JOURNAL OF
Materials
CHEMISTRY

Vibrational spectroscopy and EXAFS study of $Ti(OC_2H_5)_4$ and alcohol exchange in $Ti(\textit{iso}\text{-}OC_3H_7)_4$

Kim S. Finnie,*[a] Vittorio Luca,[a] Paul D. Moran,[b] John R. Bartlett[a] and James L. Woolfrey[a]

[a]*Materials Division, Australian Nuclear Science and Technology Organisation, Private Mail Bag 1, Menai, NSW, 2234, Australia*
[b]*Department of Chemistry, University of Auckland, Private Bag 92019, Auckland, New Zealand*

Received 17th August 1999, Accepted 26th October 1999

The vibrational spectrum of tetraethylorthotitanate (TET) has been assigned by using vibrational and structural data from the series $Ti(OEt)_yCl_{4-y}$ ($y = 1$ to 4), to distinguish between bands due to bridging and terminally coordinated ethoxide. EXAFS studies of the series showed an increase in association with increasing y, in agreement with previous cryoscopic measurements. IR bands in the spectrum of TET in the region 1300 to 800 cm^{-1} have been assigned as follows: 850 and 885 cm^{-1}, C–C stretch of bridging ethoxide; 910 and 919 cm^{-1}, C–C stretch of terminal ethoxide; 1044 cm^{-1}, C–O stretch of bridging ethoxide; 995 and 1067 cm^{-1}, C–O stretch of terminal ethoxide; 1013 cm^{-1}, C–O stretch of both bridging and terminal ethoxide. Unresolved bands in the region 1100 to 1200 cm^{-1} are assigned to in- and out-of-plane rocking modes of both bridging and terminal ethoxide. The assignment of the 885 and 1044 cm^{-1} bands to bridging ethoxide has been confirmed by comparison of the $Ti(OEt)_3(acac)$ and $Ti(OEt)_2(acac)_2$ spectra.

The vibrational assignments of TET were used to investigate the alcohol exchange reaction between tetraisopropyltitanate (TPT) and EtOH by IR and Raman spectroscopy. Ligand exchange occurred quantitatively on reaction of TPT with one mol equivalent of EtOH, the resulting $Ti(OPr^i)_3(OEt)$ being five-fold coordinated with bridging predominantly occurring through the ethoxide ligand. The second isopropoxide was also exchanged quantitatively with addition of EtOH but further exchange was slower, with the final isopropoxide remaining coordinated to the Ti(IV) site, even in an excess of EtOH.

Introduction

Sol–gel processing involves the production of metal oxides *via* hydrolysis and condensation reactions of mainly metal alkoxide precursors. In the case of titanium oxide, tetraisopropyltitanate [$Ti(OPr^i)_4$, TPT] and tetraethylorthotitanate [$Ti(OEt)_4$, TET] are widely used as precursors in the production of titania sols, gels and ceramics. Ligand modification, such as reaction with alcohols, acids, bases and other coordinating ligands, enables 'tailoring' of specific precursors and, hence, control of subsequent reactions to form the final product.

While sol–gel processing of silicates has been extensively studied, far less is known about the solution structures and reactions of transition-metal alkoxide precursors. Vibrational spectroscopy provides an important tool for probing these structures because of the distinct group frequencies of the alkoxide ligands, principally involving C–H, C–O, C–C and M–O modes. However, the vibrational spectra of even the most common precursors, such as TPT and TET, are not well understood. A detailed investigation of the vibrational spectrum of TPT has shown that interligand coupling, in which certain isopropoxide modes couple with those of other ligands through O–Ti–O linkages,[1] has a marked effect on the IR and Raman spectra, compared with spectra of molecules with a single isopropoxide group. Evidence for such coupling has been found in the vibrational spectra of the series $Ti(OPr^i)_yCl_{4-y}$, where $y = 1$ to 4.[2]

The spectrum of TPT has been fully assigned[1] and the salient features are reproduced in Table 1. In assigning the vibrational spectrum of TPT, the $Ti–O_4$ framework was assumed to have approximately tetrahedral symmetry, and four normal coordinates were assigned from the far-IR, mid-IR and Raman spectra, on the basis of T_d selection rules and depolarisation ratios.[1] The Ti–O vibrations occur in the spectral region 700–100 cm^{-1}, whereas the majority of the alkoxide modes (apart from some low-lying bending modes) occur above 800 cm^{-1}. Somewhat surprisingly, the very intense, admixed C–C–C and C–O stretching modes, which dominate the IR and Raman spectra of Pr^iOH, appear with only moderate intensity in the corresponding TPT spectra. Instead, the strongest bands in both the IR and Raman spectra of TPT are the admixed in-phase methyl rocking mode and C–O stretch, coupled with the anti-symmetric and symmetric $Ti–O_4$ stretching modes, respectively. Strong interligand coupling through the O–Ti–O linkages in TPT results in significant bandshifts and non-coincidence in the IR and Raman spectra, compared with the corresponding bands of the isolated isopropoxide ligand in $Ti(OPr^i)Cl_3$.

TPT has an average association of 1.4 by cryoscopy in benzene[3] and is generally considered to be a tetrahedral monomer, with a small degree of oligomerisation. Several weak bands in the infrared spectrum of TPT disappear on dilution in

Table 1 Band positions and assignments for the Raman (R) and infrared (IR) spectra of TPT[1]

Wavenumber/cm^{-1}	Assignment[a]
155	$\nu_2(T_d)$ [δ(O–Ti–O), R]
561	$\nu_1(T_d)$ [ν_s(Ti–O), R]
611	$\nu_3(T_d)$ [ν_{as}(Ti–O), IR]
851	ν_s(C–C–C) (R, IR)
988	ν(C–O)/$\rho(CH_3)+\nu_{as}$(Ti–O) (IR)
1024	ν(C–O)/$\rho(CH_3)+\nu_s$(Ti–O) (R)
1115	$\rho(CH_3)/\nu$(C–O)$+\nu_{as}$(Ti–O) (IR)
1124	ν_{as}(C–C–C) (R)
1180	$\rho(CH_3)/\nu$(C–O)$+\nu_s$(Ti–O) (R)

[a]Ligand assignments are approximate only, due to the strong coupling between ν(C–O) and ν(C–C) modes in secondary alcohols.

CCl_4, and have been assigned to bridging species. TET, in contrast, was found to have an average association of 2.4 by cryoscopy in benzene,[3] and is generally considered to exist as a trimer in solution. The results of a XANES and EXAFS study of TET indicate that each titanium ion is five-fold coordinated.[4] A cryoscopic study of a series of titanium compounds containing ethoxide ligands showed that for the series $Ti(OEt)_yX_{4-y}$, where X = Cl and Br, the association in solutions of 0.05 to 0.5 mol dm^{-3} [Ti(IV)] in benzene varies with y, as follows: $Ti(OEt)X_3$, monomeric; $Ti(OEt)_2X_2$, dimeric (with some admixture of trimer when X = Cl); $Ti(OEt)_3X$, trimeric; and $Ti(OEt)_4$, trimeric.[5] Therefore, the vibrational spectrum of TET is expected to be more complex than that of TPT, with contributions from bridging- as well as terminally-bonded ethoxides. In an early IR study of metal ethoxides, the C–O and Ti–O bands of TET were attributed to either bridging- or terminal-ethoxide groups.[6] This was done on the basis of: (i) comparison with the spectrum of EtOH; (ii) comparison with the spectrum of uranium hexaethoxide (monomeric); (iii) shifts in the spectra on isotopic substitution of oxygen; and (iv) the effect of donor molecules on the spectrum.

The objective of the present study is to provide an improved understanding of how the constituent ligands contribute to the vibrational spectrum of TET. The spectra of the series $Ti(OEt)_yCl_{4-y}$ ($y = 1$ to 4) contain vibrations of both terminally-bound and bridging ethoxide groups, and this fact, together with the structures determined by proton NMR and cryoscopic association data,[5] has enabled a comparison with previous assignments.

