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Oxotitanium(IV) and dichlorotitanium(IV) complexes with tetradentate Schiff bases

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Abstract

Attempts to prepare [TiO(salen)] (H_2salen = 1,2-$HOC_6H_4CH{=}NCH_2CH_2N{=}CHC_6H_4OH$-1,2) and its homologues, analogues of the well known complexes related to [VO(salen)] were only partially successful, in that all the products appear to be polymeric rather than mononuclear, and no crystalline materials were obtained. Homologues of [$TiCl_2$(salen)] were similarly difficult to obtain pure, though we determined a crystal structure for [$TiCl_2$(1,2-$OC_6H_4CMe{=}NCH_2CH_2N{=}CMeC_6H_4O$-1,2)]. This has the expected octahedral coordination, though in common with many such materials, there are molecules of solvent, thf and toluene, within the crystal. This complicates characterisation on the basis of microanalysis. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structures; Titanium complexes; Oxo complexes; Schiff base complexes

1. Introduction

Oxovanadium(IV) compounds have been extensively investigated and the chemistry of vanadium in oxidation states IV and V is really dominated by such species [1], whereas oxotitanium(IV) analogues are much less well defined [2]. The titanyl(IV) group is very labile and readily opens to form polymeric materials, based upon ···Ti–O–Ti–O··· chains. Some examples of stable Ti=O bonds are known, such as in [$TiOCl_2(NMe_3)_2$] and [$TiOCl_4$]$^{2-}$, but these are exceptional [3,4]. Furthermore, [$VO(acac)_2$] is highly soluble in most common organic solvents, but [$\{TiO(acac)_2\}_2$] is an insoluble orange powder. We have reported at some length [5] on vanadyl complexes containing the dianions derived from potentially tetradentate proligands based upon a selection of diamines, and here we describe some preliminary experiments on the formally analogous derivatives of titanium(IV).

The first examples [6] of oxotitanium(IV) tetradentate Schiff base complexes were prepared as dark microcrystalline solids, soluble in dmf and dmso, from the reaction of titanyl perchlorate with either H_2(salphen) or H_2\{salphen(3-OMe)$_2$\} in methanol. The authors mistakenly assigned ν(Ti=O) to broad absorptions at 1090 cm^{-1} but these probably arise from perchlorate stretches. These complexes actually contain an additional equivalent of acid per mole of complex, e.g. [TiO(salen)]·$HClO_4$ [7] and two interconvertible forms were isolated. They seem not to be five-coordinate complexes akin to [VO(salen)].

A further series of oxotitanium(IV) tetradentate Schiff base complexes was obtained [7] by reaction of [$\{TiO(acac)_2\}_2$] with the Schiff bases in methanol. These showed no band assignable to ν(Ti=O) in the region 1100–900 cm^{-1} and are yellow, insoluble solids, probably polymeric. Typical complexes, such as [TiO(salophen)]·MeOH and [TiO(salen)]·1/2MeOH, are easily converted into the former compounds by treatment with an aqueous solution of the appropriate acid, though the converse transformation was not possible.

Recently Floriani and co-workers isolated the first example of a linear polytitanoxane [8], prepared from [TiCl(salen)(thf)]. The crystal contains linear tetranuclear cations [$\{Ti(salen)\}_4(\mu\text{-}O)_3$]$^{2+}$, linked in an infinite chain via a titanium–oxygen (phenolate) bonds to neighbouring cation as in [$\{V(salen)\}_4(\mu\text{-}O)_3$][$BPh_4$]$_2$, isolated by Leigh and co-workers [9].

