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Studies on the synthesis of Pb-Ti-oxo-alkoxocarboxylato complexes

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Abstract—Reactions between lead carboxylates $Pb(O_2CR)_2$ and $Ti(OPr')_4$ produce complexes of empirical formulae $Pb_2Ti_2(O)(O_2CR)_2(OPr')_8$ ($R = C_3F_7$ 1; $C(CH_3)_3$ 2) in toluene and $Pb_2Ti_4(O)_2(O_2CR)_2(OPr')_{14}$ ($R = CH(CH_3)_2$ 3) in Pr'OH solution. ²⁰⁷Pb NMR evidence indicates that both types of complex form in alcoholic solution. The compound 4 having a Pb₃Ti₃ core is produced when Pb(O₂CCH(CH₃)₂)₂ reacts with Ti(OPr')₄ in toluene. Attempts to prepare acetylacetonate derivatives of compounds having 1 : 1 or 1 : 2 Pb : Ti stoichiometries by direct substitution of the compounds gave poorly soluble Pb containing products but direct reaction of Pb(O₂CCH₃)₂ or PbO with Ti-acetylacetonate-alkoxide species gave compounds of empirical formulae Pb₃Ti₃(O)₄(O₂CCH₃)₂(OPr')₇(acac) **5** and Pb₂Ti₂(O)(OEt)₈(acac)₂ **6**. Reaction of Ti(OR)₄ (R = OPr', Et) with acetic acid yields products which further react with PbO to form the previously characterised Pb—Ti compounds Pb₂Ti₂(O)(O₂CCH₃)₂(OPr')₈ **7** and Pb₂Ti₄(O)₂(O₂CCH₃)₂(OEt)₁₄ **8**. Molecular weight measurements, ²⁰⁷Pb, ¹⁹F, ¹H and ¹³C NMR and IR spectral data have been used to derive empirical formulae for the various complexes isolated. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: lead-titanium; alkoxide; carboxylate; ²⁰⁷Pb; NMR; acetylacetone.

Mixtures of hydrated lead acetate and a titanium alkoxide in alcoholic solution have been used as precursors to the formation of the piezoelectric material PbTiO₃ by sol-gel processes. [1-4]. It was recognised that some form of Pb-Ti complex would be formed in such solutions [1] and various empirical formulae were proposed (e.g. $Pb(O_2CCH_3)(O)Ti(OR)_3$ $Pb(O)_{2}Ti_{2}(OR)_{6}$). Subsequent attempts at direct syninvolving reaction between anhydrous thesis $Pb(O_2CCH_3)_2$ and $Ti(OPr')_4$ and $Ti(OEt)_4$ led to the isolation of two compounds each having a different Pb: Ti ratio depending on the alkoxide substituent. The 1:1 Pb: Ti ratio complex formed using $Ti(OPr^{i})_{4}$ as reagent [5–7], was shown to be Pb₂Ti₂(μ_4 -O)(O₂C- $(OPr')_8$ 7 by single crystal X-ray analysis [6]. This complex has also been formed by direct reaction of acetic acid on the mixed metal alkoxide $Pb_2Ti_2(\mu$ -O) $(OPr^{i})_{10}$ [8].

The formula of the 1:2 complex formed using $Ti(OEt)_4$ has been established as $Pb_2Ti_4(\mu_4-O)_2(O_2C-CH_3)_2(OEt)_{14}$ 8 by two independent X-ray studies

[7,9]. The latter complex was the only compound to be isolated whether the Pb: Ti ratio of initial reagents was 1:1 or 1:2. Each compound has a Pb: acetate ratio of 1:1 instead of the 1:2 ratio of the starting reagent i.e. acetate has been "lost" in the reaction as had previously been found [10] using various spectroscopic techniques. Moreover an acetate group bridges each of the Pb-Pb and Ti-Ti atom pairs in the 1:1 compound while in the 1:2 complex, only the pairs of Ti atoms have bridging acetate groups attached i.e. there has been acetate exchange between Pb and Ti as part of the overall reaction. Group exchange between the labile Group 4/14 precursor reagents is not unexpected although the mechanism for the exchange process is unclear. Another extreme case of such an exchange reaction has been observed in the reaction between Zn acetate and a Sn methoxide compound in an attempt to prepare a Sn-Zn heterometallic [11]. Solubility considerations presumably determined that the most readily isolated product was the polymeric homonuclear Zn-acetate-alkoxide $[Zn_2(O_2CCH_3)_3(OCH_3)]_n$

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The isolation of complexes of differing Pb—Ti stoichiometry using the same Pb carboxylate reagent but different Ti alkoxides raises the question as to whether this results from a fortuitous combination of solubility considerations or is due more fundamentally to steric or electronic differences between the alkoxy compounds of Ti, varying bridging capacities of the alkoxide groups or abilities to form oxo groups by ester elimination. Similarly the exchange of acetate groups between Pb and Ti suggests that the alkanoate group could also play a role in determining the final stoichiometry of Pb—Ti compound.

We report here the isolation and empirical formulae of complexes formed by the reactions of $Ti(OPr')_4$ with several other lead alkanoates (Pb(O₂CR)₂) where R is either strongly electronegative (C₃F₇) or large and capable of exerting steric resistance to bridge formation, (C(CH₃)₃, CH(CH₃)₂). Also, in view of the addition of acetylacetone to mixtures of a titanium alkoxide and Pb(O₂CCH₃)₂ to improve the thickness [12] and electrical properties [13] of PbTiO₃ films produced by sol-gel processes we have endeavoured to identify the acetylacetone complexes formed by its reaction with Pb—Ti alkoxide precursors.

A further feature of the two Pb—Ti complexes previously isolated has been the presence of tetrahedrally coordinated oxo groups as key structural features of each complex. In recent years, oxo groups have been found to be common structural units in many other homo- and heteronuclear alkoxides [14] and carboxylato-alkoxides compounds [15,16] even when the compounds have been prepared under scrupulously anhydrous conditions. Although such groups might still result from hydrolytic processes due to the adventitious entry of traces of water, other processes including ether elimination in alkoxides (i)

$$\mathbf{M} - \mathbf{O}\mathbf{R} + \mathbf{R}\mathbf{O} - \mathbf{M} \rightarrow \mathbf{M} - \mathbf{O} - \mathbf{M} + \mathbf{R}_2\mathbf{O} \qquad (i)$$

and ester elimination in carboxylate-alkoxide reactions (ii)

$$M \longrightarrow OR + R'COO \longrightarrow M \rightarrow M \longrightarrow OM' + R'COOR$$
(ii)

are more likely to be the routes by which oxo groups are formed. There have been reports of the formation of esters in previous studies of Pb acetate-Ti alkoxide reactions [17-19]. Hubert-Pfalzgraf et al. [6] however did not observe ester formation in the room temperature reaction which yielded the 1:1 Pb: Ti compound 7 but only when the reactants were initially heated in toluene thus suggesting ether elimination leads to oxo group formation. Extensive ester formation has been reported to occur when mixtures of Zn or other transition metal acetates are heated to high temperatures in decalin with $Al(OR)_3$ [20]. Zn—O—Al and other M—O—Al alkoxy complexes have been proposed to form although their structures are not precisely known. The generality of the formation of oxo groups in reactions leading to alkoxocarboxylato mixed metal species and indeed polynuclear alkoxides suggests that the fundamental reactions require further study.

