N,N'-Ethylenebis(acetylacetoneiminato)titanium Complexes: Synthesis, Crystal Structures, and Properties of Titanium(III) and Titanium(IV) Derivatives†

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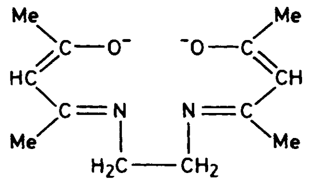
The reaction of $TiCl_4{\cdot}2thf$ and $TiCl_3{\cdot}3thf$ (thf = tetrahydrofuran) with the Na_2acen [acen = *N,N'*-ethylenebis(acetylacetoneiminate) dianion] gave the corresponding titanium(IV), $[Ti(acen)Cl_2]$ (**1**), and titanium(III), [Ti(acen)Cl(thf)] (**2**), derivatives in good yield. Complex (**2**) has a d^1 configuration and is easily oxidized to titanium(IV) derivatives. Reaction with oxygen afforded a μ-oxo complex [Cl(acen)TiOTi(acen)Cl], (**3**), having a linear Ti–O–Ti skeleton [Ti–O 1.813(1) Å; ν(Ti–O) 750 cm^{-1}]. The structures of complexes (**1**)—(**3**) have been determined by *X*-ray analysis: (**1**) space group $P2_1/n$ (monoclinic), a = 27.510(9), b = 14.347(5), c = 7.839(3) Å, β = 94.52(1)°, Z = 8, and R = 0.050 for 1 737 observed reflections; (**2**), space group $P2_12_12_1$ (orthorhombic), a = 15.403(2), b = 14.883(2), c = 8.180(1) Å, Z = 4, and R = 0.043 for 2 085 observed reflections; (**3**), space group $P2_1/n$ (monoclinic), a = 10.599(2), b = 18.392(5), c = 7.551(2) Å, β = 101.90(2°), Z = 2, and R = 0.031 for 1 961 observed reflections.

Reactivity studies on Group 4 metals have been generally limited to compounds having cyclopentadienyls as ancillary ligands around the metal.[1] Only recently the organometallic and co-ordination chemistry of these metals has moved towards the utilization of completely different anionic ancillary ligands having N or O as donor atoms attached to bulky organic residues.[2,3] These ligands can provide the appropriate environment for studying the chemistry of the M–C functionality; but not being electronically flexible like cyclopentadienyls, they cannot assure the stabilization of various oxidation states. This is a peculiar property of various macrocyclic ligands. Among the polydentate ligands, Schiff bases have numerous advantages: they provide stabilization of various oxidation states,[4,5] of M–C bonds,[4,5] and access to 'bifunctional' systems.[6]

The Schiff-base chemistry of early transition metals has been very little explored. Only very recently reports have appeared on the synthesis,[7] reduction,[8] and alkylation[9] of vanadium(III)–Schiff base complexes. The lack of appropriate starting complexes, however, did not allow reactivity studies on other metals. A few reports concern titanium–Schiff base complexes,[10] among which the only two structurally defined are $[Ti(salen)Cl_2]$[11] and [Ti(salen)Cl(py)][12] [salen = *N,N'*-ethylenebis(salicylideneiminate) dianion].

We report here the synthesis in good yield and the full structural characterization of three [Ti(acen)] derivatives [acen = *N,N'*-ethylenebis(acetylacetoneiminate) dianion]. Our attention was focused on the acen derivatives since this ligand assures a good solubility of the metal complexes in organic solvents.



acen

Experimental

All the reactions were carried out under an atmosphere of purified nitrogen. Solvents were dried and distilled before use by standard methods. The ligand $[H_2acen]$,[13] $TiCl_4{\cdot}2thf$,[14] and $TiCl_3{\cdot}3thf$[14] (thf = tetrahydrofuran) were prepared as reported. Infrared spectra were recorded with a Perkin-Elmer 883 spectrophotometer, ^1H n.m.r. spectra using a WH-360 Bruker instrument. Magnetic susceptibilities were measured using a Faraday balance. The reported synthesis of complex (**1**) is a significant improvement on that reported in ref. 10*a*.

