earlier work on $Ti_2Cl_9^-$ anion[28] for which bridging Ti–Cl stretching vibrations were reported at 268 and 230 cm^{-1} and the more recent report[5] on the $[Cl_2TiNSiMe_3]_2$ dimeric structure for which $\nu(\text{Ti–Cl})_{\text{ter}}$ occurs at 427 cm^{-1}, consistent with five-coordination at titanium, and $\nu(\text{Ti–Cl})_{\text{br}}$ was observed at 230 cm^{-1}. Interestingly, the solution infrared spectrum of the latter species reveals the terminal Ti–Cl stretching mode at 470 cm^{-1}; this increase was attributed[5] to a decrease in the coordination number of the titanium atom from five- to four-coordination. We attempted to run solution infrared spectra on the $[FCl_2Ti(acac)]_2$ species in various organic solvents in the hope of observing the terminal Ti–F stretching frequency in the elusive five-coordinate $FCl_2Ti(acac)$ species; however, the very slight solubility of this compound precluded such observations.

The results presented here contrast with the earlier observations by Thompson and co-workers[13] who suggested five-coordination for the "$Cl_3Ti(dik)$", dik = acac and bzac, species in the solid state on the basis of an increase (ca. 15–19 cm^{-1}) in the $\nu(\text{Ti–Cl})_{\text{ter}}$ stretching mode with respect to the corresponding vibration in the six-coordinate $Ti(dik)_2Cl_2$ complexes. As noted earlier, however, other data appear to suggest five-coordination at titanium(IV) for several of the above species in solution.

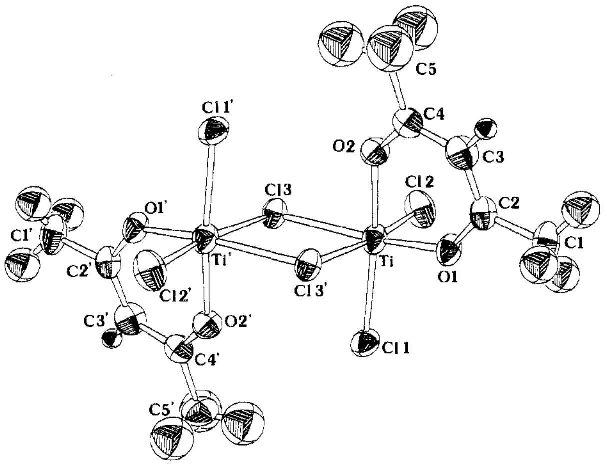

Figure 2. ORTEP plot of the molecular structure of the $[Cl_3Ti(acac)]_2$ dimer illustrating the numbering scheme.