The use of PbO as a reagent to produce "basic" lead acetate [21] suggested it be examined as a direct source of oxo groups in the synthesis of Pb-Ti complexes and as part of the present study we have successfully prepared the known 1:1 and 1:2 Pb: Ti oxoacetato-alkoxide complexes using the products of reaction of $Ti(OR)_4$ (R = Prⁱ, Et) and acetic acid as the titanium reagent. Although strenuous efforts have been made to prepare crystals of suitable quality for X-ray analysis of the new species formed in these studies so far they have been uniformly unsuccessful. Hence the empirical formulae suggested, although supported by spectroscopic and vapour phase osmometric molecular weight measurements, rely greatly on comparisons with other structurally characterised species, where available and on chemically plausible assumptions, particularly with regard to the presence and number of oxo groups in the molecules.

EXPERIMENTAL

All reactions were carried out using dry solvents and manipulations used Schlenk techniques under dry nitrogen. Alcohols were predried over molecular sieves then distilled after the formation of the appropriate Mg alkoxide or in the presence of CaH_2 then stored over molecular sieves. All other solvents were dried by standard procedures.

Molecular weights were measured by vapour phase osmometry (VPO) at 60°K using a Knauer Type II osmometer contained in a dry box facility with benzil as standard. 207Pb NMR spectra were obtained using a Bruker AM-300 spectrometer. Chemical shifts were measured in ppm using Pb(Me)₄ as external standard with high field from the standard considered negative. These values were converted to values relative to Pb(NO₃)₂ by adding 2961 [22]. ¹H, ¹³C and ¹⁹F spectra were measured at 300 K (unless otherwise stated) on a Varian EM-360A or the Bruker instrument. Tetramethylsilane was used as standard for ¹H and ¹³C spectra and CFCl₃ for ¹⁹F spectra. Mass spectra were recorded on VG Micromass 7070F or VG Trio-1 quadrupolar spectrometers. Electron microprobe analyses (EMA) were made with a Cambridge S410 SEM linked through an NEC X-ray detector and pulse processing system to a Packard multichannel analyser. A commercial sample of PbTiO₃ (Aldrich) was used as standard. Elemental analyses were by CMAS, Melbourne. $Ti(OPr')_4$ (Aldrich) was used as received.

Lead carboxylates

Anhydrous lead acetate. The preparation of 10–20 g quantities, free from evidence for O—H stretching frequencies in the 3000-4000 cm⁻¹ region was accomplished by either heating lead acetate trihydrate at 100°C under reduced pressure (10⁻³ Torr) for 5 h or

stirring the hydrate at room temperature with excess acetic anhydride for several hours then removing all volatile materials by pumping at 10^{-3} Torr and 50° C. The product is insoluble in toluene, THF and chloroform, readily soluble in methanol and 2-methoxyethanol and sparingly soluble in ethanol. A typical analysis gave; Found: C, 14.8; H, 1.85. Calc. for C₄H₆O₄Pb: C, 14.8; H, 1.85%.

Basic lead acetate $3[Pb(O_2CCH_3)_2] \cdot PbO \cdot H_2O$. The method was based on that of Kwestroo *et al.* [21]. PbO was added to a solution of the trihydrate in water in the mole ratio 1:3, oxide to acetate (a slight excess of oxide was used giving a practical mole ratio of 1.05:3. The mixture was stirred at room temperature for some hours as the bulk of the oxide slowly dissolved. The solution was finally filtered and evaporated at 40°C under reduced pressure. The powder X-ray pattern of the product was identical with the compound reported [21]. Found: C, 12.0; H, 1.50. Calc. for C₁₂H₂₀O₁₄Pb₄: C, 11.8; H, 1.60%.

Lead heptafluorobutyrate trihydrate $Pb(O_2CC_3F_7)_2$. 3H₂O. An aqueous solution of the acid was refluxed with PbO, the solution filtered and allowed to evaporate to crystallisation. Found: C, 13.7; H, 0.2; F, 38.3. Calc. for C₈H₆F₁₄O₇Pb: C, 14.0; H, 0.09; F, 38.7%.

Lead pivalate Pb($O_2CC(CH_3)_3$)₂. PbO was added to a methanol solution containing two equivalents of pivalic acid and the mixture stirred at room temperature until most of the oxide had dissolved. The solution was filtered and on further standing deposited a white solid which was filtered and dried. M.pt. 172– 174°C. Found: C, 29.2; H, 4.63. Calc. for $C_{10}H_{18}O_4Pb: C, 29.3; H, 4.40\%$.

Lead dimethylacetate $[Pb(O_2CCH(CH_3)_2)_2]_6$ · 4H₂O. This compound was prepared by the reported method [23].

1:1 Pb: Ti ratio compounds

Pb₂Ti₂(O)(O₂CR)₂(OPrⁱ)₈. Ti(OPrⁱ)₄ (usually 3.5 mmol) was added dropwise to an equimolar quantity of the carboxylate as a slurry in isopropanol (anhydrous lead acetate [7]) or toluene (lead hep-tafluorobutyrate) or a solution in toluene (lead pivalate). Volumes of solvent ca 30 cm³ were found appropriate. The mixtures were refluxed for 2–3 h, filtered, then cooled to 0°C or a lower temperature to induce crystallisation. In the case of the pivalate product the solvent was eventually removed under reduced pressure, the waxy solid remaining redissolved in the minimum of warm toluene and cooled to -20°C until crystals formed. The yields in terms of the amounts of crystalline product recovered were at least 55% in each preparation.