Syntheses.—$[Ti(acen)Cl_2]$, (**1**). Sodium hydride (4.22 g, 175.8 mmol) was added to a thf solution (500 cm^3) of H_2acen (19.80 g, 88.36 mmol). The suspension was stirred until the complete evolution of H_2, then refluxed for 1 h. A light yellow solid formed. The suspension was cooled to room temperature, then $TiCl_4{\cdot}2thf$ (29.30 g, 87.7 mmol) was added. The red solid suddenly formed was refluxed for 2 h. The suspension was evaporated to dryness and the solid extracted with the mother solution in order to remove NaCl. A suspension of a red crystalline solid was obtained. The solvent was partially evaporated to *ca.* 150 cm^3 (yield *ca.* 73%). Suitable crystals for *X*-ray analysis were obtained from the mother solution (Found: C, 41.85; H, 5.40; Cl, 21.00; N, 8.35. Calc. for $C_{12}H_{18}Cl_2N_2O_2Ti$: C, 42.20; H, 5.30; Cl, 20.80; N, 8.20%). ^1H N.m.r. ($CDCl_3$): δ 5.43 (s, 2H, CH), 3.82 (br s, 4 H, CH_2), 2.12 (s, 6 H, Me), and 2.00 (s, 6 H, Me).

[Ti(acen)Cl(thf)], (**2**). Sodium hydride (5.05 g, 210.4 mmol) was added to a thf solution (500 cm^3) of H_2acen (23.60 g, 105.20 mmol). The solution was refluxed for 0.5 h, when a light yellow solid formed. The suspension was cooled to room temperature, then $TiCl_3{\cdot}3thf$ (38.96 g, 105.2 mmol) was added. The resulting blue-violet suspension was refluxed for 1 h. The solid was extracted with the mother-liquor to remove NaCl. This normally required 1 week. The deep blue solid (*ca.* 66.7%) was filtered off (Found: C, 50.95; H, 6.95; Cl, 9.55; N, 7.30. Calc. for $C_{16}H_{26}ClN_2O_3Ti$: C, 50.85; H, 6.90; Cl, 9.40; N, 7.40%). The magnetic moment is 1.79 B.M. at 293 K.

[Cl(acen)TiOTi(acen)Cl], (**3**). The complex [Ti(acen)Cl(thf)] (4.60 g, 12.2 mmol) was dissolved in hot thf (100 cm^3). The solution was cooled to room temperature and exposed overnight to dry oxygen. A red microcrystalline solid formed (*ca.*

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: B.M. ≈ 9.27 × 10^{-24} A m^2.

Table 1. Experimental data for the *X*-ray diffraction studies on crystalline complexes (**1**)—(**3**)[a]