Table VII. Intramolecular Bond Distances (Å) and Bond Angles (deg) and Esd's

	Bond Distances		
Ti–Cl1	2.250 (1)	C1–H12	0.95 (4)
Ti–Cl2	2.214 (1)	C1–H13	0.94 (4)
Ti–Cl3	2.418 (1)	C2–C3	1.360 (6)
Ti–O1	1.888 (3)	C3–C4	1.387 (6)
Ti–O2	1.966 (3)	C3–H31	0.82 (4)
Ti–Cl3′	2.569 (1)	C4–C5	1.492 (6)
O1–C2	1.307 (5)	C5–H51	0.88 (5)
O2–C4	1.278 (4)	C5–H52	1.00 (4)
C1–C2	1.488 (6)	C5–H53	1.07 (5)
C1–H11	1.01 (4)		
	Bond Angles		
Cl1–Ti–Cl2	97.43 (5)	C2–C1–H13	107.3 (3.0)
Cl1–Ti–Cl3	94.08 (4)	H11–C1–H12	104.0 (3.7)
Cl1–Ti–Cl3′	86.74 (4)	H11–C1–H13	112.0 (3.8)
Cl1–Ti–O1	93.99 (9)	H12–C1–H13	112.2 (3.6)
Cl1–Ti–O2	168.18 (9)	O1–C2–C1	115.0 (4)
Cl2–Ti–Cl3	92.50 (5)	O1–C2–C3	120.8 (4)
Cl2–Ti–Cl3′	173.17 (5)	C1–C2–C3	124.2 (4)
Cl2–Ti–O1	97.16 (9)	C2–C3–C4	124.2 (4)
Cl2–Ti–O2	94.38 (9)	C3–C4–C5	121.7 (4)
Cl3–Ti–Cl3′	81.77 (4)	C2–C3–H31	118.4 (3.0)
Cl3–Ti–O1	166.50 (8)	C4–C3–H31	116.8 (3.0)
Cl3–Ti–O2	85.78 (8)	O2–C4–C3	121.5 (4)
O1–Ti–O2	84.10 (11)	O2–C4–C5	116.8 (4)
O1–Ti–Cl3′	87.91 (9)	C4–C5–H51	103.9 (3.7)
O2–Ti–Cl3′	81.54 (8)	C4–C5–H52	116.6 (3.0)
Ti–Cl3–Ti′	98.23 (4)	C4–C5–H53	109.8 (2.7)
Ti–O1–C2	135.59 (25)	H51–C5–H52	112.9 (4.7)
Ti–O2–C4	132.82 (26)	H51–C5–H53	110.8 (4.7)
C2–C1–H11	110.1 (2.6)	H52–C5–H53	103.0 (4.1)
C2–C1–H12	111.3 (2.9)		

The Crystal and Molecular Structure, $[Cl_3Ti(acac)]_2$. The structural analysis demonstrates that in the solid state the apparent five-coordinate $Cl_3Ti(acac)$ complex exists as the dimer, di-μ-chloro-tetrachlorobis(2,4-pentanedionato)dititanium(IV), with two chlorine atoms bridging the two titanium atoms. Figure 2 illustrates the molecular structure of the dimer and the atom numbering scheme; Figure 3 depicts a stereographic view of the molecular packing. Selected bond distances and bond angles are collected in Table VII. Only normal van der Waals contacts were observed, thereby excluding strong intermolecular interactions.

As shown in Figure 2, the two $Cl_2Ti(acac)$ fragments of the dimer are joined by Cl3 and Cl3′. The Ti_2Cl_2 ring unit is planar as required by the symmetry. The bond angle at titanium is 81.77 (4)° and at chlorine is 98.23 (4)°, while the titanium–titanium and chlorine–chlorine distances are 3.772 (1) and 3.267 (2) Å, respectively. The geometry at titanium is a distorted octahedron with bond angles between adjacent donor atoms ranging from 81.77 (4) to 97.43 (5)° while bond angles defined by the trans bonds are 166.50 (9)° (Cl3–Ti–O1), 168.18 (9)° (Cl1–Ti–O2), and 173.17 (5)° (Cl2–Ti–Cl3′). Such octahedral distortion at titanium appears common in several other chlorine-bridged titanium(IV) complexes.

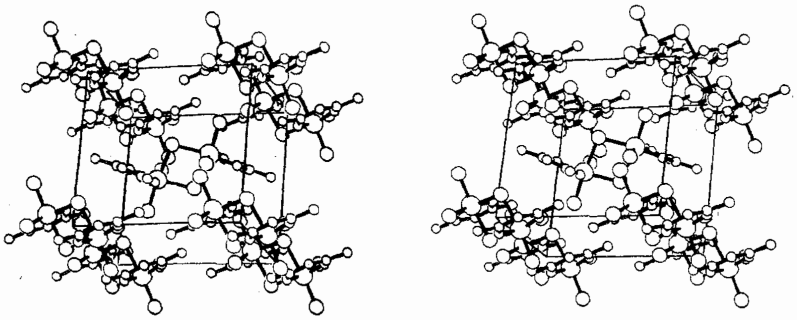

Figure 3. Stereographic view of the molecular packing.