 $\begin{array}{l} Pb_{2}Ti_{2}(O)(O_{2}CC_{3}F_{7})_{2}(OPr')_{8} \ 1. \ EMA: Pb: Ti, 1:1.\\ Found: C, 26.9; H, 4.10; F, 18.3. Calc. for \\ C_{32}H_{56}F_{14}O_{13}Pb_{2}Ti_{2}: C, 26.9; H, 3.90; F, 18.6\%. \ Mol.\\ wt. \ (benzene): 1397\pm 50 \ (theor. for \ C_{32}H_{56} \end{array}$

 $F_{14}O_{13}Pb_2Ti_2$, 1425). NMR: ¹H (CDCl₃): $\delta = 1.22$, 1.25, 1.29, 1.35, 1.39, 1.47 (d, OCH(CH₃)₂, 48H); 4.05, 4.78, 4.97, 5.05, 5.47, 5.70 (sp, OCH(CH₃)₂, 8H) ppm: ¹⁹F (CDCl₃): $\delta = -81.25$, -81.72 (t, $O_2CCF_2CF_2CF_3$; -118.0, -120.3(sext, $O_2CCF_2CF_2CF_3$; -128.1-126.5, (t, O₂CC<u>F</u>₂CF₂CF₃) ppm. IR (Nujol): 2922 (vs), 2854 (vs), 1673 (vs), 1413 (w), 1378 (s), 1337 (vs), 1227 (w), 1220 (vs), 1120 (vs), 1086 (w), 1019 (m), 966 (m), 934 (s), 838 (m), 817 (m), 718 (m), 588 (s) cm^{-1} .

Pb₂Ti₂(O)((O₂CC(CH₃)₃)₂(OPr¹)₈ **2**. EMA: Pb:Ti = 1:1. Found: C, 34.2; H, 6.31. Calc. for $C_{34}H_{74}O_{13}Pb_2Ti_2$: C, 34.0; H, 6.17%. Mol. wt. (benzene): 1165±50 (theor. for $C_{34}H_{74}O_{13}Pb_2Ti_2$, 1201). NMR: ¹H (CDCl₃): δ = 1.16 (s, O₂CC(C<u>H₃)₃); 1.28</u> (d, OCH(C<u>H₃)₂); 1.26 (d, OCH(CH₃)₂); 1.23 (d, OCH(C<u>H₃)₂); 4.86 (sp. OCH(CH₃)₂); 4.82 (sp. OC<u>H</u>(CH₃)₂); 4.50 (sp. OC<u>H</u>(CH₃)₂); 4.82 (sp. OC<u>H</u>(CH₃)₂); 4.50 (sp. OC<u>H</u>(CH₃)₂) ppm. IR (Nujol): 2922 (vs), 2854 (vs), 1557 (vs), 1483 (s), 1461 (vs), 1426 (s), 1404 (s), 1375 (vs), 1360 (vs), 1324 (m), 1224 (m), 1162 (vs), 1126 (vs), 1008 (vs), 962 (vs), 834 (m), 727 (m), 587 (vs), 470 (vs) cm⁻¹.</u></u>

 $Pb_2Ti_2(O)(O_2CCH_3)_2(OPr')_8$ 7. [8] EMA: Pb:Ti = 1:1. Found: C, 29.9; H, 5.5. Calc. for $C_{28}H_{62}O_{13}Pb_{2}Ti_{2}\colon C,\; 30.1\,;\; H,\; 5.6\%.$ Mol. wt. (benzene): 1109 ± 50 (theor. for $C_{28}H_{62}O_{13}Pb_2Ti_2$, 1117). NMR: ¹H (CDCl₃) 293 K: $\delta = 1.23$, 1.25, (d, OCH(CH₃)₂); 1.98, 2.02 (s, O₂CCH₃); 4.47, 4.99 (sp, OCH(CH₃)₂) ppm; 217 K: $\delta = 1.25$, 1.28, (d, $OCH(CH_3)_2$; 1.98, 2.01 (s, O_2CCH_3); 4.09, 4.49, 4.86, 4.99 (sp, $OCH(CH_3)_2$) ppm: C¹³ (CDCl₃): $\delta = 21.48$, 22.43 $(O_2CCH_3);$ 24.86, 25.47 (OCH(CH₃)₂; 64.10, 75.41 (OCH(CH₃)₂); 176.9, 177.0 (O₂CCH₃) ppm. IR (Nujol): 1556 (vs), 1434 (vs), 1374 (s), 1326 (m), 1126 (vs), 1010 (vs), 839 (m), 786 (m) cm⁻¹.

 $Pb_3Ti_3(O)_4(O_2CCH_3)_2(OPr')_7(acac)$ 5. Acetylacetone (0.5 g, 5 mmol) was added dropwise to a solution of $Ti(OPr')_4$ (2.84 g, 10 mmol) in Pr'OH (30 cm³). The solution was stirred at room temperature for 1 h then evaporated under reduced pressure until an oil remained. This was redissolved in Pr'OH (30 cm^3) and solid Pb(O₂CCH₃)₂ (3.25 g, 10 mmol) added. The mixture was refluxed until all solid had dissolved giving a green-yellow solution. This was filtered and allowed to stand at -20° C and crystalline material (ca 1 g) slowly deposited. Yield: 20%. EMA: Pb:Ti = 1:1. Found: C, 24.0; H, 4.09. Calc: for C₃₀H₆₂O₁₇Pb₃Ti₃: C, 24.6; H, 4.25% Mol. wt. (Pr'OH) 1500 ± 50 . (theor. for C₃₀H₆₂O₁₇Pb₃Ti₃, 1460). NMR : ¹H (CDCl₃): $\delta = 1.19 - 1.30$ (d, OCH(CH₃)₂, 42H); 1.95–2.24 (s, O_2CCH_3 and CH_3 acac total 12H); 4.01– $4.83 (sp, OCH(CH_3)_2 7H); 5.51 (s, CH acac 1H) ppm:$ ¹³C (CDCl₃): $\delta = 21.1$, 21.8, 22.5 (O₂<u>C</u>CH₃); 24.7, 25.3 (OCH(\underline{CH}_3)₂); 26.6 (\underline{CH}_3 acac); 76.6, 78.3 $(OCH(CH_3)_2)$, 102.6 (CH acac); 170.5, 178.8 (O₂CCH₃); 187.2, 191.2 (CO acac) ppm. IR (CCl₄): 1590 (s), 1567 (s), 1526 (s), 1419 (s), 1372 (s), 1127 (m), 1019 (m), 663 (s), 650 (s) cm^{-1} .

 $Pb_{3}Ti_{3}(O)_{4}(O_{2}CCH(CH_{3})_{2})_{2}(OPr^{i})_{8}$ 4. $Pb(O_{2}C-$

CH(CH₃)₂)₂ (1.91 g, 5 mmol) was dissolved in toluene (20 cm³) then Ti(OPrⁱ)₄ (1.5 ml, 5 mmol) added dropwise. The mixture was warmed at 60 °C for several hours then filtered and allowed to stand at room temperature for some days until a small crop (ca 500 mg) of crystals appeared. EMA : Pb : Ti = 1 : 1. Found : C, 24.8 ; H, 4.56. Calc. for $C_{32}H_{70}O_{16}Pb_3Ti_3$: C. 26.0 ; H, 4.74% M. wt. (benzene) : 1445±50 (theor. for $C_{32}H_{70}O_{16}Pb_3Ti_3$, 1476). IR (Nujol) : 2926 (vs), 2855 (vs), 1561 (vs), 1532 (vs), 1410 (vs), 1360 (vs), 1274 (vs), 1167 (s), 1117 (vs), 1094 (vs), 972 (s), 928 (m), 850 (s), 811 (s), 765 (m), 727 (vs), 694 (m), 627 (vs) cm⁻¹.