	(**1**)	(**2**)	(**3**)
Formula	$C_{12}H_{18}Cl_2N_2O_2Ti$	$C_{16}H_{26}ClN_2O_3Ti$	$C_{24}H_{36}Cl_2N_4O_5Ti_2$
M	341.1	377.7	627.3
System	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/n$	$P2_12_12_1$	$P2_1/n$
Cell parameters at 295 K[b]			
a/Å	27.510(9)	15.403(2)	10.599(2)
b/Å	14.347(5)	14.883(2)	18.392(5)
c/Å	7.839(3)	8.180(1)	7.551(2)
α/°	90	90	90
β/°	94.52(1)	90	101.90(2)
γ/°	90	90	90
U/Å^3	3 084(2)	1 875.2(5)	1 440.3(6)
Z	8	4	2
D_c/g cm^{-3}	1.469	1.338	1.446
Crystal dimensions/mm	0.15 × 0.26 × 0.30	0.32 × 0.35 × 0.56	0.32 × 0.45 × 0.61
μ(Mo-K_α)/cm^{-1}	8.97	6.08	7.74
Scan type	ω	ω—2θ	ω—2θ
Scan width/°	1.60	1.40	1.30
2θ range/°	6—46	6—50	6—51
Reflections measured	$\pm h, \pm k, l$	$\pm h, k, l$	$\pm h, \pm k, l$
Data measured	4 581	3 379	3 784
Data unique	3 610	3 379	2 676
Data observed [$I > 3\sigma(I)$]	1 737	2 085	1 961
Agreement between equiv. reflections	0.030		0.022
No. of variables	343	208	169
Weighting parameter[c]	0.0001	Unit	Unit
Overdetermination ratio	5.1	10.0	11.6
Maximum shift/error on last cycle	0.2	0.2	0.01
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.050	0.043	0.031
$R' = \Sigma w^{\frac{1}{2}}\|\|F_o\| - \|F_c\|\|/\Sigma w^{\frac{1}{2}}\|F_o\|$	0.045		
Goodness of fit = $[\Sigma w(\|F_o\| - \|F_c\|)^2/(N_o - N_v)]^{\frac{1}{2}d}$	1.15		

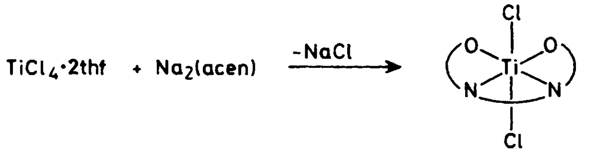
[a] Details common to all three complexes: scan speed 0.100° s^{-1}; all H atoms localized in ΔF map, included as fixed contributors with U_{iso} fixed at 0.10, 0.12, and 0.08 Å^2 for (**1**), (**2**), and (**3**) respectively. [b] Obtained by least-squares analysis of the setting angles of 30 carefully centred reflections chosen from diverse regions of reciprocal space. [c] $w = 1/[\sigma^2(F_o) + F_o^2]$. [d] N_o, N_v = Number of observations and variables respectively.

75.0%). Crystals suitable for *X*-ray analysis were obtained from the mother-liquor. Complex (**3**) can be recrystallized from thf. The i.r. spectrum shows a very strong Ti–O band at 750 cm^{-1} (Found: C, 46.20; H, 5.95; Cl, 10.90; N, 8.80. Calc. for $C_{24}H_{36}Cl_2N_4O_5Ti_2$: C, 45.90; H, 5.75; Cl, 11.00; N, 8.95%). ^{1}H N.m.r. ($CDCl_3$); δ 5.12 (s, 2 H, CH), 3.72 (m, 4 H, CH_2), 1.99 (s, 6 H, Me), and 1.88 (s, 6 H, Me).

X-Ray Crystallography.—All crystallographic measurements were made on crystals sealed under nitrogen in glass capillaries, using a Philips PW 1100 diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å) as previously described.[15] The crystal quality was tested by ψ scans showing that crystal absorption could not be neglected for complex (**3**). So the data for this compound were corrected for absorption following a semiempirical method.[16] The structures were solved by standard heavy-atom procedures and refined using full-matrix least squares,[17] with scattering factors calculated using data from ref. 18*a*. Anomalous scattering corrections were included in all structure-factor calculations.[18b] In complex (**2**) disorder seems to affect the thf molecule, showing highly anisotropic thermal motion. Refinement of this structure stopped at R = 0.043 (R_g = 0.045). Since the space group is polar the structure was refined again to convergence by inverting all the co-ordinates ($x,y,z \longrightarrow -x,-y,-z$). The final R values (R = 0.046, R_g = 0.048) indicated the previous choice to be the correct one. Details of crystal data, intensity recording, and refinement are given in Table 1, final atomic co-ordinates in Tables 2—4.