Table VIII. Deviations from the Least-Squares Plane for the Acetylacetonate Group

Atom	Dev, Å	Atom	Dev, Å
Ti	0.042	C2	−0.042
O1	−0.002	C3	0.041
O2	−0.067	C4	0.028

Thus, for example, bond angles between adjacent donor atoms range from 79.08 (5) to 100.23 (7)° in $[TiCl_4{\cdot}CH_3COOC_2H_5]_2$ and 78.5 (3) to 98.2 (4)° in $[TiCl_4{\cdot}OPCl_3]_2$; the corresponding bond angles across the trans bonds are 166.28 (5)–169.77 (10)° for the former ethyl acetate dimer[29] and 165.0 (4)–173.0 (6)° in the latter compound.[30] Similar distortions have also been reported in the oxygen-bridged titanium(IV) dimer, $[TiCl(acac)_2]_2O{\cdot}CHCl_3$[31] and $[TiO(acac)_2]_2$.[32]

The bond lengths in the planar (see Table VIII) chelated (acac) ligand are O1–C2, 1.307 (5) Å; C2–C3, 1.360 (6) Å; C3–C4, 1.387 (6) Å; and O2–C4, 1.278 (4) Å. The mean values for the corresponding bond distances for a variety of metal acetylacetonates of varying geometry and oxidation state of the central metal ion are,[33] respectively, d(O–C) = 1.27 (1) Å and $d(C–C_i)$ = 1.40 (2) Å. Thus, O1–C2 is significantly longer and C2–C3 significantly shorter. Of more importance are the titanium–donor atom bond distances. For example, the Ti–O1 distance is 1.888 (3) Å and the Ti–O2 is 1.966 (3) Å, shorter than the Ti–O(acac) distances of 1.97 and 2.06 Å in $[TiO(acac)_2]_2$[32] and 1.985 (5) Å in bis(2,4-pentanedionato)bis(2,6-diisopropylphenoxo)titanium(IV).[34] Interestingly, the Ti–O1 bond is trans to the longer (and therefore weaker) Ti–Cl3 bond (2.418 (1) Å), and the Ti–O2 is trans to the shorter (and stronger) titanium–terminal chlorine bond Ti–Cl1 (2.250 (1) Å). Also, the titanium–terminal chlorine bond lengths show some differences which are outside experimental error; the longer Ti–Cl1 (2.250 (1) Å) is opposite to the Ti–O2 bond while the shorter Ti–Cl2 (2.214 (1) Å) is trans to the bridge Cl3′. These variations in bond lengths afford two possible explanations. First, the oxygen donor atoms O1 and O2 have a greater trans influence than the chlorine donor atoms. Such trans influence has also been postulated to explain the variations in the lengths of the three Ti–O bonds in the $[TiO(acac)]_2$ dimer.[32] Secondly, titanium(IV) has available vacant 3d orbitals that are potential π acceptors; the presence of such electronegative substituents as chlorine should increase the effective nuclear charge at titanium resulting in some contraction of the 3d orbitals. This contraction will reduce the energies between the d orbitals and the oxygen lone pair and thereby enhance pπ–dπ bonding. Considerable π-type bonding in titanium acetylacetonate complexes has also been suggested earlier in the $Ti(acac)_3^+$ cation[35] as being partially responsible for the low-field shift in the proton NMR resonances, and in a variety of titanium(IV) diketonates with regard to spectral shifts in the charge-transfer band.[22] Finally, it is interesting to note that the Ti-terminal chlorine distances in the present six-coordinate titanium dimer are longer than those in $TiCl_4$ (2.185 Å)[36] and comparable to those in the five-coordinate $[TiCl_2{\cdot}NSiMe_3]_2$ dimer (2.21–2.22 Å)[5] while the difference of 0.15 Å in the titanium–bridge chlorine distances is larger than the 0.07 Å difference found in the chlorine-bridged dimer $[TiCl_2{\cdot}NSiMe_3]_2$.[5]