1:2 Pb: Ti ratio compounds

Pb₂Ti₄(O)₂(O₂CCH(CH₃)₂)₂(OPr')₁₄ **3**. Ti(OPr')₄ (2.83 g, 10 mmol) was added dropwise to a suspension of Pb(O₂CCH(CH₃)₂)₂ (3.81 g, 10 mmol) in Pr'OH (30 cm³) and the mixture refluxed for 20 min. The resulting solution was filtered hot and crystals grew as it cooled to room temperature. Yield: 91%. M.pt. 72–72°C. EMA: Pb: Ti, 1:2. found: C, 36.7; H, 6.85. Calc. for C₅₀H₁₁₂O₂₀Pb₂Ti₄: C, 36.6; H, 6.84%. Mol. wt. (toluene): 1620 ± 50 (theor. for C₅₀H₁₁₂O₂₀Pb₂Ti₄. 1639). NMR: ¹H (d⁸-toluene): δ = 1.19 (d, O₂CCH(CH₃)₂, 12H, J = 7.0 Hz); 1.25, 1.35, 1.52, 1.55 (d OCH(CH₃)₂, 84H, J = 6.1 Hz); 2.46 (sp O₂CCH(CH₃)₂ 2H, J = 6.1 Hz) ppm.

Pb₂Ti₄(O)₂(O₂CCH₃)₂(OEt)₁₄ 8 from "basic" lead acetate. Ti(OPrⁱ)₄ (2.86 g, 10 mmol) was dissolved in ethanol (30 cm³) and the solution stirred at room temperature for 30 min before evaporating under reduced pressure until an oily "waxy" solid remained. This was redissolved in ethanol (30 cm³) and the solution added dropwise to a suspension of "basic" lead acetate (3.04 g, 2.50 mmol) in EtOH (50 cm³). The resulting mixture was refluxed for 1 h then allowed to cool to room temperature and colourless crystals separated. The complex is readily soluble in hexane, benzene and toluene. Yield: 70%. EMA: Pb: Ti, 1:2. Found : C, 27.8; H, 5.40. Calc. for C₃₂H₇₆O₂₀Pb₂Ti₄: C, 27.7; H, 5.48%. Mol. wt. (benzene): 1350 ± 50 (theor. for $C_{32}H_{76}O_{20}Pb_2Ti_4$, 1387). NMR: ¹H (CDCl₃) 300 K : $\delta = 1.22$, 1.24, 1.26 (t, OCH₂CH₃); 1.98 (s, O₂CCH₃); 3.72-4.56 (broad band of poorly resolved quartets, OCH₂CH₃): 217 K : $\delta = 1.20, 1.23,$ 1.25 (t, OCH_2CH_3); 1.98 (s, O_2CCH_3); 3.70, 4.09, 4.44, 4.51, 5.14 (q, OCH₂CH₃) ppm; (C_6D_6) 300 K: $\delta = 1.30, 1.35, 1.54$ (t, OCH₂CH₃); 2.01 s, O₂CCH₃); 4.53, 4.68, 4.90 (q, OCH_2CH_3) ppm. ¹³C (CDCl₃): $\delta = 17.8, 18.4, 19.2 \text{ (OCH}_2\text{CH}_3); 26.2 \text{ (O}_2\text{CCH}_3);$ 68.5, 69.2, 71.0, 72.2 (OCH₂CH₃); 183.0 (O₂CCH₃) ppm. IR (Nujol): 1564 (vs), 1434 (vs), 1372 (s), 1131 (s), 1094 (s), 1052 (s), 925 (m), 895 (m), 663 (m) cm^{-1} .

Reaction with Ti(OPrⁿ)₄-"[Pb₂(O₂CCH₃)₃(OPrⁿ)]"

Ti(OPr")₄ (2.84 g, 10 mmol) was dissolved in Pr"OH (50 cm³) and Pb(O₂CCH₃)₂ (3.25 g, 10 mmol) added.

The mixture was refluxed for 1 h as the acetate dissolved. The resulting clear yellow solution was cooled to room temperature and a white solid precipitated. It recrystallised from Pr"OH. EMA : Pb only. Found : C, 16.7; H, 2.66. Calc. for $C_9H_{16}O_7Pb_2$: C, 16.6; H, 2.46%. NMR : ¹H(CDCl₃): $\delta = 0.94$ (t, OCH₂CH₂CH₃, 3H); 1.60 (sex, OCH₂CH₂CH₃, 2H); 2.04 (O₂CCH₃, 9H); 3.61 (t, OCH₂CH₂CH₃, 2H). IR (Nujol): 1159 (s), 1423 (s), 1227 (m), 1105 (m), 1070 (s), 1017 (s), 888 (w), 721 (s), 665 (s) cm⁻¹. MS: m/z = 593 (Pb₂(O₂CCH₃)⁺, 5%); 489 (Pb₂O(O₂CCH₃)⁺, 3%); 267 (Pb(O₂CH₃)⁺ 100%).

Reactions with PbO

Pb₂Ti₄(μ -O)₂(O₂CCH₃)₂(OEt)₁₄ **8**. Ti(OEt)₄ (0.82 g, 3.60 mmol) was dissolved in ethanol (30 cm³) and glacial acetic acid (0.22 g, 3.60 mmol) added. The mixture was heated under reflux for 30 min, cooled, then PbO (0.8 g, 3.6 mmol) added and the mixture returned to reflux for 3 h. The solution was filtered and left until crystallisation occurred. Found : C, 27.8 ; H, 5.40. Calc. for C₃₂H₇₆O₂₂Pb₂Ti₄: C, 27.7 : H, 5.48%. EMA : Pb:Ti, 1:2. ²⁰⁷Pb NMR (toluene) : sharp peak at 2868 ppm.