In order to verify the assignment of bridging-ethoxide vibrational bands in species identified as being oligomeric, the IR spectra of complexes obtained by modifying TET with acetylacetone, [*i.e.* $Ti(OEt)_3(acac)$ and $Ti(OEt)_2(acac)_2$], have been compared. The disubstituted complex, $Ti(OEt)_2(acac)_2$, is mononuclear and octahedral, with two terminally bound ethoxide ligands.[7] However, the structure of $Ti(OEt)_3(acac)$ is less well established. The crystal structure shows that the solid has a binuclear centrosymmetric structure, $[\{Ti(OEt)_3(acac)\}_2]$, with two bridging and four terminally bound ethoxides per dimer. However, NMR studies suggest that in solution, partial disproportionation to $Ti(OEt)_4$ and $Ti(OEt)_2(acac)_2$ occurs, giving an equilibrium mixture of the three species.[7] An alternative structure has also been proposed, following XANES–EXAFS, NMR and IR studies, consisting of an equilibrium mixture of monomeric (five-fold coordinate) and oligomeric (six-fold coordinate) $Ti(OEt)_3(acac)$, *e.g.* $Ti(OEt)_3(acac) \leftrightharpoons [\{Ti(OEt)_3(acac)\}_2]$.[8]

The vibrational assignments have also been used in an investigation of the sequential alcohol-exchange reaction in which TPT is reacted with EtOH to form $Ti(OPr^i)_{4-y}(OEt)_y$ and Pr^iOH, in order to gain insight into the changes in structure which occur with exchange of alkoxide ligands.

In addition to using the published structural data,[5] the structures of the mixed chloroethoxide species have been examined here by X-ray absorption spectroscopy (XAS) of solutions in CCl_4, exploiting the ability of XAS to provide direct structural information on the Ti-ligand environment. The preedge XANES region arises from transitions of electrons to bound excited electronic states, but this electronic excitation, occurring at the absorbing atom, is strongly modulated by the surrounding atoms in the short to medium environment range (< 100 absorbing atoms). The preedge transitions are dipole allowed (3s→4p) and quadrupolar forbidden (1s→3d). In the case of Ti, p–d mixing results in a non-negligible intensity of preedge features. For a centrosymmetric structure (octahedral coordination), their intensity is very small, but increases as the degree of distortion increases. Therefore, for Ti in tetrahedral symmetry, a single intense transition is observed. As the coordination number, and hence symmetry, increases, the intensity of the preedge peak decreases. For Ti in octahedral coordination, a weak triplet structure is usually observed. Recently, Farges *et al.*[9,10] showed empirically that the average coordination number of Ti in a range of titanium oxide reference materials and titanium silicate glasses can be extracted reasonably well from plots of preedge intensity against peak energy. In addition to observation of the preedge structure, it is possible to analyse EXAFS data in detail, in order to extract precise bond distances and approximate coordination numbers.

Experimental

Samples

TPT (Hüls Troisdorf) and TET (solution containing 5 wt% EtOH, Merck) were used as-received. The ethanol concentration in TET corresponds to a molar ratio of 1 : 15 ethanol : ethoxide, and is, therefore, not expected to contribute significantly to the spectra. The titanium chloroethoxide solutions, $Ti(OEt)_yCl_{4-y}$, (y = 1 to 4), were prepared by mixing stoichiometric quantities of $TiCl_4$ and TET solutions (0.4 mol dm^{-3} in dry CCl_4 at ambient temperature).[11] A solution of TPT (0.4 mol dm^{-3} in dry CCl_4) served as a tetrahedral standard for the XAS measurements of the corresponding chloroethoxide solutions. Partially exchanged $Ti(OPr^i)_y(OEt)_{4-y}$ samples were prepared by mixing TPT and dry ethanol in molar ratios of (TPT : EtOH) 1 : 0, 1 : 1, 1 : 2, 1 : 3, 1 : 4 and 1 : 5. The refractive index of each $Ti(OPr^i)_y(OEt)_{4-y}$ sample was measured using an Abbey refractometer to enable correction of IR ATR data for dilution effects. Both $Ti(OEt)_yCl_{4-y}$ and $Ti(OPr^i)_y(OEt)_{4-y}$ samples were prepared and handled under dry N_2 at all times. $Ti(OEt)_3(acac)$ and $Ti(OEt)_2(acac)_2$ were synthesized by mixing stoichiometric quantities of TET and acetylacetone, followed by distillation (under dry N_2) to remove the released ethanol, as confirmed by the absence of the characteristic ν(C–C–O) Raman band at 881 cm^{-1}.[12]

Spectroscopy

IR spectra were obtained using a Digilab FTS-40 spectrometer, equipped with a liquid-N_2-cooled-MCT detector. A linearised detector was used for the $Ti(OEt)_yCl_{4-y}$ and $Ti(OEt)_y(acac)_{4-y}$ spectra. Absorption spectra of the mixed chloroethoxide samples were measured in the range 4000 to 400 cm^{-1} (4 cm^{-1} resolution, 256 scans) using a liquid cell with KRS-5 windows and 20 μm pathlength. Spectra of $Ti(OPr^i)_y(OEt)_{4-y}$ and $Ti(OEt)_y(acac)_{4-y}$ were measured in the range 4000 to 530 cm^{-1} (4 cm^{-1} resolution, 256 scans) using an attenuated total reflectance (ATR) accessory equipped with a single reflection ZnSe element. All $Ti(OPr^i)_y(OEt)_{4-y}$ ATR spectra were corrected for the change in sample refractive index due to increasing dilution with alcohol.

FT-Raman spectra in the range 3500–100 cm^{-1} were obtained using a Digilab FT-Raman II spectrometer, with a liquid-N_2-cooled-germanium detector and holographic notch filter. A reproducible sample alignment was used for all samples, which were sealed in 20 ml glass vials. The $Ti(OEt)_yCl_{4-y}$ spectra were normalised using the 790 and 760 cm^{-1} bands of the CCl_4 solvent. The 1064 nm exciting line of a Spectra-Physics Nd-YAG diode laser was used, with 500 mW power incident at the sample; 1024 scans were coadded for each unpolarised Raman spectrum (resolution 4 cm^{-1}), while parallel and perpendicularly polarised spectra were measured by coaddition of 2048 scans. Spectral data were processed using Win-IR (Digilab) software, incorporating a curve-fitting procedure.

X-Ray absorption spectra were recorded on beam line 20B of the Australian National Beam line facility (ANBF) at The Photon Factory, Tsukuba, Japan, using a Si(111) monochromator. The EXAFS data were recorded in fluorescence mode using a Canberra 11 element detector. Normalizations of the spectra were performed using the program WINXAS, which fits a zero-order spline to a specified region after the edge step.[13] Analyses of the EXAFS data were performed with the program XFIT.[14] To fit the EXAFS data, initial values of E_0, the energy zero, and S_0^2, the amplitude reduction factor, were obtained by fitting the EXAFS data of titanium isopropoxide, and using the number of nearest-neighbour atoms (N), their distance (R) and the Debye–Waller factor (σ^2), fixed at their expected values, and allowing the energy zero (E_0) and amplitude reduction factor (S_0^2) to float simultaneously. These values of E_0 and S_0^2 were then used as initial values for the modelling of the $Ti(OEt)_yCl_{4-y}$ samples. The various shells observed in the FT-EXAFS data were initially isolated using a Gaussian window and fitted separately. In the final fits the window was increased to include all the FT peaks to be fitted and the N, R, and σ^2 values of each shell were allowed to float.

Results and discussion

The Raman and IR spectra of TET in the range 1500–500 cm^{-1} are shown in Fig. 1. The vibrational spectrum of TET is complicated by the presence of bands arising from bridging- as well as terminally-bonded ethoxides. In contrast to TPT, in which the vibrations of the $Ti–O_4$ framework can be characterised by four normal modes of the relatively highly symmetrical (T_d) monomer, there are twelve Ti–O normal modes arising from a (theoretical) lone, five-fold coordinated Ti, assuming a distorted trigonal bipyramidal symmetry (C_{2v}). Hence, a detailed assignment of the Ti–O modes has not been attempted here. The intense Raman band at 608 cm^{-1} is fully polarised and is assigned as a totally symmetric Ti–O stretching mode. This band position is close to that of the corresponding mode in tetrabutylorthotitanate (TBT) at 618 cm^{-1}, in which the coordination of Ti has also been determined to be five-fold.[4] It is interesting to note that the totally symmetric stretching mode of tetrahedrally-coordinated Ti is found at 561 cm^{-1} in TPT. This is contrary to expectations that a decreased coordination number (from five to four) results in a higher stretching frequency. A probable reason for the discrepancy is that this mode is strongly coupled with C–O and CH_3 modes in TPT, resulting in a shift to lower wavenumber.[1] This would suggest that such coupling does not occur as strongly in TET.