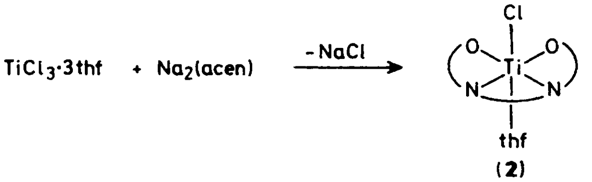
Results and Discussion

Reaction of $TiCl_4$·2thf and $TiCl_3$·3thf with the sodium salt of H_2acen leads to titanium(IV) and titanium(III) derivatives in good yield [equations (1) and (2)]. The crude solids formed in



(**1**)

(1)



(**2**)

(2)

reactions (1) and (2) must be extracted with thf in order to free complexes (**1**) and (**2**) from NaCl. The complexes have been fully characterized including an *X*-ray analysis (see below). A significant difference was observed in the C=N stretching vibration which moves down to 1 560 cm^{-1} [complex (**2**)] from 1 600 cm^{-1} [complex (**1**)] with the decrease in the oxidation state of the metal. Complex (**2**) has a normal magnetic moment of 1.79 B.M. at 293 K as expected for titanium(III). Complexes

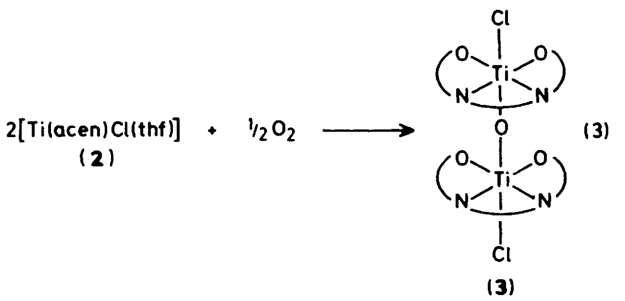
Table 2. Fractional atomic co-ordinates (× 10^4) for complex (**1**)

	Molecule A			Molecule B		
Atom	X/a	Y/b	Z/c	X/a	Y/b	Z/c
Ti	−66(1)	−2 385(1)	−2 599(3)	2 466(1)	2 976(1)	5 128(3)
Cl(1)	−342(1)	−993(2)	−3 950(4)	2 890(1)	2 679(2)	2 697(4)
Cl(2)	289(1)	−3 697(2)	−1 248(4)	1 983(1)	3 233(2)	7 426(4)
O(1)	−430(2)	−2 138(5)	−768(9)	2 696(2)	4 194(5)	5 222(9)
O(2)	−438(2)	−3 138(5)	−4 167(9)	2 892(2)	2 200(4)	6 427(9)
N(1)	496(3)	−1 582(6)	−1 305(11)	1 892(2)	3 498(5)	3 392(10)
N(2)	483(2)	−2 440(6)	−4 370(11)	2 049(2)	1 749(5)	4 599(10)
C(1)	−785(3)	−1 712(9)	1 742(14)	2 873(4)	5 812(8)	5 082(16)
C(2)	−373(3)	−1 665(7)	660(13)	2 551(4)	5 016(7)	4 593(13)
C(3)	46(3)	−1 188(7)	1 079(13)	2 143(4)	5 112(7)	3 508(13)
C(4)	461(3)	−1 162(7)	110(15)	1 838(4)	4 348(8)	2 886(13)
C(5)	891(4)	−621(7)	983(15)	1 430(4)	4 608(8)	1 501(15)
C(6)	960(4)	−1 576(9)	−2 139(16)	1 583(3)	2 747(7)	2 592(14)
C(7)	860(4)	−1 716(8)	−4 026(16)	1 547(3)	1 950(7)	3 801(13)
C(8)	889(4)	−2 969(8)	−6 854(14)	1 825(4)	61(7)	4 681(14)
C(9)	483(3)	−2 980(7)	−5 687(13)	2 163(3)	897(7)	5 039(12)
C(10)	99(4)	−3 610(7)	−6 140(13)	2 628(4)	680(7)	5 905(13)
C(11)	−334(4)	−3 670(7)	−5 447(12)	2 952(3)	1 303(7)	6 577(15)
C(12)	−737(4)	−4 319(8)	−6 033(16)	3 408(4)	1 000(7)	7 598(16)