 $Pb_2Ti_2(\mu-O)(OEt)_8(acac)_2$ 6. Acetylacetone (1 g, 10 mmol) was added to a solution of Ti(OEt)₄ (2.29 g, 10 mmol) in EtOH (50 cm³), the mixture refluxed for 30 min then cooled to room temperature. PbO (2.23 g, 10 mmol) was then added and the mixture heated at reflux for a further 3 h. The solution was filtered, reduced to half its volume under reduced pressure and allowed to stand whereupon a white solid slowly precipitated. It was recovered by filtration, washed with EtOH and dried under reduced pressure. EMA: Pb:Ti = 1:1. Found: C, 26.3; H, 4.45. Calc. for C₂₆H₅₄O₁₃Pb₂Ti₂: C, 28.7; H, 5.02%. Mol. wt. (benzene): 900 ± 50 (theor. for $C_{26}H_{54}O_{13}Pb_2Ti_2$, 1085). NMR: ¹H (CDCl₃): $\delta = 1.19$, 1.22, 1.24 (t, OCH₂CH₃, 24H); 1.94, 2.05 (s, CH₃ acac, 12H); 4.42, 4.46 (q, OCH₂CH₃, 16H); 5.55 (s, CH acac, 2H) ppm. ¹³C (CDCl₃): $\delta = 18.3$, 20.2, 20.8, 26.8 (CH₃ (acac and OEt); 68.7, 72.2 (OCH₂CH₃); 102.9 (CH acac); 188.0 (CO acac) ppm. IR (Nujol): 1594 (bvs), 1521 (vs), 1442 (vs), 1372 (vs), 1271 (vs), 1146 (vs), 1099 (vs), 1057 (vs), 897 (s) cm^{-1} .

RESULTS AND DISCUSSION

The lead carboxylates

The various lead carboxylates were conveniently prepared by the reactions of PbO, suspended in an organic solvent or water, with the appropriate acid. The heptafluorobutyrate was isolated as a trihydrate similar to the acetate whose structure has been shown to be based on chelated acetate groups bridging Pb atoms [24–26] while the anhydrous trimethylacetate was isolated from methanol solution. The dime-

Synthesis of Pb-Ti-oxo-alkoxo-carboxylato complexes

		²⁰⁷ Pb chemical shifts (ppm)		
Compound	Solvent	300 K	(TK)	
Pb(O ₂ CCH ₃) ₂ ·3H ₂ O	H ₂ O	1552		
	MeOH	1973	1776(276) 1679(256)	
	DMSO	2327 broad		
	MeOC₂H₄OH	1601 broad		
$Pb(O_2CCH_3)_2$	H ₂ O	1552		
	DMSO	2384		
$3Pb(O_2CCH_3)_2 \cdot PbO \cdot H_2O$	MeOH	no signal	3121, 2818, 1861(250)	2591,
$Pb(O_2CC_3F_7)_2 \cdot 3H_2O$	H ₂ O	126 broad		
	MeOH	606	116(226)	
	DMSO	608		
	MeOC ₂ H₄OH	436	68(226)	
	THF	1087	771(226)	
$[Pb(O_2CCH(CH_3)_2)_2] \cdot 4H_2O$	$C_6D_5CD_3$		2709, 2661, 1667	2170,
$Pb(O_2CC(CH_3)_3)_2$	H ₂ O		1426	

Table 1. ²⁰⁷ Pb NMR spectra of lead carboxylates (concentrations were as close to 0.1 mol
dm^{-3} as solubilities allowed)

thylacetate, containing 2/3 of a mole of water per Pb, has been shown [23] to exist in the solid state as the cyclic hexamer $[Pb_6(O_2CCH(CH_3)_2)_{12}] \cdot 4H_2O$ soluble in solvents such as toluene. ²⁰⁷Pb NMR data on the compounds are given in Table 1 together with that for the acetate and "basic" acetate. Single resonances were observed for the C_3F_7 , $C(CH_3)_3$ and acetate compounds in water. The 4 resonances found in toluene for the sparingly water insoluble dimethylacetate have been previously discussed in terms of its hexanuclear structure [23]. Harrison et al. [27] have previously measured the ²⁰⁷Pb chemical shifts of a number of lead(II) compounds PbX₂ in water, including lead acetate, and concluded that the single resonances observed were due to very rapid equilibration between cation anion complexes as in eqn. (iii). They showed that in consequence the shift values varied quite markedly with concentration unless the salt is completely ionised at all concentrations as is the perchlorate.

$$PbX_{2}(H_{2}O)_{x} \leftrightarrow [PbX(H_{2}O)_{y}]^{+} + X^{-} \qquad (iii)$$

No study of the variation with concentration was made for any of the compounds examined in the present work but as far as permitted by solubility considerations, NMR measurements were made at concentrations close to 0.3 mol dm⁻³. Allowing for conversion to chemical shifts relative to Pb(NO₃)₂ the value of 1552 ppm found in the present work for the acetate at 0.3 M is in good agreement with that of 1557 ppm previously reported [27].

Single ²⁰⁷Pb resonances were also observed for the acetate and heptafluorobutyrate in several ionising

coordinating solvents at 300 K and at 226 K in methanol. This implies rapid exchange between the various possible solvated species $[Pb(O_2CR)_2(solv)_x]$ and $[Pb(O_2CR)(solv)_y]^+$, the variation of chemical shift with alkanoate group indicating a difference in equilibrium constants between the complexes of the various alkanoate complexes. The presence of the highly electronegative fluorocarbon group results in a considerable shift to higher field of the observed resonances in each solvent compared to the hydrated acetate.

The "basic" acetate fails to display any resonances in MeOH at 300 K, but multiple resonances were observed at 250 K suggesting either that the compound dissociates in solution giving species that can exchange with each other sufficiently rapidly to prevent NMR detection except at low temperatures or that a single species exists with differently coordinated lead atoms which undergoes such rapid fluxional behaviour at room temperature that single atom resonances are not detected. The crystal structure of the compound has not yet been reported but the tetranuclear empirical formula of the compound, 3Pb(O₂C-CH₃)₂·PbO·H₂O [21] may suggest some structural relationship with other tetranuclear, "basic" carboxylates $M_4(\mu_4-O)(O_2CR)_6$ [28] of Zn, Be and Co which have been structurally characterised and found to have four tetrahedrally arranged metal ions coordinated to a central oxo group with carboxylate ions coordinated in O-O bridging mode to pairs of metal ions. The additional water molecule associated with the empirical formula of the Pb compound could be

coordinated at a single Pb site leading to an overall trigonal pyramidal configuration for the four Pb atoms. Ready displacement of coordinated water from one site and reattachment of MeOH solvent at other Pb sites or the changing of coordination partners of each Pb atom by "opening" and "shutting" of the acetate bridges provides plausible mechanisms of fluxional exchange for such a labile system and even for distinguishing individual Pb atoms when the exchange processes are slowed at low temperatures. The empirical formulation of an oxo group and discrete water molecule however may alternatively represent two OH groups. The only "basic" Pb unit so far structurally defined is the hexanuclear cationic species $[Pb_6O(OH)_6]^{4+}$ found in the "basic" perchlorate salt [29]. It contains one oxo group coordinated to four tetrahedrally arranged Pb atoms with the remaining two Pb atoms linked to two faces of the tetrahedron each by three triply bridging OH groups. This array leads to the presence of three differently coordinated types of Pb atoms in the solid state structure.