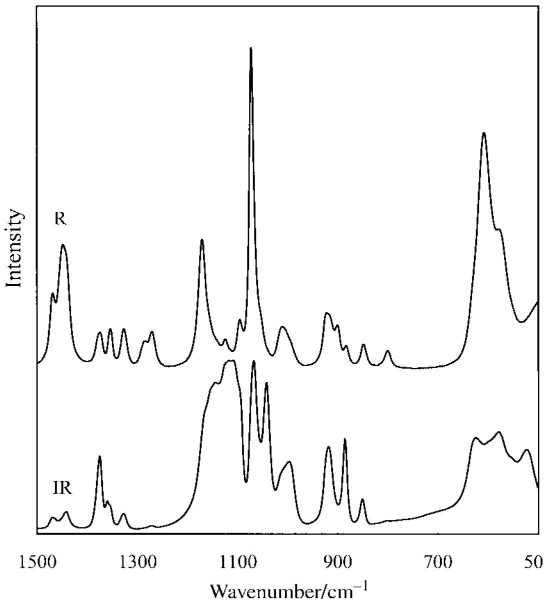

Fig. 1 Raman and IR spectra of TET in the region 1500 to 500 cm^{-1}.

The alkoxide bands in the range 1300–800 cm^{-1} have been assigned using the spectra of mixed chloroethoxide titanate species as described below.

X-Ray absorption spectroscopy of the series $Ti(OEt)_yCl_{4-y}$

In the present series of samples, the most intense preedge peak is observed for the solution of TPT, which is known to be tetrahedral and monomeric at this concentration,[1] and can, therefore, be used as a standard (Fig. 2). The preedge of $Ti(OEt)Cl_3$ has comparable intensity to that of TPT, indicating that $Ti(OEt)Cl_3$ is also a tetrahedral monomer. This is emphasized in the EXAFS data of both of these compounds.

The FT-EXAFS spectrum of TPT clearly shows a single Ti–O correlation, best fitted with a single Ti–O bond length of *ca.* 1.81 Å, which is appropriate for four-coordinate Ti (Fig. 3, Table 2). There is a possible weak contribution from carbon backscatterers at 2.93 Å although the signal-to-noise (*S*/*N*) of the data makes this somewhat uncertain. Likewise, the FT-EXAFS analysis of $Ti(OEt)Cl_3$ indicates that this complex is also tetrahedral and monomeric. The first shell correlation is best fitted as the sum of O and Cl backscatterers and the observed Ti–O and Ti–Cl bond lengths are 1.72 and 2.18 Å, respectively. Ti–Ti correlations are not observed, as expected for a monomeric species. The Ti–O bond length is consistent with terminal ethoxide, as observed for TPT.

The preedge peak in the XANES trace of $Ti(OEt)_2Cl_2$ has a much reduced intensity compared to either $Ti(OEt)Cl_3$ or TPT, indicating that the coordination number has increased to at least five, and possibly six. This trend continues as the ethoxide to chloride ratio increases (Fig. 2). The FT-EXAFS spectra of both $Ti(OEt)_2Cl_2$ and $Ti(OEt)_3Cl$ show clear evidence of higher shells. It was possible to fit these higher shells as Ti–Ti, Ti–O, and Ti–C correlations, using the single-scattering theory (Feff 4.0). However, the poor *S*/*N* of the spectra, together with the possibility of multiple-scattering contributions at these longer distances, makes determination of the exact coordination environment beyond the first atomic shell uncertain. In the case of $Ti(OEt)_2Cl_2$, we were unable to observe a long Ti–O shell [2.20 Å in $Ti(OEt)_3Cl$] corresponding to bridging oxygen, due to overlap with the terminal Ti–Cl shell at 2.30 Å. However, the

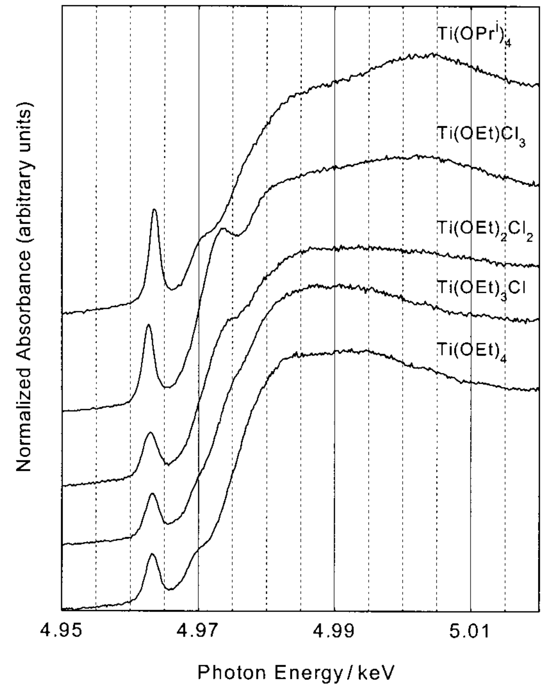

Fig. 2 Ti K-edge XANES spectra of solutions of $Ti(OEt)_yCl_{4-y}$ and TPT, 0.4 mol dm^{-3} in dry CCl_4.

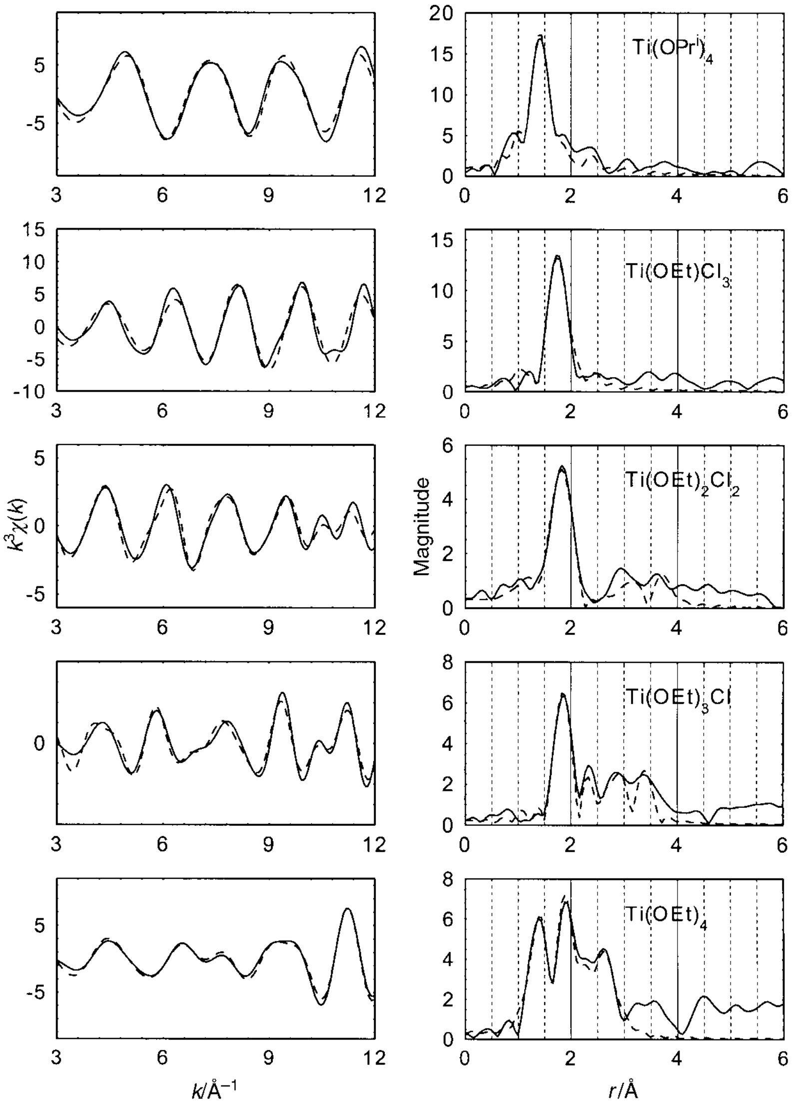

Fig. 3 Ti K-edge EXAFS spectra of solutions of Ti(OEt)$_y$Cl$_{4-y}$ and TPT, 0.4 mol dm^{-3} in dry CCl$_4$. (—) experimental, (- - - -) simulated. Left side—k-space data. Right side—r-space data (not corrected for phase shift).

data are inconsistent with the presence of a long Ti–Cl bond, expected to be 2.5–2.6 Å for bridging chloride,[15] and thus we conclude that bridging preferentially occurs through the ethoxide ligands, consistent with the increased donor ability of the alkoxide oxygen compared with chloride.