Table 3. Fractional atomic co-ordinates (× 10^4) for complex (**2**)

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Ti	−11(1)	99(1)	−1 029(1)	C(7)	−1 695(5)	68(6)	789(15)
Cl	−820(1)	−137(1)	−3 521(2)	C(8)	−1 531(5)	−1 598(5)	2 514(9)
O(1)	753(2)	985(3)	−1 984(4)	C(9)	−860(4)	−1 292(4)	1 291(7)
O(2)	559(2)	−1 071(2)	−1 053(5)	C(10)	−154(4)	−1 889(4)	1 030(8)
N(1)	−784(3)	1 204(3)	−281(5)	C(11)	499(4)	−1 766(4)	−87(7)
N(2)	−933(3)	−530(3)	525(6)	C(12)	1 197(5)	−2 458(4)	−295(9)
C(1)	1 599(4)	2 277(5)	−2 638(9)	O(3)	770(2)	335(3)	1 195(4)
C(2)	812(4)	1 857(4)	−1 858(7)	C(13)	508(4)	400(5)	2 878(8)
C(3)	202(4)	2 383(4)	−1 120(8)	C(14)	1 317(5)	488(6)	3 831(9)
C(4)	−592(4)	2 064(4)	−418(7)	C(15)	2 006(6)	515(8)	2 706(12)
C(5)	−1 217(5)	2 796(5)	103(10)	C(16)	1 711(4)	343(6)	1 152(9)
C(6)	−1 613(5)	947(5)	432(10)				

(**1**) and (**2**), unlike other Schiff-base derivatives, are quite soluble in organic solvents, *i.e.* acetone, $CHCl_3$, thf, *etc.* Complex (**1**) is very sensitive to hydrolysis and complex (**2**) is sensitive to oxygen. Other synthetic methods for producing Schiff-base derivatives of Ti^{IV} and Ti^{III} were either very tedious or require the presence of a ligand like pyridine which limits reactivity studies.[10b,12] Moreover, direct reaction of $TiCl_3$ with H_2salen occurred with oxidation of the metal and hydrogenation of the ligand.[19] Complex (**2**) participates in various oxidation reactions.[20] Its reaction with molecular oxygen gave the μ-oxo dimer (3) [equation (3)].



(**3**)

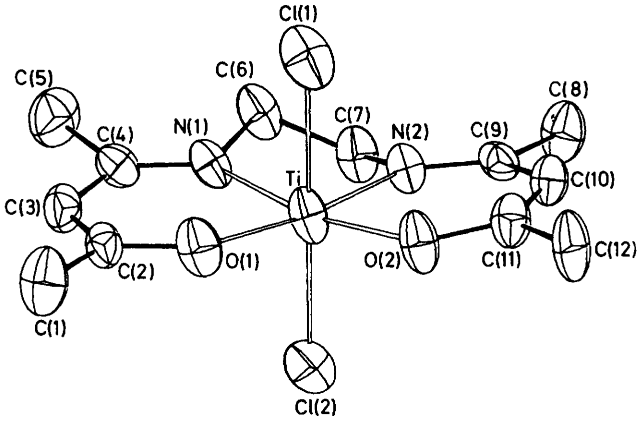


Figure 1. An ORTEP view of complex (**1**) (molecule B) (48% probability ellipsoids)

Complex (**3**) was fully characterized (see Experimental section) including an *X*-ray analysis (see below). The strong Ti–O bond interaction in (**3**) is revealed by the strong Ti–O band at 750 cm^{-1} and the linearity of the Ti–O–Ti fragment in agreement with a Ti–O multiple bond. Similar geometry was found in related μ-oxo complexes like $[\{TiCl_2(cp)\}_2(\mu\text{-}O)]$[21] (cp = $\eta\text{-}C_5H_5$), $[\{Ti(cp)_2(OH_2)_2\}_2(\mu\text{-}O)][ClO_4]_2$,[22] and $[\{Ti(acac)_2(Cl)\}_2(\mu\text{-}O)]$ (acac = acetylacetonate).[23] The structures of complexes (**1**)—(**3**) are shown in Figures 1—3. Selected bond distances and angles are compared in Table 5.