Reactions of lead carboxylates with $Ti(OPr')_4$

1:1 Pb: Ti *ratio complexes*. New complexes having a 1:1 Pb: Ti ratio have been obtained from reactions between Pb(O₂CC₃F₇)₂ or Pb(O₂CC(CH₃)₃)₂ and Ti(OPr')₄ in hot toluene solution. The solution molecular weights measured for the complexes indicate that they are of comparable stoichiometries to the structurally characterised acetate-isopropoxide complex 7 [6,7] and suggest they have the empirical formulae Pb₂Ti₂(μ -O)(O₂CC₃F₇)₂(OPr')₈ 1 and Pb₂Ti₂(μ -O)(O₂CC(CH₃)₃)₂(OPr')₈ 2. The ²⁰⁷Pb NMR spectrum of each complex 1, 2, 7, in toluene (and 7 in Pr'OH) shows two sharp resonances (Table 2), those for the heptafluorobutyrate compound being at notably higher field than for the pivalate or acetate in line with the high field shift shown by the Pb fluoroalkanoate compared to other alkanoates. The structure of complex 7 determined by Hubert-Pfalzgraf et al. [5,6] showed a central μ_4 -O-(Pb₂-Ti₂) unit with one Pb atom (Pb(1)) 4 coordinate and the other, (Pb(2)), 5 coordinate in the solid state. The pairs of Pb and Ti atoms are each bridged by acetate groups so that there are two differently coordinated carboxylate groups in the crystal structure. The ²⁰⁷Pb NMR spectra are in agreement with the presence of two differently coordinated Pb atoms in each of the Pb-Ti complexes. The 4coordinate site (Pb(1)) will have a relatively lower electron density than the 5-coordinate (Pb(2)), is therefore less shielded, suggesting that the lower field (2824 ppm) resonance be tentatively assigned to Pb(1) and that at 2447 ppm to Pb(2).



(2430, 2110, 1780, EtOH)

Pb : Tì ratio	Complex	²⁰⁷ Pb chemical shifts" (ppm)
1:1	$1 \text{ Pb}_{2}\text{Ti}_{2}(O)(O_{2}\text{CC}_{3}F_{7})_{2}(OPr^{i})_{8}$	1822, 1717 (1876, 1682, 224 K)
	2 $Pb_2Ti_2(O)(O_2CC(CH_3)_3)_2(OPr')_8$	2814, 2336
	4 Pb ₃ Ti ₃ (O) ₄ (O ₂ CCH(CH ₃) ₂) ₂ (O'Pr) ₈	2397, 2189
		(2534, 2397, 2189 Pr'OH)
	5 Pb ₃ Ti ₃ (O) ₄ (O ₂ CCH ₃) ₂ (OPr ^{i}) ₇ (acac)	2561, 2161
	6 Pb ₂ Ti ₂ (μ -O)(OEt) ₈ (acac) ₂	2688
	$7 Pb_2Ti_2(O)(O_2CCH_3)_2(OPr')_4$	2824, 2447
		2750, 2438 (Pr'OH)
1:2	3 Pb ₂ Ti ₄ (O) ₂ (O ₂ CCH(CH ₃) ₂) ₂ (OPr ⁱ) ₁₄	2599, 2374, 2176
		(2556 Pr'OH)
	8 Pb ₂ Ti ₄ (O) ₂ (O ₂ CCH ₃) ₂ (OEt) ₁₄	2868

Table 2. Empirical formulae of Pb-Ti compounds and ²⁰⁷Pb NMR spectra

"Spectra measured at 300 K in toluene solution unless otherwise indicated.

Compounds 1 and 7 show ${}^{19}F$ and ${}^{13}C$ (1) and ${}^{1}H$ (7) NMR resonances indicative of two separate carboxylate groups at room temperature (see Experimental). However only one ¹H resonance was clearly observed for the pivalate in compound 2. The 7 differing isopropoxide ligands seen in the solid state structure of the acetate (7) are not individually distinguishable in the clusters of overlapping doublets $(OCH(CH_3)_2)$ and septets $(OCH(CH_3)_2)$ due to these groups in the acetate complex or either of compounds 1 or 2. While the NMR data reported here were obtained using a spectrometer working at 300 MHz, Hubert-Pfalzgraf et al. [6] only detected one ²⁰⁷Pb resonance and one CH3 acetate 1H resonance for compound 7 at 200 MHz. They have moreover presented evidence for the existence of two fluxional species in solution based on the 'H NMR detection of additional acetate resonances at -50° C. In support of this we have observed an increase in the number of resonances ascribable to isopropyl CH groups for compound 7 at 217 K. The molecular weights of the compounds in benzene measured in the present work indicates that little or no dissociation occurs in solution.

The 'H spectrum of the heptafluorobutyrate compound also showed groups of overlapping isopropoxide CH₃ and CH signals but neither showed any marked increase in separation or increase in number at 217 K indicating a lower degree of fluxional behaviour for this complex.

1:2 Pb: Ti ratio complexes

The structural studies [7,9] of the 1:2 Pb-Ti complex containing acetate and ethoxide groups have established its formula to be $Pb_2Ti_4(\mu_4-O)_2(O_2C CH_{3}_{2}(OEt)_{14}$ 8 with equivalently sited 5 coordinate Pb atoms. The molecular weight measured in toluene is in agreement with such an empirical formula while the observation of a single ²⁰⁷Pb NMR resonance [7,9] (Table 2) indicates that it does not dissociate rapidly in that solvent. The 'H NMR spectrum in CDCl₃ at 300 K shows three broad, partially overlapping triplets in the region expected for ethoxide CH₃ resonances. A single broad band of unresolved quartets is observed in the region expected to show methylene protons. At 217 K five peaks can be clearly seen in the methylene region but no resolution of the methyl protons was observed. The spectrum in C₆D₆ shows sets of overlapping resonances in each of the methyl and methylene regions. A single resonance due to the acetate methyl is however clearly recognised in both solvents. At lower temperatures the resonances broaden and the acetate methyl resonance shifts until it merges with the residual toluene methyl resonance at 2.1 ppm. These observations indicate a degree of fluxional behaviour for the molecule in solution probably involving interconversion of bridging and terminal alkoxide groups.