The observed coordination expansion with the formation of bridging-ethoxide ligands for Ti(OEt)$_y$Cl$_{4-y}$ species, where $y > 1$, is in general agreement with the structures derived from association data determined cryoscopically at concentrations of 0.4 mol dm^{-3} in benzene, and ^{1}H NMR spectra.[5]

Vibrational spectra of the series Ti(OEt)$_y$Cl$_{4-y}$

Raman and IR spectra of the Ti(OEt)$_y$Cl$_{4-y}$ solutions in the range 1300 to 800 cm^{-1} are shown in Fig. 4 and 5, respectively, and band positions (± 2 cm^{-1}), integrated intensities ($\pm 5\%$) and assignments are tabulated in Table 3. The region 800 to 700 cm^{-1} is obscured by solvent bands in both the Raman and IR spectra, but Ti–O bands observed in the region 700 to 500 cm^{-1} in the Raman and IR spectra are shown in Fig. 6 and 7 respectively, and are included in Table 3. Ti–Cl vibrations were observed at 479 (IR), 386 (R), 378 (R), 134 (R) and 120 (R) cm^{-1} in Ti(OEt)Cl$_3$ and more weakly in Ti(OEt)$_2$Cl$_2$. The positions of the ethoxide CH$_2$ and CH$_3$ bands in the range 1500–1200 cm^{-1} remain relatively unchanged throughout the Ti(OEt)$_y$Cl$_{4-y}$ series, and the intensities are essentially additive. However, bands due to vibrations involving the C–C–O and Ti–O bonds are expected to show more variation with chloride substitution due to:

(1) increased electropositivity of the Ti^{4+} ion with increasing chloride substitution;

(2) varying degrees of association, as discussed above;

(3) possible interligand coupling effects as observed in TPT,[1] and for the corresponding Ti(OPr^i)$_y$Cl$_{4-y}$ series.[2]

Comparison of the spectra of simple molecules—those observed during sequential addition of ethoxide to Ti(OEt)$_y$Cl$_{4-y}$—has enabled identification of some TET bands. In the following discussion, the association data and structures from Weingarten and Van Wazer[5] have been employed.

Ti(OEt)Cl$_3$. The degree of association of Ti(OEt)Cl$_3$ has been determined by cryoscopy to be slightly >1, at a concentration of 0.4 mol dm^{-3}, indicating that this complex is largely monomeric.[5] The X-ray absorption data presented here support this conclusion. Hence, the vibrational spectrum will be dominated by bands due to terminally-coordinated ethoxide, possibly with some weak bands due to a small fraction of bridging ligands, and should, therefore, be the simplest of the series to interpret. The major IR and Raman bands are all coincident (Table 3), as expected for a low-symmetry molecule, and can be assigned by comparison with IR band assignments for the parent alcohol. As noted in an

Table 2 EXAFS fit parameters for TPT, TET and titanium ethoxychlorides in CCl_4 solutions

Sample	Scatter	Fit parameters[a] N	r/Å	σ^2/Å^2	$\chi^{2\,b}$
$Ti(OPr^i)_4$	O	4	1.81	0.0005	12.3
	C	3.0	2.93	0.004	
$Ti(OEt)Cl_3$	O	1.0	1.72	0.002	8.6
	Cl	1.7	2.18	0.002	
	C	1.0	2.87	0.002	
$Ti(OEt)_2Cl_2$	O	0.4	1.79	0.003	2.6
	Cl	2.7	2.30	0.009	
	Ti	0.4	3.53	0.002	
	C	1.0	3.24	0.002	
	O	0.9	4.18	0.002	
$Ti(OEt)_3Cl$	Cl	0.5	2.05	0.002	3.6
	O	1.9	2.20	0.002	
	Ti	4.0	3.05	0.02	
	O	2.9	3.27	0.002	
	Cl	1.1	3.70	0.002	
$Ti(OEt)_4$	O	1.7	1.79	0.002	1.9
	O	2.8	2.11	0.002	
	C	7.0	2.38	0.002	
	C	6.2	2.94	0.002	
	Ti	1.4	3.18	0.002	

[a] The program XFIT uses the goodness-of-fit parameter (χ^2) defined as $\chi^2 = \int_{k=0}^{\infty} [W\{\chi_{obs}(k) - \chi_{calc}(k)\}]^2$ where W is a weighting parameter, χ^2_{obs} is the observed datum, and χ^2_{calc} is the calculated datum. [b] Typical uncertainty on N is ± 1, on r it is ± 0.05, and on σ^2 it is ± 0.005.

analysis of the ethanol IR spectrum,[16] the C–C and C–O stretching modes of alcohols are highly mixed, and the band at 881 cm^{-1}, assigned there as a C–O stretch, is more appropriately assigned as a symmetric C–C–O stretch, with the corresponding antisymmetric C–C–O stretch being found at 1049 cm^{-1}.[12] Consequently, the symmetric C–C–O stretch dominates the Raman spectrum of ethanol, with a depolarisation ratio (ρ) of 0.2, whereas the 1049 cm^{-1} band has $\rho = 0.61$, reflecting the symmetry difference between the two modes. However, significant variations in the Raman intensities are observed following coordination of a single ethoxide ligand to Ti(IV). The band at 942 cm^{-1} is the only significant feature in the region 1000 to 850 cm^{-1} and, presumably, corresponds to the 881 cm^{-1} band of ethanol. The band at 1072 cm^{-1} has considerable intensity in both Raman and IR spectra and, therefore, arises from the 1049 cm^{-1} ethanol mode. However, the significantly reduced intensity of the 942 cm^{-1} band with an increased ρ of 0.37, compared with the intense, and now fully polarised band at 1072 cm^{-1} ($\rho < 0.1$), suggests that formation of a Ti–O bond has resulted in some decoupling of the C–C and C–O vibrations, leading to assignments of the 942 and 1072 cm^{-1} bands as predominantly ν(C–C) and ν(C–O), respectively (Table 3).

Additional bands to note are the Ti–O stretching mode, which is observed at 630 cm^{-1}, and the strong IR band at 1101 cm^{-1} (1104 cm^{-1} R), which is assigned to the out-of-plane methyl rock, $\rho(CH_3)$, found at 1088 cm^{-1} (1094 cm^{-1} R) in ethanol. The corresponding IR band in $Ti(OPr^i)Cl_3$, assigned to an in-phase-methyl rock (also coupled with C–O stretching), is similarly intense.[2] The Raman spectrum of 0.4 mol dm^{-3} TET in a large excess of $TiCl_4$ (molar ratio 1 : 7) was found to be identical to that of $Ti(OEt)Cl_3$ over the range 1300 to 500 cm^{-1}, confirming that the features described above do correspond to an isolated ethoxide ligand.

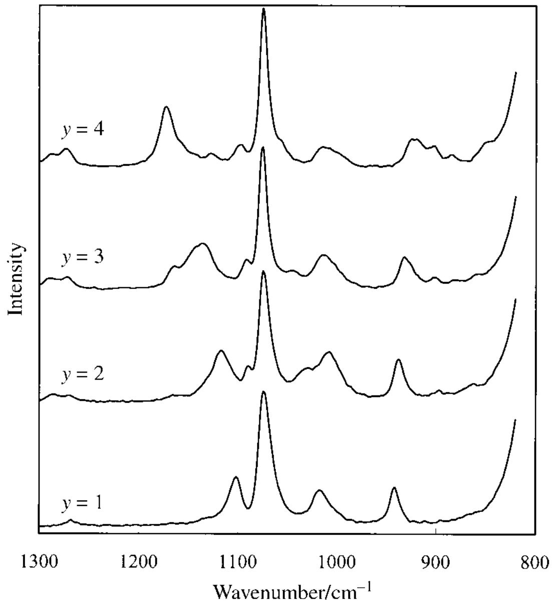

Fig. 4 Raman spectra of solutions of $Ti(OEt)_yCl_{4-y}$ in CCl_4 (0.4 mol dm^{-3}), in the region 1300–800 cm^{-1}.

$Ti(OEt)_2Cl_2$. The association of $Ti(OEt)_2Cl_2$ was determined as approximately 2.3 at a concentration of 0.4 mol dm^{-3}, and the solution considered to be a mixture of dimers and trimers.[5] The most favoured structures (on dipole moment and steric grounds) both consist of five-fold coordinated Ti ions, each with two shared (bridging) ethoxides, a terminal ethoxide and two chlorides.[5] The first shell EXAFS of this complex can be fitted to a Ti–O correlation with a distance of 1.79 Å, indicative of a terminal ethoxide, and a Ti–Cl correlation at 2.30 Å (Table 2). No attempt was made to try to fit an additional shell of oxygen scatterers to this first FT peak, because the number of adjustable parameters would exceed the number of independent parameters permitted by information theory.[17] Comparison of the vibrational spectrum of $Ti(OEt)_2Cl_2$ with that of $Ti(OEt)Cl_3$ should, in the first instance, reflect the contribution of one bridging ethoxide per Ti(IV) site. The most notable difference in comparing IR spectra is the appearance of relatively strong bands at 878 and 863 cm^{-1} (unresolved, Fig. 5), and at 577 and 550 cm^{-1} (unresolved, Fig. 7), whereas the 942 cm^{-1} band

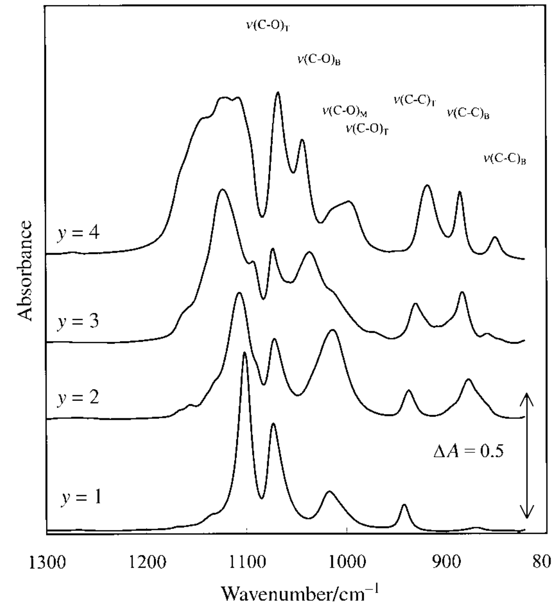

Fig. 5 IR spectra of solutions of $Ti(OEt)_yCl_{4-y}$ in CCl_4 (0.4 mol dm^{-3}), in the region 1300–800 cm^{-1}. The main bands are denoted as follows: T = terminal, B = bridging, and M = mixed (terminal + bridging), ethoxide.