Table 4. Fractional atomic co-ordinates ($\times 10^4$) for complex (**3**)

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Ti	111(0)	912(0)	930(1)	C(4)	1 732(3)	1 715(2)	−1 449(4)
Cl	143(1)	2 142(0)	2 159(1)	C(5)	1 930(3)	2 142(2)	−3 066(5)
O(1)	1 914(2)	886(1)	1 882(3)	C(6)	−467(3)	1 464(2)	−2 943(4)
O(2)	−815(2)	623(1)	2 742(3)	C(7)	−1 669(3)	1 639(2)	−2 252(5)
O(3)	0(0)	0(0)	0(0)	C(8)	−4 046(3)	971(2)	−1 906(5)
N(1)	621(2)	1 417(1)	−1 377(3)	C(9)	−2 805(2)	856(2)	−530(4)
N(2)	−1 722(2)	1 149(1)	−733(3)	C(10)	−2 886(3)	417(2)	992(4)
C(1)	4 099(3)	1 209(2)	2 996(5)	C(11)	−1 967(3)	324(2)	2 515(4)
C(2)	2 893(3)	1 262(2)	1 544(4)	C(12)	−2 206(3)	−102(2)	4 099(5)
C(3)	2 831(3)	1 655(2)	24(4)				

Table 5. Selected bond distances (Å) and angles (°) [X = Cl(2) for (**1**) and O(3) for (**2**) and (**3**)]

	Complex (**1**)			
	Molecule A	B	Complex (**2**)	Complex (**3**)
Ti–O(1)	1.848(7)	1.858(7)	1.932(4)	1.899(2)
Ti–O(2)	1.878(7)	1.861(6)	1.950(3)	1.916(3)
Ti–N(1)	2.121(9)	2.137(7)	2.121(5)	2.140(2)
Ti–N(2)	2.132(8)	2.124(7)	2.124(5)	2.130(2)
Ti–Cl(1)	2.358(3)	2.350(4)	2.415(2)	2.443(1)
Ti–X	2.336(4)	2.350(4)	2.209(3)	1.813(1)
N(1)–Ti–N(2)	78.7(3)	78.8(3)	78.1(2)	77.5(1)
O(2)–Ti–N(2)	86.0(3)	85.3(3)	85.0(2)	86.5(1)
O(2)–Ti–N(1)	164.7(3)	163.8(3)	161.5(2)	162.6(1)
O(1)–Ti–N(2)	165.5(3)	164.6(3)	161.8(2)	162.4(1)
O(1)–Ti–N(1)	86.8(3)	85.9(3)	86.0(2)	85.2(1)
O(1)–Ti–O(2)	108.5(3)	110.1(3)	109.3(2)	110.3(1)

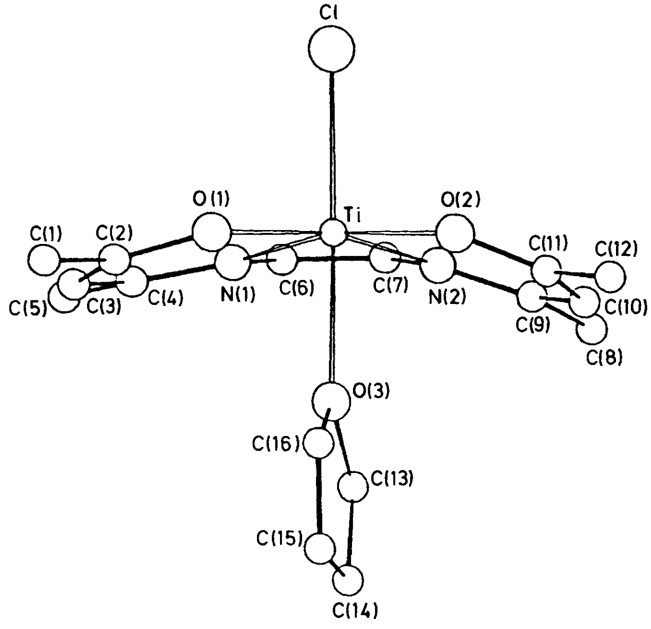


Figure 2. A perspective view of complex (**2**)