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The titanium compound *trans*-[$TiCl_2$(salen)] is not clearly defined though the vanadium analogues *trans*-[VX_2(salen)] (X = Cl, Br, or I) [10] are well known. The red complex *cis*-[$TiCl_2$(salen)] was first prepared by reaction of H_2(salen) with titanium tetrachloride in ethanol [11]. The salophen derivative was also described. Ghose and Lasisi then extended this work to a wider range of tetradentate Schiff bases [12]. However, the [$TiCl_2$(salen)] reported in their work is pale yellow rather than the red we found, though the microanalyses were consistent with this formulation. [$TiCl_2$(salen)] was later isolated by Gilli and Cruickshank from the reaction of [$TiCl_3(thf)_3$] with H_2(salen) in tetrahydrofuran [13]. They were attempting to isolate the Ti^{III} complex [Ti(salen)Cl], but the green solid isolated changed to red after 12 h. This red material, recrystallised from tetrahydrofuran and characterised by X-ray diffraction studies, was shown to be *trans*-[$TiCl_2$(salen)]·thf. The analogous Ti^{IV} complex from H_2(salphen) is a brown solid.

In this paper we also present some new data on complexes [$TiCl_2$(L)] (L = tetradentate Schiff base dianion).

2. Results and discussion

Following the method of Biradar et al. [5,11], we formed oxotitanium(IV) tetradentate Schiff base complexes by heating equimolar amounts of the soluble di(isopropoxo)bis(pentane-2,4-dionato)titanium and the Schiff base in methanol, acetonitrile, or dichloromethane under reflux, from 4 h to 3.5 days. The products were then isolated by concentrating the orange solutions and precipitating them as yellow powders by addition of diethyl ether.

A series of additional formally titanyl(IV) complexes was prepared. Their poor solubilities in organic solvents has meant that we were unable to isolate crystals suitable for X-ray diffraction studies, nor, indeed, for NMR studies. To date there is no example of a crystallographically characterised mononuclear or polynuclear oxotitanium(IV) tetradentate Schiff base complex of the type [TiO(L)].

These Schiff bases dianions coordinate in the equatorial via both phenolate oxygen and imine nitrogen groups and remain quasi-planar. The coordination via imine nitrogen in the present compounds is inferred by comparison of the IR spectra with those of the proligands. All except one show a reduction in ν(C=N). The exception to this is the compound formed from H_2\{salen(3-OMe)$_2$\} and di(isopropoxo)bis(pentane-2,4-dionato) titanium, which shows ν(C=N) 6 cm^{-1} higher than ν(C=N) in the proligand, implying that nitrogen is not coordinated in this compound. The titanium–oxygen stretch is assigned to a broad absorption in the 800–910 cm^{-1} region, though the yellow complex formed from H_2(hap-1,2-pn) and di(isopropoxo)-bis(pentane-2,4-dionato)titanium showed no obvious band assignable to ν(Ti=O).

Oxotitanium(IV) Schiff base complexes differ from the oxovanadium(IV) Schiff base complexes described earlier in having a d^0 configuration, and are therefore diamagnetic. They should be amenable to NMR studies, but their poor solubilities makes this difficult to realise. Furthermore, neither H_2(hapen) nor H_2(hap-1,3-pn) appeared to react despite heating the reaction mixtures under reflux for long periods. In contrast, the analogous vanadium complexes, [VO(hapen)] and [VO(hap-1,3-pn)] were readily synthesised [14], although we were unable to prepare [VO(hap-1,3-pn)] in a pure form.

Formation of the oxotitanium(IV) tetradentate Schiff base complexes was confirmed by their mass spectra. The poor solubilities of these complexes suggests that they are polymeric, and it is evident that Ti(IV) Schiff base complexes prefer to be six coordinate, rather than five coordinate. The microanalyses of all complexes prepared are also in poor agreement with the required values, with the exception of [TiO(sal-1,3-pn)] and [TiO(sal-1,2-pn)], which were isolated with solvent of crystallisation. It is not clear in general what the impurities might be.