Table 3 Raman and IR bands of Ti(OEt)$_{4-y}$Cl$_y$, $y=1$ to 4 (0.4 mol dm^{-3} in CCl$_4$), 500 to 1200 cm^{-1}

Ti(OEt)Cl$_3$				Ti(OEt)$_2$Cl$_2$				Ti(OEt)$_3$Cl				Ti(OEt)$_4$				
IR/cm^{-1}	Area	R/cm^{-1}	Area	IR/cm^{-1}	Area	R/cm^{-1}	Area	IR/cm^{-1}	Area	R/cm^{-1}	Area	IR/cm^{-1}	Area	R/cm^{-1}	Area	Assignment
								529	3.1			521	7.4			ν(Ti–O)
				550	4.4			559	7.6			553	3.5			ν(Ti–O)
565	0.16			577	3.6							576	8.4	578	9.3	ν(Ti–O)
		610	0.1			608	3.8	614	12.4	613	30.7	600	13.6	611	20.3	ν(Ti–O)
631	1.6	630	7.1	623	4.8	627	12.3			642	1.7	628	6	632	1.9	ν(Ti–O)
				863	0.6			857	0.5			850	1.5			ν(C–C), bridging
871	0.2			878	4.4			883	2.6			885	3	884	2.4	ν(C–C), bridging
				895	0.2	897	0.2	897	2.1	901	2			902	1	ν(C–C), bridging
												910	4.9			ν(C–C), terminal
942	1.4	942	3.7	937	1.7	937	4.1	928	2.2	933	4.8	919	3.5	920	4	ν(C–C), terminal
								931	0.5					927	0.6	ν(C–C), terminal
								971	0.1							
								1006	2.2	1003	4.4	995	5.9	1003	2.2	ν(C–O), terminal
1015	5.5	1016	7	1015	15.8	1008	9.4			1015	3.8	1013	2.6	1016	2.5	ν(C–O), mixed
						1033	3.3	1037	20.3	1044	3	1044	11			ν(C–O), bridging
														1064	5.3	ν(C–O), terminal
1072	11.2	1073	19.1	1071	8.8	1075	17.1	1072	5.8	1076	16.2	1067	10.9	1075	12.6	ν(C–O), terminal
				1090	0.43	1090	1.9	1093	1.5	1092	1.7					
												1099	7.8	1098	1.8	
1101	8.9	1104	2.0	1106	11.1	1117	8.6	1121	25.1			1120	18.9	1127	1.9	Out-of-plane ρ(CH$_3$)
1113	1.4	1108	1.9													
1129	3.1	1126	1.2	1129	3.3	1137	0.6			1133	10.2	1147	11.3	1143	0.2	
										1147	3			1156	1.7	
				1158	1.9	1162	0.5	1160	2.1	1166	1.9	1167	6.4	1172	9.1	In-plane ρ(CH$_3$)

remains basically unchanged, apart from a small shift to 937 cm^{-1}. Therefore, the 878 and 863 cm^{-1} bands are assigned to C–C stretching modes, and the 577 and 550 cm^{-1} bands to Ti–O stretching modes of bridging ethoxide, with the adjacent ligands in the dimer resulting in a small splitting of the bands. A closer examination of the IR spectrum of Ti(OEt)Cl$_3$ reveals weak bands at 871 and 565 cm^{-1}, indicating that a small amount (*ca.* 3%) of bridging ethoxide is present. It should be noted that there is a significant increase in the 630 cm^{-1} band intensity on addition of the second ethoxide, despite the unambiguous assignment to terminal ethoxide in the first spectrum. Clearly, the Ti–O bands in particular will be coupled, so that assignments to either terminal- or bridging-species are less meaningful than for vibrations localised on the ethoxide ligand.

In addition to the 1072 cm^{-1} band in Ti(OEt)Cl$_3$, there is a weaker band at 1015 cm^{-1}; coordination of a bridging ethoxide results in a significant increase in the IR intensity of this band. However, the band in the Ti(OEt)Cl$_3$ spectrum has *ca.* 35% of the intensity of that in Ti(OEt)$_2$Cl$_2$, which is too intense to be assigned to the fraction of bridging ethoxide (*ca.* 3%) present in the first sample. Therefore, we must conclude that both bridging and terminal ethoxides have a C–O band in this region; it is not, however, clear why terminally-bound ethoxide should exhibit two C–O stretching bands. For Ti(OEt)$_2$Cl$_2$, two Raman bands at 1008 and 1033 cm^{-1} lie under the 1015 cm^{-1} IR band envelope, compared with the single Raman band at 1016 cm^{-1} in Ti(OEt)Cl$_3$ (Fig. 4), indicating that there are several possible components to the IR band.

Ti(OEt)$_3$Cl and Ti(OEt)$_4$. Ti(OEt)$_3$Cl is trimeric,[5] and according to the structural model discussed above, the difference between Ti(OEt)$_2$Cl$_2$ and Ti(OEt)$_3$Cl should be the addition of one terminal ethoxide. However, the spectra do not

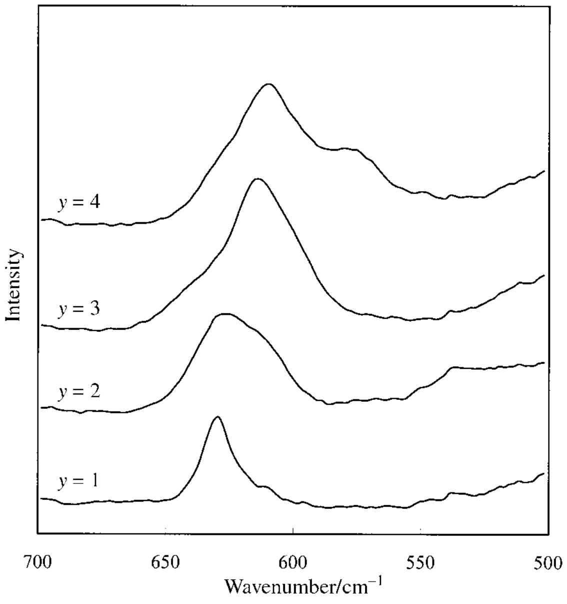

Fig. 6 Raman spectra of solutions of Ti(OEt)$_y$Cl$_{4-y}$ in CCl$_4$ (0.4 mol dm^{-3}), in the region 700–500 cm^{-1}.

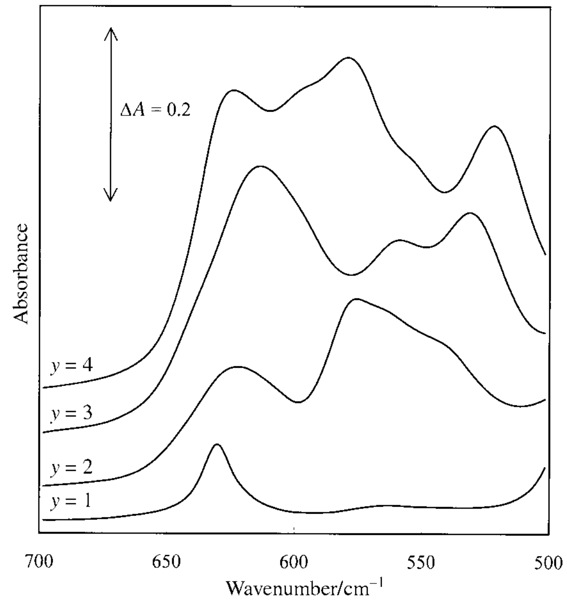

Fig. 7 IR spectra of solutions Ti(OEt)$_y$Cl$_{4-y}$ in CCl$_4$ (0.4 mol dm^{-3}), in the region 700–500 cm^{-1}.

conclusively show an increase in the intensity of these bands. In the C–C stretching region of Fig. 4 and 5, there is a new IR band at 897 cm^{-1} (901 cm^{-1} R), situated *between* the assigned bridging and terminal bands. There is no increase in the 1072 cm^{-1} band assigned to the C–O stretch of terminal ethoxide; indeed there is even a small decrease in the intensity. However, there is significantly increased intensity at 1037 cm^{-1}, one of several bands which have split from the band originally at 1015 cm^{-1} in Ti(OEt)$_2$Cl$_2$, with a second band shifting to lower wavenumber, at 1006 cm^{-1}. The 1015 cm^{-1} band was present in terminal ethoxide but appeared more intense for the bridging ligand. Thus, there is some ambiguity in determining whether the third ligand is terminal or bridging. Assignment to bridging, however, would suggest an increase of the Ti coordination number to six.