In complex (**1**), titanium exhibits a bipyramidal co-ordination with the donor atoms from the acen ligand in the equatorial plane and two chlorine atoms in *trans* axial positions. In the asymmetric unit there are two crystallographically independent molecules (A and B) having the same geometry (Figure 1). Hereafter the values involving molecule B are given in square brackets. The N_2O_2 core is nearly planar, titanium not deviating from the mean plane in molecule A, while it shows small but significant tetrahedral distortion, with titanium displaced by 0.028(3) Å in molecule B. The directions of the two Ti–Cl bonds are nearly perpendicular to the co-ordination plane, the angles they form with the normal to that plane being 3.5(2) [2.2(1)] and 2.6(2) [2.7(1)]°.

The O(1) ··· N(1) six-membered chelation ring is nearly planar, titanium being displaced by 0.044(2) [0.053(3)] Å from the plane through the other five atoms, and it is almost coplanar with the co-ordination plane {dihedral angle 1.8(3) [2.1(3)]°}. A greater distortion is shown by the N(2) ··· O(2) chelation ring, titanium being 0.305(2) [0.210(3)] Å out of the plane through N(2),C(9),C(10),C(11),O(2) which forms a dihedral angle of 11.9(3) [9.3(3)]° with the co-ordination plane. Most of the methyl carbons deviate from planarity. The most significant difference between molecules A and B concerns the conformation. The ethylene bridge has the usual *gauche* conformation, the N(1)–C(6)–C(7)–N(2) torsion angle being 41.8(10) [−45.5(10)]°. Excluding N(1A), the nitrogen atoms are slightly but significantly pyramidal. The distances of N(1) and N(2) from the planes through the bonded atoms are 0.023(9) [0.064(7)] and 0.040(8) [0.058(7)] Å. There are no intermolecular contacts less than 3.5 Å.

In complex (**2**) an oxygen atom from a thf molecule replaces a chlorine atom of complex (**1**). The co-ordination of acen is not strictly planar, titanium being displaced by 0.166(1) Å from the N_2O_2 plane towards chlorine. The directions of the Ti–Cl and Ti–O(3) bonds are perpendicular to the co-ordination plane, the dihedral angles they form with the normal to the plane being 1.0(1) and 1.6(1)° respectively. The torsion angle around the C(6)–C(7) bond is 3.7(11)°, so that the five-membered chelate ring is folded along the N(1) ··· N(2) line, C(6) and C(7) being out of the N(1),N(2),Ti plane by 0.371(8) and 0.410(11) Å on the same side. The planarity of the N(1),N(2),C(6),C(7) system as well as the short value of the C(6)–C(7) bond [1.35(1) Å] reflect the high thermal motion (or disorder) of the ethylene bridge. The Ti(acen) fragment shows an 'umbrella'-shaped conformation: the dihedral angles between the co-ordination plane (including titanium) and the three nearly planar groups N(1),N(2),C(6),C(7); N(1),C(4),C(3),C(2),O(1); and N(2),C(9),-C(10),C(11),O(2) are 10.9(3), 13.5(2), and 20.3(2)° respectively. The dihedral angle between the two six-membered chelation rings is 33.7(2)°. Titanium is 0.204(1) and 0.342(1) Å out of these planes. The N(2) atom is slightly pyramidal, being 0.042(5) Å out of the Ti,C(7),C(9) plane. The three bonds around N(1) are strictly coplanar.