In addition to the materials firmly identified (see Section 4), reactions were also carried out between di(isopropoxo)bis(pentane-2,4-dionato)titanium and H_2\{salen(3,5-Cl_2)$_2$\} and H_2\{salen(5-Br)$_2$\}. The reactions in methanol at reflux give highly insoluble mustard powders with a strong absorption band at 869 cm^{-1} in the first case and at 824 cm^{-1} in the second. These were assigned to ν(Ti=O). The FAB mass spectra of the products were uninformative, due to the poor solubility in the 3-nitrobenzyl alcohol matrix. The EI mass spectra show ions at $m/z = 463$ and 483 both five mass units less than those of the expected parent ions. We are unable to explain this. However the isotopic distribution suggested that the ion at 463 from [TiO\{salen(3,5-Cl_2)$_2$] contains four chlorine atoms, as expected. The microanalyses were in poor agreement with the required values. The IR spectrum of the second product shows ν(C=N) is at 1640 cm^{-1}, unchanged from the value in the proligand, and implying that coordination to titanium may not be via the imine nitrogen atoms.

A similar reaction between di(isopropoxo)bis-(pentane-2,4-dionato)titanium and H_2\{salen(5-Br)$_2$\}but in acetonitrile gave a brick red solid in 66% yield. The EI mass spectrum of this product shows an ion at $m/z = 488$, relative intensity 63%, consistent with [TiO\{salen(5-Br)$_2$\}]$^+$. There are also ions at $m/z = 486$,

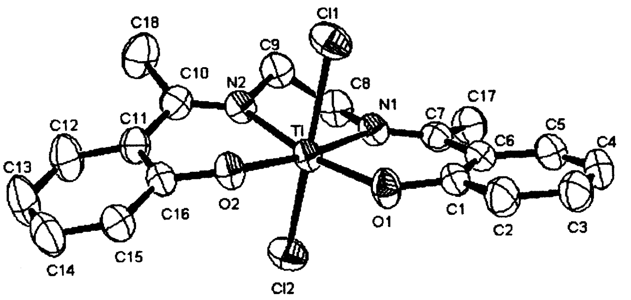

Fig. 1. The molecular structure of [TiCl$_2$(hapen)] in the crystal of [TiCl$_2$(hapen)·thf·0.5toluene.

Table 1
Selected bond lengths (Å) and angles (°) in [TiCl$_2$(hapen)]·thf·0.5toluene [a]

Ti(1)–O(1)	1.827(2)
Ti(1)–O(2)	1.823(2)
Ti(1)–N(1)	2.172(2)
Ti(1)–N(2)	2.151(2)
Ti(1)–Cl(1)	2.360(1)
Ti(1)–Cl(2)	2.355(1)
Cl(1)–Ti(1)–Cl(2)	168.59(4)
Cl(1)–Ti(1)–O(1)	90.26(8)
Cl(1)–Ti(1)–O(2)	91.49(7)
Cl(1)–Ti(1)–N(1)	85.10(7)
Cl(1)–Ti(1)–N(2)	84.94(7)
Cl(2)–Ti(1)–O(1)	95.21(8)
Cl(2)–Ti(1)–O(2)	96.03(7)
Cl(2)–Ti(1)–N(1)	85.37(7)
Cl(2)–Ti(1)–N(2)	87.10(7)

[a] Ti removed from mean plane of coordinating N$_2$O$_2$ atoms by 0.01 Å.

488, and 490 with the expected isotopic distribution for two bromine atoms. The microanalyses are reasonably consistent with this formulation. The IR spectrum shows the strongest band in the 800–1000 cm $^{-1}$ region at 809 cm $^{-1}$, which we assign to ν(Ti=O), and ν(C=N) is at 1632 cm^{-1} compared to 1638 cm^{-1} in the proligand. If the band at 809 cm^{-1} is due to ν(Ti=O) this is ca. 100 cm^{-1} lower than expected.