In Bradley and Westlake's assignment of the IR spectrum of TET, six bands between 1138 and 882 cm^{-1} were attributed to C–O modes.[6] Our assignments show a significant departure from those of the earlier study. However, in the division of bands between terminal and bridging ethoxides, the two studies are largely in agreement. In the early study, the 1064, 913 and 623 cm^{-1} bands were attributed to terminal ethoxide, and the 882 and 577 cm^{-1} bands to bridging ethoxide, as confirmed here. In addition, the 1040 cm^{-1} band was assigned to bridging ethoxide. There is some ambiguity here in the assignment of this band from the mixed Ti chloroethoxide spectra, with both terminal and bridging ethoxide giving rise to bands in this region of the spectrum. However, analysis of the IR spectrum of Ti(OEt)$_3$(acac) (discussed below), suggests that the 1044 cm^{-1} band is indeed due to bridging ethoxide. This implies that four bridging and one terminal ethoxide are coordinated to each Ti(IV) centre in Ti(OEt)$_3$Cl, such as would be observed in a cyclic trimer with two ethoxides bridging each Ti(IV) ion, for example.

The final member of the series, TET, has also been found to be trimeric.[5] A six membered ring of three (five-fold coordinated) Ti and three bridging ethoxides, was the preferred structure from NMR[5] and more recently, XANES and EXAFS data.[4] Comparison of the IR spectra of Ti(OEt)$_3$Cl and TET shows a large increase in the intensity of the IR bands at 1067, 1013, 995, 919 and 910 cm^{-1}, and a sharp drop in the 1044 cm^{-1} band intensity (Fig. 5). There is clearly a marked increase in the amount of terminal ethoxide present in TET compared with Ti(OEt)$_3$Cl. However, the results are somewhat more equivocal for the bridging species; the decrease in C–O stretching intensity suggests that the concentration of bridging ethoxide is reduced in TET compared with Ti(OEt)$_3$Cl, whereas there is little change in the corresponding C–C stretching band intensities. Hence, while there is a suggestion of six-fold coordination in Ti(OEt)$_3$Cl, the possibility of fewer bridging ethoxides in TET means there is no strong evidence to challenge the previous determination of five-fold coordination in this species.

It is interesting to note the changes in the Raman spectra in the region 1100 to 1200 cm^{-1} (Fig. 4), over the Ti(OEt)$_y$Cl$_{4-y}$ series, with a systematic shift in the most intense band from 1104 cm^{-1} in Ti(OEt)Cl$_3$, to 1172 cm^{-1} in TET. This shift confirms that unique compounds have been obtained following the ligand redistribution reaction, rather than an equilibrium mixture of species, which would all contribute to the vibrational spectrum. The band at 1104 cm^{-1} was attributed to the out-of-plane methyl rock (1088 cm^{-1} for ethanol); however it appears that the *in-plane* methyl rock (1150 cm^{-1} for ethanol) is more intense in the Raman spectrum of TET, the out-of-plane rock appearing only weakly (in Raman) at 1127 cm^{-1}. The IR spectra in this region (Fig. 5) are quite complex, consisting of a number of unresolved bands, including a band at *ca.* 1160–1170 cm^{-1} attributed to the in-plane methyl rock, which grows more intense with increasing amounts of ethoxide.

Comparison of the TET spectra with those of Ti(OEt)Cl$_3$ suggests that the individual band intensities are not strictly additive; for example, the IR C–C stretching band intensities in TET (summed bridging and terminal bands) are not four times that in Ti(OEt)Cl$_3$. However, summation of the *total* intensities in the region 500–1200 cm^{-1} shows that, for the IR spectra at least, the sum scales nearly linearly with the number of ligands. Comparison of the IR spectra of Ti(OEt)Cl$_3$ and TET indicates that the bands which have essentially C–H character (sum of in- and out-of-plane methyl rocking modes) scale roughly linearly with number of ethoxides, whereas the summed Ti–O bands of TET (and to a lesser extent the C–C bands) have increased intensities at the expense of the C–O stretching bands. This redistribution of band intensities is indicative of interligand coupling and, in the absence of strict additivity of the separate modes, care should be taken to systematically vary the ligand concentration when attempting to use vibrational spectra to quantify ligands in species with mixed alkoxide compositions, such as in the alcohol exchange study below.

IR spectra of Ti(OEt)$_3$(acac) and Ti(OEt)$_2$(acac)$_2$

The assignment of several bridging-ethoxide bands has been verified by examination of two compounds formed by reacting TET with acetylacetone. The IR spectra of Ti(OEt)$_3$(acac) and Ti(OEt)$_2$(acac)$_2$, in the range 1200–800 cm^{-1}, are shown in Fig. 8. The addition of an acetylacetonate ligand results in a significantly more complex vibrational spectrum, particularly in the region 1200–1700 cm^{-1}, which includes the intense, coupled carbon–carbon and carbon–oxygen stretching modes of acac. Hence, a full assignment of the spectrum has not been attempted here.

Using either of the two proposed structures of Ti(OEt)$_3$(acac) discussed above, comparison of the Ti(OEt)$_3$(acac) and Ti(OEt)$_2$(acac)$_2$ spectra should reveal the contribution of bridging ethoxide ligands, which are not present in the latter compound. Note that the intense 327 cm^{-1} mode of TET was not observed in the Raman spectrum of Ti(OEt)$_3$(acac) (not shown here), suggesting that the most probable structure is the equilibrium mixture Ti(OEt)$_3$(acac)$\leftrightharpoons$[{Ti(OEt)$_3$(acac)}$_2$]. Comparison of the ethoxide band region clearly shows the appearance of two bands (shown marked with arrows), at 1040 and 886 cm^{-1} in the spectrum of Ti(OEt)$_3$(acac). The absence of these bands in Ti(OEt)$_2$(acac)$_2$ confirms the assignment to C–O and C–C stretching modes, respectively, of bridging ethoxide, in agreement with the assignments by Bradley and Westlake.[6] Comparison of the corresponding Raman spectra

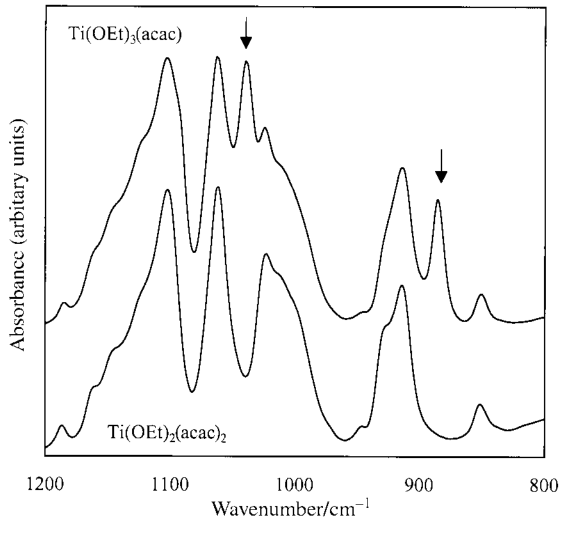

Fig. 8 IR spectra of Ti(OEt)$_3$(acac) and Ti(OEt)$_2$(acac)$_2$ in the region 1200–800 cm^{-1}. Bridging ethoxide bands marked with arrows.

shows very little difference between the two samples, indicating that the bridging ethoxide bands are only weakly Raman active.