The structure of complex (**3**) shows a μ-oxo ligand [O(3)] bridging two Ti(acen)Cl units. This oxygen atom lies on a crystallographic centre of symmetry, so the Ti–O(3)–Ti′ angle equals 180° for crystallographic requirements, indicating an *sp* hybridization state for oxygen, in agreement with the short

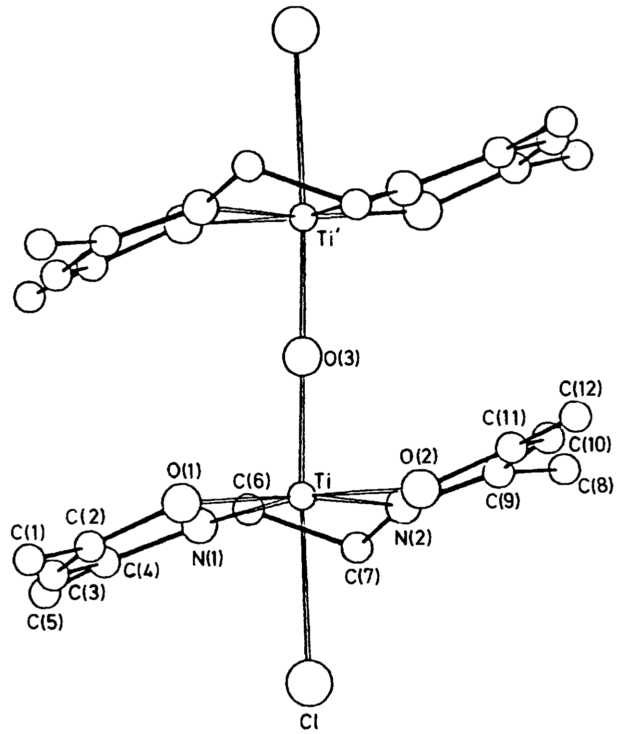


Figure 3. A perspective view of the dimer in complex (**3**). The prime indicates the transformation to $-x$, $-y$, $-z$

value of the Ti–O(3) distance [1.813(1) Å] which is consistent with multiple bonding. The Ti–Cl distance [2.443(1) Å] is longer than those observed in (**2**) [2.415(2) Å] and (**1**) [mean 2.349(5) Å] reflecting the *trans* influence of the oxo-oxygen ligand. The Ti–Cl bonds, which are not *trans* to the μ-oxo group in $[\{Ti(acac)_2(Cl)\}_2(\mu\text{-}O)]$,[23] are significantly shorter [2.32(2) and 2.30(1) Å], while the Ti–O (bridging) distances are very similar [average 1.80(2) Å]. The atoms in the equatorial plane show small but significant tetrahedral distortions with titanium displaced by 0.102(1) Å towards O(3). The directions of the Ti–Cl and Ti–O(3) bonds form angles of 1.2(1) and 3.9(1)° with the normal to the N_2O_2 core.

The C(6)–C(7) ethylenic bridge assumes the usual *gauche* conformation with a N(1)–C(6)–C(7)–N(2) torsion angle of −47.6(3)°. The C(6)–C(7) distance [1.507(5) Å] corresponds well to a single C sp^3–C sp^3 bond. The Ti(acen) fragment has a step conformation with dihedral angles of 19.1(1) and 19.2(1)° between the co-ordination plane and the groups O(1),C(2),C(3),C(4),N(1) and O(2),C(11),C(10),C(9),N(2) respectively. Titanium is 0.390(1) and 0.578(1) Å out of these planes, which form a dihedral angle of 4.3(1)°. Both nitrogen atoms are slightly pyramidal: the distances of N(1) and N(2) from the plane through Ti,C(6),C(4) and Ti,C(7),C(9) are 0.040(2) and 0.035(3) Å, respectively. Intermolecular contacts are consistent with van der Waals interactions for all compounds. The structural parameters within the acen ligand fall in the usual range.[7]

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