Dichlorotitanium Schiff base complexes were prepared by the method of Floriani and co-workers [8], the reaction of the Schiff base in tetrahydrofuran with titanium tetrachloride in toluene [15]. The red suspension was heated under reflux, reduced to dryness and the crude product washed with a 1:1 mixture of acetone and water and rapidly filtered in air to remove any residual traces of hydrochloric acid. Whilst this method worked well for both [TiCl$_2$(salen)] and [TiCl$_2${salen(3-OMe)$_2$}], washing the crude red products containing [TiCl$_2$(hapen)] and [TiCl$_2$(hapnptn)] with an acetone–water mixture led to decomposition.

All four complexes prepared were isolated as brick red powders in high yield. The IR spectra showed a reduction in ν(C=N) compared to ν(C=N) in the proligand, consistent with co ordination to titanium via imine nitrogen. The three complexes [TiCl$_2${salen-(3-OMe)$_2$}], [TiCl$_2$(hapen)] and [TiCl$_2$(hapnptn)] are new. It is noteworthy that although we were unable to prepare [VO(hapnptn)] we have been able to coordinate (hapnptn)$^{2-}$ to Ti(IV) to yield [TiCl$_2$(hapnptn)]. However only microanalyses for [TiCl$_2${salen(3-OMe)$_2$}] were in good agreement with the required values, and for both [TiCl$_2$(hapen)] and [TiCl$_2$(hapnptn)] the C and N contents are consistently low, perhaps due to traces of hydrochloric acid in the final product. The product [TiCl$_2$(hapen)]·thf·0.5toluene was crystallographically characterised, though surprisingly, the microanalysis of the red crystals from the same crop that was used for X-ray studies was also poor.

Deep red needles of [TiCl$_2$(hapen)]·thf·0.5toluene suitable for X-ray structure analysis were isolated from the filtrate of the preparative reaction mixture. In contrast to [TiCl$_2$(salen)], which is moisture-sensitive, these are stable in air for a short period. The structure shows six-coordinate titanium in a distorted octahedral environment, with the Schiff base in the equatorial plane and the two chlorides mutually *trans* in axial sites (Fig. 1 and Table 1).

Two dichlorotitanium tetradentate Schiff base complexes have been previously characterised crystallography, [TiCl$_2$(salen)] [13] and [TiCl$_2${salen(3-Bu^t-5-Me)$_2$}] [16] and Table 2 compares selected bond lengths and angles of the three complexes [TiCl$_2$(L)].The Ti–O(phenolate) and Ti–N bond distance in all three complexes are similar, the latter being the shorter. The dimensions do not vary much and are essentially as expected.

Table 2
A comparison of selected bond lengths and angles in [TiCl$_2$(salen)], [TiCl$_2$(hapen)] and [TiCl$_2${salen(3-Bu^t-5-Me)$_2$}]

Selected bond lengths (Å) and angles (°)	[TiCl$_2$(salen)][14]	[TiCl$_2$(hapen)]	[TiCl$_2${salen(3-^{t}Bu,5-Me)$_2$}][17]
Ti(IV) removed from the mean plane of N$_2$O$_2$ by	not reported	0.011(1)	0.003(2)
Cl–Ti–Cl	168.7(1)	168.59(4)	169.18(10)
Ti–Cl(1), Ti–Cl(2)	2.346(2)	2.355(1), 2.360(1)	2.345(3), 2.353(3)
Ti–O(phenolate)	1.835(5)	1.823(2), 1.827(2)	1.816(4), 1.820(5)
Ti–N	2.141(5)	2.151(2), 2.172(2)	2.110(6), 2.136(5)

Table 3
Crystal data and structure refinement [$TiCl_2$(hapen)]·thf·0.5toluene

Empirical formula	$C_{18}H_{18}Cl_2N_2O_2Ti\cdot(C_4H_8O)\cdot0.5(C_7H_8)$
Formula weight	531.3
Crystal system	monoclinic
Space group	$P2_1/c$ (no.14)
Unit cell dimensions	
a (Å)	13.426(4)
b (Å)	13.880(2)
c (Å)	14.250(2)
β (°)	108.58(2)
V ($Å^3$)	2517.1(9)
Z	4
μ (mm^{-1})	0.58
Reflections collected	4613
Independent reflections	4423 [$R_{int} = 0.019$]
Reflections with $I > 2\sigma_I$	3485
Final R_1, wR_2 [$I > 2\sigma_I$]	0.047, 0.117
All data	0.064, 0.130