Ethoxide speciation in Ti(OEt)$_y$(OPr$^{\text{i}}$)$_{4-y}$

With an understanding of the TET and TPT spectra, it is possible to investigate ligand speciation in Ti(OEt)$_y$(OPr$^{\text{i}}$)$_{4-y}$ produced when the isopropoxide ligands in TPT are partially exchanged with ethoxide ligands. The Raman spectra of TPT–EtOH solutions (with TPT : EtOH molar ratios of 1 : 0, 1 : 1, 1 : 2, 1 : 3, 1 : 4 and 1 : 5) in the range 700–100 cm^{-1} (encompassing Ti–O and alkoxide bending modes) are shown in Fig. 9. It is evident that the most dramatic change has occurred on addition of one molar equivalent of EtOH. From the rapid increase in the intensity of the peak at 608 cm^{-1} [ν(Ti–O) of ≡Ti–OEt] in the spectrum of the 1 : 1 mixture, and the corresponding decrease in the intensities of ν_1(TPT) and ν_2(TPT) at 561 and 155 cm^{-1}, respectively (T_{d} symmetry), it may be inferred that the majority of titanium sites are five-fold coordinate in this solution. The residual TPT bands were not evident in the spectrum of the 1 : 2 mixture in Fig. 9, suggesting that the transformation to five-fold coordination was complete on addition of two molar equivalents of EtOH. The corresponding IR spectra (not shown here) are consistent with this interpretation; the 577 cm^{-1} band of TET was observed after the addition of one molar equivalent of EtOH, but it was not until the addition of two molar equivalents of EtOH that ν_3(TPT) at 611 cm^{-1} completely disappeared.

The Raman and IR spectra of the TPT–EtOH solutions in the range 1500 to 700 cm^{-1} are shown in Fig. 10 and 11, respectively. Complicating these spectra are contributions from both Pr$^{\text{i}}$OH, released on substitution of isopropoxide with ethoxide, and unreacted EtOH. While there was considerable overlap of the alcohol and alkoxide bands in the IR spectra, there were isolated bands in the Raman spectra that allowed semi-quantitative analyses of the concentrations of the different species present in solution. As for the emerging ethoxide bands, those assigned to bridging ethoxide are overlapped by EtOH bands in both IR and Raman, and are thus only observable in the spectra of the 1 : 1 solution, where the amount of free EtOH is minimal.

The intense symmetric C–C–C stretching mode of Pr$^{\text{i}}$OH, which occurs in the Raman spectrum at 817 cm^{-1} (Fig. 10), was used to calculate the concentration of Pr$^{\text{i}}$OH present in each solution and hence the stoichiometry of the Ti(OEt)$_y$(OPr$^{\text{i}}$)$_{4-y}$ species formed on addition of EtOH. In the 1 : 1 solution, where one molar equivalent of EtOH was added, this concentration corresponds to *ca.* 26% of the original isopropoxide ligand concentration (*i.e.* there has been complete exchange of isopropoxide with ethoxide ligands to form Ti(OPr$^{\text{i}}$)$_3$(OEt), as also found in an earlier IR study).[18] This is confirmed by the absence of a Raman band at 881 cm^{-1} (corresponding to the intense C–C symmetric stretch of EtOH, Fig. 10). With mostly five-fold coordinated Ti(IV) in this product, the quantitative release of Pr$^{\text{i}}$OH precludes a possible solvation reaction in which EtOH coordinates *via* donation of oxygen lone electron pairs to vacant Ti(IV) orbitals.[18] Instead, there must exist one bridging alkoxide per Ti(IV) site.

Comparison of the C–C IR stretching bands clearly shows that the majority of ethoxide ligands in Ti(OPr$^{\text{i}}$)$_3$(OEt) are bridging rather than terminally coordinated. EtOH has a strong IR band at 881 cm^{-1} which could obscure the bridging ethoxide band at this position; however, the absence of the corresponding band in the Raman spectrum of the 1 : 1 solution (Fig. 10) indicates that there is very little free EtOH remaining on reaction with TPT. Thus, the intensities of the 885 and 919 cm^{-1} IR bands in the spectrum of the 1 : 1 mixture in Fig. 11, which correspond to bridging and terminal ethoxide C–C stretching bands, respectively, may be compared. The band at 885 cm^{-1} has approximately 10 times the intensity of the 919 cm^{-1} band in the solution, whereas the 919 cm^{-1} band is the stronger of the two in the TET spectrum (Table 3). Hence, substitution with the first ethoxide results in mostly bridging coordination, with a small fraction terminally coordinated.

In the 1080 to 950 cm^{-1} region of the Ti(OPr^{i})$_3$(OEt) IR spectrum, there are two remaining ethoxide bands which are not obscured by TPT or Pr$^{\text{i}}$OH bands, at 1043 and 1070 cm^{-1} in the spectrum of the 1 : 1 mixture (Fig. 11). While the corresponding bands have similar intensities in TET (at 1044 and 1067 cm^{-1}, respectively, Table 3), the first features far more strongly in this spectrum, suggesting assignment to bridging ethoxide. Note that in solutions in which larger

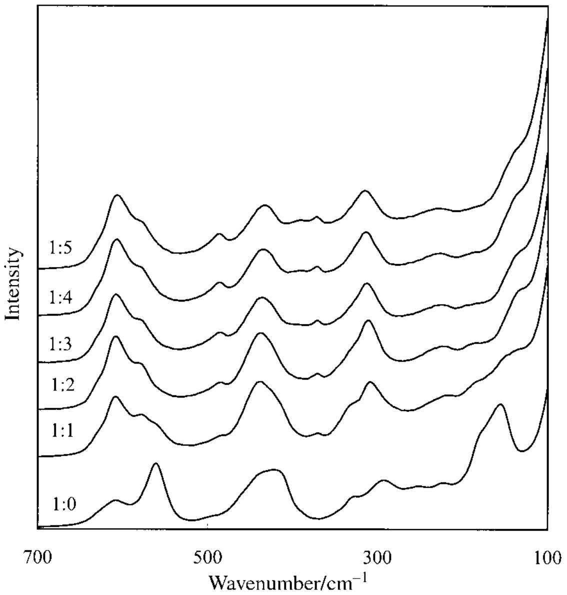

Fig. 9 Raman spectra of TPT–EtOH solutions in the region 700–100 cm^{-1} with molar ratios (TPT : EtOH) of 1 : 0, 1 : 1, 1 : 2, 1 : 3, 1 : 4 and 1 : 5. The spectra are adjusted to a constant Ti(IV) concentration of 3.4 mol dm^{-3}.

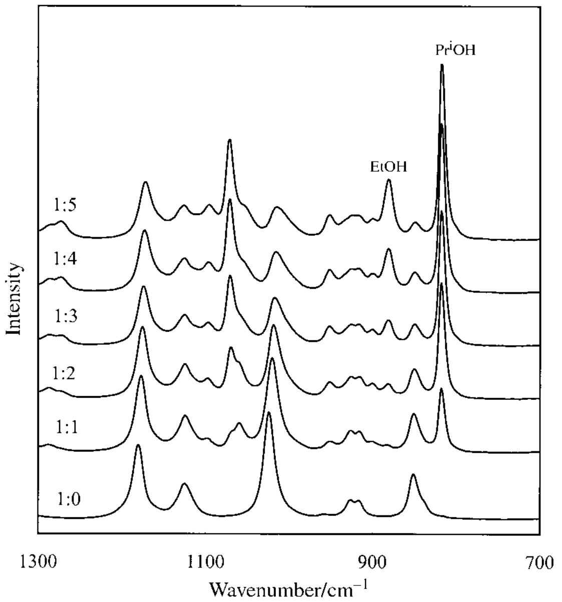

Fig. 10 Raman spectra of TPT–EtOH solutions in the region 1300–700 cm^{-1} with molar ratios (TPT : EtOH) of 1 : 0, 1 : 1, 1 : 2, 1 : 3, 1 : 4 and 1 : 5. The spectra are adjusted to a constant Ti(IV) concentration of 3.4 mol dm^{-3}. The characteristic ν(C–C–C) of Pr$^{\text{i}}$OH and ν(C–C–O) of EtOH are labelled at 817 and 885 cm^{-1} respectively.