When $Pb(O_2CCH(CH_3)_2)_2$ reacts with $Ti(OPr')_4$ in isopropanol even in a 1:1 mole ratio a high yield of complex 3 having a 1:2 ratio of Pb: Ti is obtained. Its ¹H NMR spectrum shows a cluster of resonances that may be assigned to the methyl and methylene groups respectively of the isopropoxide groups together with peaks having chemical shifts representative of the dimethylacetate CH and CH₃ protons. Integration of these regions provides a ratio of OPrⁱ to $O_2CCH(CH_3)_2$ groups of 7:1. The molecular weight for the compound in toluene solution indicated the empirical formula $Pb_2Ti_4(\mu-O)_2(O_2CCH(CH_3)_2)_2$ $(OPr^{i})_{14}$ 3, similar to that of the 1:2 Pb: Ti acetate/ethoxide product 8. However three ²⁰⁷Pb resonances were observed for the compound in toluene solution and a single resonance in Pr'OH (Table 2). This contrasts with the single resonance shown by the 1:2 acetate-ethoxide compound 8. The reaction between equimolar quantities of $Pb(O_2CCH(CH_3)_2)_2$ and $Ti(OPr^{i})_{4}$ in toluene allowed isolation of a very small quantity of a complex 4 having a Pb: Ti ratio of 1:1. In contrast to the other 1:1 ratio compounds isolated which have a Pb₂Ti₂ composition the molecular weight of this product in toluene indicated that it contains a Pb₃Ti₃ core. Insufficient quantity of the product was isolated to allow the full range of NMR measurements to be made but the compound shows two ²⁰⁷Pb NMR resonances in toluene solution and three in Pr'OH (Table 2) one of the latter (2534 ppm) having close to the same chemical shift as given by the 1:2 complex (2556 ppm) prepared and measured in that solvent.

The influence of solvent on the formation of mixtures of Pb—Ti complexes

The reaction of $Pb(O_2CCH(CH_3)_2)_2$ and $Ti(OPr^{i})_4$ in both isopropanol and toluene was further examined by removing samples from reaction mixtures containing equimolar amounts of the reagents after some hours of reflux and measuring their ²⁰⁷Pb NMR spectra. In the case of the toluene reaction, three strong peaks at 2599, 2374 and 2176 ppm were observed in the ratio 1:2:2 together with some far less intense peaks. The sample from the isopropanol reaction similarly showed three strong resonances with almost the same chemical shifts 2529, 2343, and 2195 ppm together with several weaker peaks at lower field. Comparison with the spectra of the isolated compounds measured in each solvent thus indicates that both types of compounds with Pb₂Ti₄ and Pb₃Ti₃ cores are formed whether the reaction solvent is isopropanol or toluene. Each type of complex appears stable in one solvent but undergoes some degree of rearrangement in the other to form the second type of complex, possibly reaching an equilibrium condition. A plausible empirical formula for the 1:1 species formed with this combination of reagents in agreement with the various data is $Pb_3Ti_3(O)_4(O_2CCH(CH_3)_2)_2(OPr')_8$ 4. The ²⁰⁷Pb NMR examination of the reaction mixtures shows the presence of other Pb containing species which were not identified. None of these peaks could be ascribed to the unreacted carboxylate.

X-ray structural data on the two different products is necessary if a detailed understanding of their apparent interconvertability is to be obtained. The structural features so far defined by the acetate/ethoxide 1:2 Pb: Ti compound **8** may not be found for the dimethylacetate/isopropoxide complex despite their similar metal ratios and ²⁰⁷Pb NMR features while the Pb₃Ti₃ compound represents a new structural type.

The ²⁰⁷Pb NMR spectral examination of several other reaction mixtures has also disclosed the coincident formation of other Pb: Ti ratio complexes to those which were most readily isolated. Thus a freshly prepared equimolar mixture of anhydrous $Pb(O_2CCH_3)_2$ and $Ti(OPr^i)_4$ in Pr^iOH showed not only two peaks representative of the 1:1 Pb: Ti compound 7 isolated but also an additional strong peak at 2987 ppm which may well be due to the parallel formation of a 1:2 complex similar to 8 formed by reaction between $Pb(O_2CCH_3)_2$ and $Ti(OEt)_4$. The relatively easy isolation of the 1:1 species 7 could be due to its lower solubility and formation in greater amount under the reaction conditions employed. The detection of only two peaks in the ²⁰⁷Pb NMR spectrum of the pure complex dissolved in isopropanol, the solvent used in the reaction, indicates that the 1:1 compound retains its stoichiometry and possibly its solid state structure in the alcohol, and does not rearrange to give some 1:2 product. However the ²⁰⁷Pb spectrum of the 1:2 Pb:Ti acetate/ethoxide complex 8 which displays only one resonance in toluene solution, shows three resonances when measured in ethanol solution indicating some form of decomposition or rearrangement of the 1:2 Pb: Ti compound occurs in that solvent. Samples removed at various time intervals from a refluxing equimolar mixture of $Pb(O_2CCH_3)_2$ and $Ti(OEt)_4$ in ethanol, from which can be isolated the 1:2 compound 8 show the same three resonances and may well indicate the parallel formation of both 1:2 and 1:1 ratio acetate-ethoxide species.

Similarly, the reaction between Ti(OPr⁴)₄ and Pb(O₂CC(CH₃)₃)₂, which favoured the isolation of the 1:1 ratio Pb: Ti complex **2** in toluene, was also studied in refluxing isopropanol by measuring the ²⁰⁷Pb spectra of samples of the reaction mixture withdrawn at intervals. After 30 min reaction time 5 peaks of equal intensity were observed at 2261, 2336, 2682, 2814 and 3069 ppm. These resonances occur downfield of the resonance shown by the carboxylate alone and indicate that the carboxylate had already reacted to form new species. Further refluxing for up to 3 h, showed an increase in intensity of the peaks at 2336 and 2814 ppm had become the dominant features of the spectrum. These were comparable to the chemical shifts measured in toluene for the 1:1 complex **2** sub-

sequently isolated. The other peaks initially observed, although much reduced in intensity, were still detectable.

Such qualitative experiments indicate that a variety of compounds can form from reactions between Pb carboxylates and Ti alkoxides in a given solvent. The complex most readily isolated must depend on its solubility in that solvent and the concentration which it can attain because of the solvent influence on the reaction pathway. The different Pb: Ti ratio complexes may or may not be formed in equilibrium with each other.

Reactions with other Ti alkoxides

Solubility considerations appeared to dominate several other reactions attempted with Ti(OMe)₄, $Ti(OBu^n)_4$ or $Ti(OPr')_{4}$. Reaction between Pb(O₂CCH₃)₂ and either of the first two alkoxides resulted in solids shown by EMA to be mixtures of Pb and Pb-Ti products which could not be separated. Ti(OPr")₄ formed a sparingly soluble product containing only Pb whose mass spectrum showed an ion of mass 593 possibly $[Pb_2(O_2CCH_3)_3]^+$ or $[Pb_2(O_2C (CH_3)_{3-x}(OPr^n)_x]^+$. Its ¹H NMR spectrum indicated the presence of acetate and alkoxide groups in the ratio 3:1. It appears to be $\{Pb_2(O_2CCH_3)_3(OPr'')\}_n$ a similar type of compound to $\{Zn_2(O_2CCH_3)_3(OMe)\}_n$ [11].