3. Conclusions

The colour, mass spectra data and IR data of the yellow solids TiO(L) imply that they are all basically of the same form, though presumably polynuclear. Mononuclear titanyl(IV) complexes show ν(Ti=O) in the region 1050–950 cm^{-1}, whereas our complexes show ν(Ti=O) at much lower values, 910–865 cm^{-1}. Probably the structures contain –O–Ti–O–Ti–O– polymers. The three novel dichlorotitanium(IV) complexes proved more tractable and at least one structure was unequivocally determined.

The propensity for the formation of M=O appears to increase across the first row of d-block metals, perhaps due to the increase in ionisation potentials. Although Ti^{IV} is the most stable state for titanium under normal ambient conditions, the double bond structure is considerably stabler for vanadium(IV) and for vanadium(V). Subsequent elements form stable M=O species only in higher oxidation states. The stability of such bonds in 'normal' oxidation states of the metals seems to be maximal in the middle of the row, with chromium and manganese.

4. Experimental

All reactions were all carried out under dinitrogen, using standard Schlenk techniques unless otherwise stated. Solvents used were dried as follows and distilled under dinitrogen by conventional methods. All reagents received from commercial suppliers were used as supplied. IR spectra were obtained as dispersions in potassium bromide, or as Nujol mulls using a Perkin–Elmer model 1710 FT IR spectrophotometer. Carbon, nitrogen and hydrogen analyses were carried out by Ms. Nicola Walker at the University of Surrey on a Leeman CE 440 Elemental Analyser. Mass spectra were recorded by Dr Ali Abdul Sada on a VG Autospec spectrometer for Electron Impact spectra (EI source at 70 eV) and on a Kratos MS80RF for fast atom bombardment spectra (FAB source at 80 kV, with xenon gas and a FAB matrix of 3-nitrobenzyl alcohol).

Details of the X-ray structure analysis are given in Table 3. There is a molecule of thf solvate; and also a molecule of toluene solvate lying across an inversion centre for which the methyl group could not be located and is presumably disordered equally over the three possible sites. All non-H atoms were anisotropic. H atoms were included in riding mode with $U_{iso(H)}$ equal to $1.2U_{eq(C)}$ or $1.5U_{eq(C)}$ for methyl groups. The programs used for data collection and structure analysis are given in Refs. [17–19].

4.1. Preparation of [TiO(salen)]

H_2(salen) (3.90 g, 14.5 mmol) was dissolved in acetonitrile (100 cm^3) and di(isopropoxo)bis(pentane-2,4-dionato)titanium (5.30 cm^3, 14.5 mmol) was added. The solution was heated under reflux for 13 h, to give an orange powder, which was filtered off and washed with diethyl ether (30 cm^3). Yield: 2.20 g, 46%. IR (KBr disc, cm^{-1}): 1631 ν(C=N), 911 ν(Ti=O) (s).

4.2. Preparation of [Ti(O(sal-1,3-pn)] · 1.5MeOH

H_2(sal-1,3-pn) (2.50 g, 8.85 mmol) was dissolved in methanol (50 cm^3) to afford a yellow solution. Di(isopropoxo)bis(pentane-2,4-dionato)titanium (3.2 cm^3, 8.74 mmol) was then added via syringe and the solution heated under reflux for 6 h. A change to red occurred, and a yellow–brown precipitate formed. This was filtered off and washed with diethyl ether (40 cm^3). Additional product was isolated after reducing the filtrate to approximately 15 cm^3 and adding diethyl ether (100 cm^3). [SL1]Yield: 1.22 g, 40%. IR (KBr disc, cm^{-1}): 1629 ν(C=N)(s), 905 (m) ν(Ti=O). Found: C, 56.4; H, 4.7; N 7.6. $C_{17}H_{16}N_2O_3Ti\cdot1.5MeOH$ requires: C, 56.6; H, 5.6; N, 7.1%. MS (FAB): $m/z = 345$, $[MH]^+$, (56%), based on $m/z = 136$, 100%.