The O1–O2(acac) bite in $[Cl_3Ti(acac)]_2$ is considerably shorter (2.582 (4) Å) than that found in other acetylacetonate systems. Lingafelter[33] has indicated that, in several of the first-row transition metal acetylacetonates, the only effect on the geometrical parameters in the acetylacetonate residue of varying the metal ion is a variation in the O–O bite distance and that such a variation is clearly not due to differences in the metal radii. Rather, the O–O bite distance is shortened by increased oxidation state of the metal (e.g., Co(II) 2.96 Å, Mn(III) 2.81 Å, and Zr(IV) 2.67 Å). Also, the O–O bite in the bis(diisopropylphenoxo)bis(2,4-pentanedionato)titanium(IV) complex is 2.66 Å,[37] nearly the same as that of $Zr(acac)_4$. That the O–O bite is comparatively short in the present Ti(IV) dimer suggests an increased effective nuclear charge at titanium and supports our notion of significant pπ–dπ bonding in the Ti(acac) heterochelated rings.

Solution Structure. There is no doubt that in solution this $[Cl_3Ti(acac)]_2$ dimer undergoes cleavage to give a true five-coordinate species as suggested for the benzoylacetonate analogue from conductivity, molecular weight, and NMR spectral data.[13] A more complete NMR spectral investigation in these types of complexes will be reported in a forthcoming publication.[38] Suffice it to note that in solution, $[X_3Ti(dik)]_2$ breaks up to yield $X_3Ti(dik)$ which subsequently disproportionates into the well-known six-coordinate $Ti(dik)_2X_2$ and TiX_4. This cleavage is not unexpected for chlorine-bridged dimers. It occurs in $[TiCl_2{\cdot}NSiMe_3]_2$[5] for which the solution species appear to be discrete $(Ti–N)_2$ rings based on four-coordinate titanium. These species react with pyridine to form a bispyridine adduct. Similar observations have been reported in the case of $Cl_3Ti(bzac)$.[13] In contrast, dissolution of the oxygen-bridged $[TiOCl(acac)]_2$ dimer in excess pyridine results in no bispyridine adduct formation; evidently, the titanium–oxygen bridge bonds are too strong.[39] The dimer $[TiO(acac)_2]_2$ also appears to be stable toward cleavage and pyridine adduct formation.[40]

The question as to how the $[X_3Ti(dik)]_2$ dimers cleave in solution is enigmatic. From inspection of the two titanium–bridge chlorine bond distances (Table VII), Ti–Cl3 and Ti–Cl3′, it is tempting to suggest that cleavage occurs at the longer (and weaker) Ti–Cl3′ bond and at the symmetry-related Ti′–Cl3 bond. Disproportionation accompanied by intermolecular ligand exchange or preceded by intramolecular ligand exchange may lead to the observed six- and four-coordinate compounds.

Acknowledgment. Support of this research by the National Research Council of Canada is gratefully appreciated. N. S. wishes to thank Concordia University for a sabbatic leave (1975–1976).

Registry No. $[Cl_3Ti(acac)]_2$, 36482-44-7; $Ti(acac)_2F_2$, 19289-15-7; $[FCl_2Ti(acac)]_2$, 63181-02-2; $Ti(acac)_2Cl_2$, 17099-86-4.