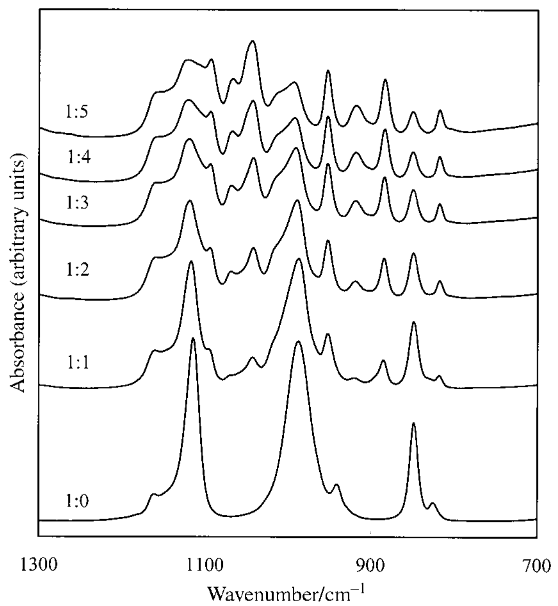

Fig. 11 IR spectra of TPT–EtOH solutions in the region 1300–700 cm^{-1} with molar ratios (TPT : EtOH) of 1 : 0, 1 : 1, 1 : 2, 1 : 3, 1 : 4 and 1 : 5. The spectra are adjusted to a constant Ti(IV) concentration of 3.4 mol dm^{-3}.

quantities of EtOH have been added, this band appears intense due to absorption by EtOH at 1046 cm^{-1}. In the Raman spectrum of Ti(OPr^i)$_3$(OEt), the band at 1059 cm^{-1} has greater intensity than that at 1071 cm^{-1}. However, with further addition of ethanol, the 1059 cm^{-1} band appears as a weaker shoulder to the main 1072 cm^{-1} band, suggesting an assignment to bridging ethoxide.

The Pr^{i}OH concentration in the 1 : 2 solution, in which two molar equivalents of EtOH have been added (calculated using the Raman band at 817 cm^{-1}), again suggests that nearly quantitative exchange has occurred, with 48% of the original isopropoxide ligands released. (However, the emergence of the EtOH band at 881 cm^{-1} in the Raman spectrum suggests that this figure may be somewhat overestimated.) The addition of three, four and five molar equivalents of EtOH resulted in 55, 71 and 74% Pr^{i}OH released respectively. There was a significant increase in the intensity of the 919 cm^{-1} band assigned to terminal ethoxide on addition of the second and third molar equivalent of EtOH, and smaller increases thereafter. The concentrations of released Pr^{i}OH suggest that the first and second isopropoxide ligands of TPT are easily exchanged with ethoxide ligands (due both to the higher nucleophilicity of the ethoxide ligand and the resulting coordination expansion), the third is exchanged with more difficulty, and even in an excess of EtOH, the final isopropoxide is not removed under these experimental conditions. This is in agreement with an earlier study, which found that the isopropoxide ligands were not fully exchanged when TPT was mixed with a five-fold excess of EtOH.[18]

Conclusion

The coordination of ethoxide to Ti(IV) ions in the series Ti(OEt)$_y$Cl$_{4-y}$, $y = 1$ to 4, has been investigated by IR, Raman and X-ray absorption spectroscopy, resulting in assignments of the TET vibrational bands in the region 1300 to 700 cm^{-1}, and in particular, the identification of characteristic modes of terminal and bridging ethoxide. The assignments have been employed to investigate the alcohol exchange reaction between TPT and EtOH using vibrational spectroscopy:

(1) Coordination expansion was observed with increasing y in the series Ti(OEt)$_y$Cl$_{4-y}$ ($y = 1$ to 4, 0.4 mol dm^{-3} in CCl$_4$). Ti(OEt)Cl$_3$ was determined to be four-coordinate as in Ti(OPr^i)$_4$, but the coordination number increased to at least five and possibly six for $y = 2$ to 4. The EXAFS results are in agreement with previous association data determined cryoscopically for the series.[5]

(2) The characteristic IR modes of bridging and terminal ethoxide in TET were identified as follows:

Bridging

- C–C stretch at 850 and 885 cm^{-1}.
- C–O stretch at 1044 cm^{-1}.

Terminal

- C–C stretch at 910 and 919 cm^{-1}.
- C–O stretch at 995 and 1067 cm^{-1}.

An additional C–O stretching mode observed at 1013 cm^{-1} contains contributions from both bridging and terminal ethoxide.

(3) Comparison of the IR band intensities of the series Ti(OEt)$_{4-y}$Cl$_y$ indicates that while the overall (summed) intensities increase linearly with addition of ethoxide, only the C–H modes are approximately additive. The Ti–O and C–C intensities increase disproportionately whereas the C–O intensities appear lower than expected with increasing ethoxide content, suggesting coupling of the ethoxide vibrations. As the Ti–O, C–C and C–O band intensities do not therefore accurately reflect the number of bonds present per molecule, caution should be exercised in using particular vibrational bands to quantify absolute ligand concentrations.

(4) The coupling of ethoxide vibrations in the series Ti(OEt)$_{4-y}$Cl$_y$ has a minimal effect on the IR and Raman spectra, in contrast to the corresponding isopropoxide series. The most significant effect of ethoxide coupling is the shift of Raman band intensity from the out-of-plane methyl rock at 1104 cm^{-1} in Ti(OEt)Cl$_3$, to the in-plane methyl rock at 1172 cm^{-1} in TET. Both in- and out-of-plane rocking modes appear in the IR spectrum, resulting in an intense cluster of bands in the region 1100 to 1200 cm^{-1}.

(5) The appearance of certain ethoxide bands in the IR spectrum of Ti(OEt)$_3$(acac) which are not in that of Ti(OEt)$_2$(acac)$_2$, has confirmed the assignment of several bridging ethoxide bands made for TET. In particular, the assignment of a *ca.* 1040 cm^{-1} band to bridging ethoxide results in the prediction of one terminal and four bridging ethoxides per Ti(IV) ion in Ti(OEt)$_3$Cl, suggesting a six-coordinate structure for this compound.

(6) The coordination of the majority of titanium species was observed to increase from four in TPT, to five after the exchange of only one isopropoxide ligand with ethoxide, which occurred quantitatively with addition of one molar equivalent of EtOH. Bridging predominantly occurred through the ethoxide ligand. The second isopropoxide was also exchanged quantitatively (or nearly so) with addition of EtOH, but further exchange was more sluggish, with an equilibrium existing between the mixed titanium species, EtOH and Pr^{i}OH. The final isopropoxide was not exchanged, even in an excess of EtOH.

Acknowledgements

P.D.M. thanks the NZ Vice-Chancellors' Committee for the award of a post-graduate scholarship. This work was supported by the Australian Research Council. Access to the Photon Factory was provided by the Australian Synchrotron Research Program which has been funded by the Commonwealth of Australia *via* the Major National Research Facilities Program.

References

1 P. D. Moran, G. A. Bowmaker, R. P. Cooney, K. S. Finnie, J. R. Bartlett and J. L. Woolfrey, *Inorg. Chem.*, 1998, **37**, 2741.

2 P. D. Moran, Ph.D. Thesis, The University of Auckland, 1996, ch. 6.

3 D. C. Bradley, R. C. Mehrotra and D. P. Gaur, *Metal Alkoxides*, Academic Press, London, 1978 and references therein.

4 F. Babonneau, S. Doeuff, A. Léaustic, C. Sanchez, C. Cartier and M. Verdaguer, *Inorg. Chem.*, 1998, **27**, 3166.

5 H. Weingarten and J. R. Van Wazer, *J. Am. Chem. Soc.*, 1965, **87**, 724.

6 D. C. Bradley and A. H. Westlake, *Proc. Symp. Coord. Chem.*, 1964, 309.

7 R. J. Errington, J. Ridland, W. Clegg, R. A. Coxall and J. M. Sherwood, *Polyhedron*, 1998, **17**, 659.

8 A. Léaustic, F. Babonneau and J. Livage, *Chem. Mater.*, 1989, **1**, 240.

9 F. Farges, *Am. Mineral.*, 1997, **92**, 44.

10 F. Farges, G. E. Brown, Jnr. and J. J. Rehr, *Geochim. Cosmochim. Acta*, 1996, **60**, 3023.

11 O. Poncelet, J.-C. Robert and J. Guilment, *Mater. Res. Soc. Symp. Proc.*, 1992, **271**, 249.

12 D. Lin-Vein, N. B. Colthup, W. G. Fateley and J. G. Grasselli, *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, Academic Press, San Diego, 1991, p. 57.

13 T. Ressler, *J. Phys. IV*, 1997, **7**, 269.

14 P. A. Ellis and H. C. Freeman, *J. Synchrotron Radiat.*, 1995, **2**, 190.

15 H.-M. Gau, C.-S. Lee, C.-C. Lin, M.-K. Jiang, Y.-C. Hou and C.-N. Kuo, *J. Am. Chem. Soc.*, 1996, **118**, 2936.

16 Y. Mikawa, J. W. Brasch and R. J. Jacobsen, *Spectrochim. Acta, Part A*, 1971, **27**, 529.

17 E. A. Stern, *Am. Phys. Soc.*, 1993, **48**, 9825.

18 J. R. Bartlett and J. L. Woolfrey, *Chem. Mater.*, 1996, **8**, 1167.

Paper a906662d