The product [Ti(O(sal-1,3-pn)] MeCN can be prepared similarly using acetonitrile as solvent.

4.3. Preparation of [TiO{salnptn(3-OMe)$_2$}]

H_2{salnptn(3-OMe)$_2$} (3.33 g, 9.0 mmol) was partially dissolved in methanol (75 cm^3) to afford a yellow suspension. Di(isopropoxo)bis(pentane-2,4-dionato)titanium (3.39 cm^3, 9.0 mmol) was added and the suspension heated under reflux for 6 h. A yellow precipitate was formed, which was then filtered off and washed with diethyl ether (40 cm^3). Yield: 0.71 g, 18%. IR (KBr disc, cm^{-1}): 1615 ν(C=N)(s), 865 ν(Ti=O)(s). MS (EI): $m/z = 432$, $[M]^+$, (100%), $m/z = 864$, $[M_2]^+$, (35%).

4.4. Preparation of [TiO(hap-1,2-pn)]

H_2(hap-1,2-pn) (2.40 g, 7.78 mmol) was added to di(isopropoxo)bis(pentane-2,4-dionato) titanium (2.83 cm^3, 7.73 mmol) in methanol (75 cm^3). The suspension was heated under reflux for 3.5 days during which time the solution turned orange. After cooling the solution to room temperature, diethyl ether (150 cm^3) was added and a yellow clay-like substance was isolated. The suspension was stirred for 1 h, before the solid was filtered off and washed with diethyl ether (40 cm^3). Yield: 1.00 g, 35%. IR (KBr disc, cm^{-1}): 1595 ν(C=N)(s). MS (EI): $m/z = 372$, $[M]^+$ (100%).

4.5. Preparation of [TiO(salnptn)]

H_2(salnptn) (6.0g, 19 mmol) was suspended in methanol (50 cm^3) and di(isopropoxo)bis(pentane-2,4-dionato)titanium (7.2 cm^3, 20 mmol) was added. The suspension was heated under reflux for 16 h to give a red oil. The volume of the solution was reduced to 10 cm^3, and petroleum ether (60–80°C, 30 cm^3) was added. This gave a mixture of a lemon powder with a brown impurity, which was subsequently washed out using cold methanol (30 cm^3) to give the lemon powder. Yield: 4.17 g, 58%. IR (KBr disc, cm^{-1}): 1618 ν(C=N)(s), 901 ν(Ti=O)(s). MS (EI): $m/z = 372$, $[M]^+$ (90%), based on $m/z = 45$ (100%).

4.6. Preparation of [TiO(sal-1,2-pn)]·MeOH

H_2(sal-1,2-pn) (10.0 g, 35 mmol) was dissolved in methanol (280 cm^3) to afford a yellow solution and di(isopropoxo)-bis(pentane-2,4-dionato) titanium (13.0 cm^3, 35 mmol) was added. The solution was then heated under reflux overnight to give a red solution, which was then reduced in volume to 20 cm^3 and diethyl ether (150 cm^3) was added to precipitate the complex as an orange powder. This was filtered off and washed with diethyl ether (40 cm^3). Yield: 8.40 g, 69%. IR (KBr disc, cm^{-1}): 1631 ν(C=N)(s), 904 ν(Ti=O)(m). Found: C, 58.0; H, 4.9; N, 7.3. $C_{17}H_{16}N_2O_3Ti \cdot MeOH$ requires: C, 57.4; H, 5.4; N, 7.4% $C_{17}H_{16}N_2O_3$-Ti·0.5MeOH requires: C, 58.3; H, 5.0; N, 7.8%. MS (EI): $m/z = 344$, $[M]^+$ (100%).