Supplementary Material Available: Table V, a listing of structure factor amplitudes (3 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843

Self-Consistent Field Xα Scattered-Wave Treatment of the Electronic Structures of Octachlorodimetalate Anions of Technetium and Tungsten

F. ALBERT COTTON* and BARBARA J. KALBACHER

Received December 29, 1976 AIC60931T

The ground-state electronic structures of the anions $Tc_2Cl_8^{3-}$ and $W_2Cl_8^{4-}$ have been calculated using the SCF–Xα–SW method. The results are discussed and compared with those already published for $Mo_2Cl_8^{4-}$ and $Re_2Cl_8^{2-}$. The electronic structure predicted for $W_2Cl_8^{4-}$ is very similar to that for $Mo_2Cl_8^{4-}$ and there does not appear to be any qualitative reason that $W_2Cl_8^{4-}$ should not be capable of existence. For the $Tc_2Cl_8^{3-}$ ion the excess electron, over the quota required for the formation of the quadruple bond between the metal atoms, occupies the $\delta^*(2b_{1u})$ orbital, making the net Tc–Tc bond order here 3.5. The calculation on $Tc_2Cl_8^{3-}$ has been carried through to a prediction, via the transition-state formalism, of the optical spectrum, apparently in good accord with the limited data available. Overall trends observed when the results of calculations for $Tc_2Cl_8^{3-}$, $Mo_2Cl_8^{4-}$, $W_2Cl_8^{4-}$, and $Re_2Cl_8^{2-}$ are all compared are discussed and found to be reasonable.

The existence of quadruple bonds between atoms of transition metals has been recognized since 1964.[1,2] In general, quadruply bonded systems have been characterized by their short metal–metal bond lengths and, in the case of $M_2X_8^{n-}$ species with eight separate ligands, by their eclipsed conformation.[3] Only recently, however, have quantitative theoretical studies been undertaken on these systems. This has occurred, in part, because of the advent of a first-principles theoretical method capable of handling multi-electron systems with the expenditure of acceptable amounts of computer time.

We report here the study of two complexes by the self-consistent field Xα scattered-wave (SCF–Xα–SW) method.[4-8] Calculations on octachloroditechnetate(2.5) and the hypothetical species, octachloroditungstate(II), were undertaken. Our purpose in treating the first one was to obtain as reliable a theoretical basis as possible on which to analyze the available experimental data for $Tc_2Cl_8^{3-}$, both published[9-15] and unpublished.[16] For $W_2Cl_8^{4-}$ we were looking for indications concerning the likelihood of its existence since it has not been reported even though it is vertically homologous to $Mo_2Cl_8^{4-}$ and horizontally homologous to $Re_2Cl_8^{2-}$, both of which are quite stable and very well characterized.

We have been mindful of the interesting and useful results already obtained on the octachlorodimolybdate[17,18] and octachlorodirhenate[19] systems by others, and we shall later compare our results in detail with these others in order to see what trends and regularities there may be as a function of net charge and position in the periodic table for the four $M_2Cl_8^{n-}$ species.

Procedures

General Data. The SCF–Xα scattered-wave method as developed by Slater and Johnson[5] was used to determine the ground-state electronic structures of $Tc_2Cl_8^{3-}$ and the hypothetical species $W_2Cl_8^{4-}$. The coordinate system was in each case applied to an ion of idealized D_{4h} symmetry with the metal–metal bond along the z axis and chlorine–metal bond directions chosen to project upon the x and y axes. The calculation of the technetium system included the use of s-, p-, and d-type spherical harmonics on the central metal and s- and p-type spherical harmonics on the chlorine ligands. For the tungsten system, s-, p-, d-, and f-type spherical harmonics were used. For the extramolecular region, spherical harmonics up to $l = 5$ were used for both systems. Throughout the calculations, the stablizing influence of a surrounding crystal lattice on the anionic complexes was stimulated by adding to the potential that of a "Watson sphere" with radius equal to that of the outer sphere.[20] All calculations were carried out on a model 470V/6 Amdahl computer. Typically, one iteration on the spin-restricted $Tc_2Cl_8^{3-}$ system required 16 s of computer time. A single iteration on the spin-unrestricted system required approximately 27 s.

Calculation on $Tc_2Cl_8^{3-}$. Coordinates for $Tc_2Cl_8^{3-}$ were taken from the crystallographic data of Cotton and Shive.[15] The averaged di-