4.7. Reaction between di(isopropoxo)bis(pentane-2,4-dionato)titanium and H_2\{salen(3-OMe)$_2$\}

H_2\{salen(3-OMe)$_2$\} (2.50 g, 7.6 mmol) was dissolved in methanol (70 cm^3) to afford a yellow solution. Di(isopropoxo)bis(pentane-2,4-dionato)titanium (2.50 cm^3, 6.8 mmol) was added, and the solution was heated under reflux for 13 h during which time the colour of the solution changed from yellow to orange to red. On cooling to room temperature, diethyl ether (100 cm^3) was added to precipitate the yellow Schiff base complex. This was then filtered off and washed with diethyl ether (50 cm^3) Yield: 2.35 g, 79%. IR (KBr disc, cm^{-1}): 1639 ν(C=N)(s), 866 ν(Ti=O)(s). MS (EI): $m/z = 390$, $[M]^+$, (100%).

4.8. Reaction of di(isopropoxo)bis(pentane-2,4-dionato)titanium with H_2\{salen(3,5-Cl)$_2$\}

H_2\{salen(3,5-Cl)$_2$\} (4.20 g, 11.3 mmol) was suspended in methanol (75 cm^3) and di(isopropoxo)-bis(pentane-2,4-dionato)titanium (3.79 cm^3, 10.4 mmol) was added. The yellow suspension was heated under reflux for 4 h to give a mustard powder which was then filtered off and washed with copious amounts of diethyl ether until the washings were colourless. Yield: 3.48 g, 72%. IR (KBr disc, cm^{-1}): 1639 ν(C=N)(s), 869 ν(Ti=O)(s). Found: C, 44.1; H, 2.4; N 6.3. $C_{16}H_{10}Cl_4N_2O_3Ti$ (corresponding to[TiO\{salen(3,5-Cl)$_2$\}]) requires: C, 41.0; H, 2.1; N, 6.0%. MS (EI): $m/z = 463$ $[M-5]^+$ (100%).

4.9. Reaction of di(isopropoxo)bis(pentane-2,4-dionato)titanium with H_2\{salen(5-Br)$_2$

(a) H_2\{salen(5-Br)$_2$\} (5.0 g, 11.7 mmol) was partially dissolved in methanol (75 cm^3) to afford a yellow suspension. Di(isopropoxo)bis(pentane-2,4-dionato)titanium (4.2 cm^3, 11.5 mmol) was added and the suspension heated under reflux for 5 h to give a mustard solid. This was filtered off and washed with diethyl ether (50 cm^3) and dried. Yield: 3.60 g, 63%. IR (KBr disc, cm^{-1}): 1640 ν(C=N)(s), 824 ν(Ti=O)(m). Found: C, 40.6; H, 2.5; N, 5.8. $C_{16}H_{12}Br_2N_2O_3Ti$ requires: C, 39.3; H, 2.5; N. 5.7%. MS (EI): $m/z = 483$ $[M-5]^+$ (27%), based on $m/z = 227$ (100%).

4.10. Reaction of di(isopropoxo)bis(pentane-2,4-dionato)titanium with H_2\{salen(5-Br)$_2$\} (b)

H_2\{salen(5-Br)$_2$\} (2.97 g, 7.0 mmol) was partially dissolved in acetonitrile (100 cm^3) to afford a yellow suspension. Di(isopropoxo)bis(pentane-2,4-dionato)titanium (3.0 cm^3, 8.5 mmol) was added and the suspension heated under reflux for 4 h to give a brick red solid. This was then filtered off and washed with diethyl ether (30 cm^3). Yield: 2.24 g, 66%. IR (KBr disc, cm^{-1}): 1632 ν(C=N)(s). Found: C, 42.2; H, 2.7; N, 5.8. $C_{16}H_{12}Br_2N_2O_3Ti$ (corresponding to [TiO\{salen(5-Br)$_2$\}]) requires: C, 39.4; H, 2.5; N, 5.7%. $C_{16}H_{12}Br_2N_2O_3Ti \cdot MeCN$ requires: C, 40.8; H, 2.8; N, 5.3%. MS (EI): $m/z = 488$, $[M]^+$, (61%), based on $m/z = 80$ (100%).

4.11. Preparation of [TiCl$_2$(salen)]

H$_2$(salen) (16.6 g, 60 mmol) was dissolved in thf (250 cm^3) to afford a yellow solution which was cooled to −30°C using an acetone–liquid nitrogen bath. An orange solution of titanium tetrachloride (6.5 cm^3, 60 mmol) in toluene (40 cm^3) was added with an immediate change to dark red. This red suspension was heated under reflux for 3 h, and the solid was then filtered off, washed with diethyl ether (50 cm^3), and then with a 1:1 mixture of acetone–water and filtered rapidly in air. Yield: 17.40 g, 73%. IR (KBr disc, cm^{-1}): 1613 ν(C=N)(s).

4.12. Preparation of [TiCl$_2${salen(3-OMe)$_2$}]

H$_2${salen(3-OMe)$_2$} (6.0 g, 20 mmol) was dissolved in thf (100 cm^3) to afford a yellow solution. An orange solution of titanium tetrachloride (1.60 cm^3, 20 mmol) in toluene (20 cm^3) was then added to give a magenta coloured suspension. This suspension was then heated under reflux for 2.5 h, filtered and the precipitate washed with tetrahydrofuran (20 cm^3) and diethyl ether (30 cm^3). Yield: 7.73 g, 95%. IR (KBr disc, cm^{-1}): 1625 ν(C=N)(s). Found: C, 48.6; H, 4.1; N, 6.2. $C_{18}H_{18}Cl_2N_2O_4Ti$ requires: C, 48.6; H, 4.1; N, 6.3%.

4.13. Preparation of [TiCl$_2$(hapen)] 2HCl

H$_2$(hapen) (5.0 g, 17 mmol) was partially dissolved in thf (200 cm^3) to afford a yellow suspension. An orange solution of titanium tetrachloride (1.8 cm^3, 16 mmol) in toluene (40 cm^3) was added to give a brick red suspension. This suspension was then heated under reflux for 3.5 h, and stirred at room temperature for 3 days. The brick red solid was filtered off, and washed with diethyl ether (50 cm^3). Yield: 6.00 g, 86%. IR (KBr disc, cm^{-1}): 1607 ν(C=N)(s). Found: C, 42.4; H, 4.5; N, 5.3. $C_{18}H_{18}Cl_2N_2O_2Ti\cdot 2HCl$ requires: C, 44.4; H, 4.1; N, 5.8%.

4.14. Preparation of [TiCl$_2$(hapnptn)]·2HCl

H$_2$(hapnptn) (3.4 g, 10 mmol) was dissolved in thf (120 cm^3) to afford a yellow solution. An orange solution of titanium tetrachloride (1.0 cm^3, 9 mmol) in toluene (40 cm^3) was then added to give to brick red suspension. This red suspension was then heated under reflux for 40 min, and then stirred at room temperature for 3 d. The red solid was then filtered off and washed with tetrahydrofuran and diethyl ether (60 cm^3). Yield: 4.39 g, 96%. IR (KBr disc, cm^{-1}): 1609 ν(C=N)(s). Found: C, 47.2; H, 5.2; N, 5.2. $C_{21}H_{24}Cl_2N_2O_2Ti\cdot 2HCl$ requires: C, 47.8; H, 5.0; N, 5.3%.

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