Action of acetylacetone

Only one Pb-Ti complex containing acetylacetone $Pb_2Ti_2(O)(acac)_2(OPr')_8$ has previously been reported [8] resulting from the direct reaction of acetylacetone with the "single source" compound $Pb_2Ti_2(O)(OPr')_{10}$ in hexane solution. We have attempted the direct substitution of acetylacetone for other coordinated groups by reaction with $Pb_2Ti_2(O)(O_2CCH_3)_2(OPr')_8$ 7 in Pr^iOH and $Pb_2Ti_4(O)_2(O_2CCH_3)_2(OEt)_{14}$ 8 in EtOH. In each reaction a precipitate formed which only contained Pb together with acetate, alkoxide and acetylacetonate groups as indicated by IR spectral examination. Hubert-Pfalzgraf et al. [6] have reported that $Pb(O_2CCH_3)_2$ is precipitated following reaction of acetylacetone with 7 in toluene. The pretreatment of a slurry of $Pb(O_2CCH_3)_2$ in isopropanol with a solution of the ligand produced a similar insoluble Pb containing product which did not dissolve in the presence of $Ti(OPr^{i})_{4}$ even under reflux.

A successful procedure involved the dissolution of solid $Pb(O_2CCH_3)_2$ in a Pr'OH solution of $Ti(OPr')_4$ containing acac in the ratio acacH : Ti, 0.5 : 1 allowing isolation of a product having a 1 : 1 Pb : Ti ratio. The molecular weight of the complex in Pr'OH indicated a Pb_3Ti_3 core was present. The ¹³C NMR spectrum of the product contained peaks that could be assigned



to isopropoxide, acetate and acetylacetonate groups. The shifts assigned to the acetylacetonate group were similar to those reported for that ligand in Ti(OP $r'_{3}(acac)$ [30] and $Pb_{2}Ti_{2}(O)(acac)_{2}(OPr')_{8}$ [8] with 2 separate CO resonances being identified suggesting unsymmetrical binding of the acetylacetonate ligand. Non-symmetric bonding of acac has been observed in the dimeric [Al(OPr')₂(acac)]₂ [31]. Two intense IR spectral bands shown by the Pb-Ti compound at 1567 cm⁻¹ and 1419 cm⁻¹ are assigned as $v_{as}(CO_2)$ and $v_{sym}(CO_2)$ respectively, characteristic of an acetate group symmetrically attached to a metal while the difference $\Delta v = 148 \text{ cm}^{-1}$ between these frequencies indicates a bridging mode of coordination [32]. Strong metal alkoxide vibrations are observed in the 1000-1200 cm⁻¹ region. The ¹H NMR spectrum showed three septets assigned to CH protons of isopropyl groups which integrated to give a ratio of 4:2:1 from higher to lower field suggesting the presence of nonequivalent isopropyl groups. The splitting of the isopropyl methyl doublets confirms this inequivalence. The methyl resonances of the acac and acetate groups are likely to have similar chemical shifts [33] around 2 ppm. Three peaks are shown by the complex in that region. One sharp (1.95 ppm), the other two broad (2.03 and 2.09 ppm) with integration giving a 2:1:1 ratio of intensities. Since the IR spectral evidence suggests equivalent acetate coordination, the sharp NMR peak at 1.95 ppm is assigned to an acetate CH₃ resonance with the remaining broader peaks due to dissimilarly placed acac methyl groups. The sharp peak at 5.51 ppm is then assigned to the acac CH proton, the value being similar to that reported for $Ti(OPr')_{3}$ (acac) [30]. The ²⁰⁷Pb NMR spectrum of the complex in toluene showed two broad diffuse peaks at 2561 and 2161 ppm in the ratio 2:1 according to the peak

width at half height. This would accord with a 2:1 ratio of three Pb atoms in the molecule dispersed over two different types of coordination sites but the broad nature of the peaks does not preclude the existence of more separate Pb sites in the molecule with fluxional properties. These data taken in conjunction with its elemental analysis suggest the empirical formula Pb₃Ti₃(O)₄(O₂CCH₃)₂(OPrⁱ)₇(acac) **5** with acac coordinated to Ti in an unsymmetrical mode.

Reactions involving PbO

Initial experiments showed that no reaction occurred between PbO and Ti(OPrⁱ)₄ or Ti(OEt)₄ when the components were refluxed in the parent alcohols but prior reaction of the alkoxide with one equivalent of either acetic acid or acetylacetone gave products which readily dissolved the oxide. Thus a Pr'OH solution of Ti(OPr')₄, previously treated with one equivalent of acetic acid, reacted with an equimolar quantity of PbO to give a solution displaying the same ²⁰⁷Pb NMR spectrum as a solution of $Pb(O_2CCH_3)_2$ and $Ti(OPr')_4$ refluxed in Pr'OH. This was considered above to indicate a mixture of the known 1:1 Pb:Ti complex $Pb_2Ti_2(\mu-O)(O_2C CH_3)_2(OPr')_8$ 7 together with the as yet uncharacterised 1:2 compound $Pb_2Ti_4(\mu-O)_2(O_2CCH_3)_2$ (OPr')14. Reaction of PbO with a similarly formed Tiacetate-ethoxide species in ethanol allowed the isolation of the known compound $Pb_2Ti_4(\mu-O)_2(O_2C CH_3)_2(OEt)_{14}$, 8 identified by its IR, ²⁰⁷Pb and ¹H NMR spectra and elemental analysis. Similarly, a solution containing the product formed by reaction of equimolar amounts of Ti(OEt)₄ and acetylacetone in ethanol was refluxed with sufficient PbO to give a 1:1 Pb: Ti mole ratio. A product isolated from the mixture had a Pb: Ti ratio of 1:1 and showed only a single ²⁰⁷Pb resonance in toluene solution (Table 2). Its ¹H and ¹³C NMR spectra showed peaks assignable to ethoxide and coordinated acetylacetonate ions. Its integrated ¹H NMR spectrum and molecular weight suggest it is the ethoxy analogue of the isopropoxy-acetylacetonate compound previously reported by Hubert-Pfalzgraf *et al.* [8] with empirical formula Pb₂Ti₂(O)(OEt)₈(acac)₂ **6**. PbO failed to dissolve in a solution in which Ti(OPr')₄ had been first reacted with one mole equivalent or acetylacetone.

Although simple stoichiometric formulae Ti $(OR)_{4-n}(O_2CR)_n$ (n = 1, 2) have been assigned [34] earlier to the products formed when Ti(OR)4 react with carboxylic acids, recent structural studies have shown that more complex species are formed. Although the specific product formed on reaction of acetic acid with Ti(OEt)₄ has not yet been structurally characterised, the compounds formed in other related reactions have been found to be hexanuclear oxo Ti species of the form $Ti_6(\mu-O)_4(O_2CR)_8(OR')_8$ $(R = CH_3, R' = Bu^n$ [35], $R = CH_3, R' = Et$ [36], $R = C_6H_5$, R' = Pr'' [37]). The oxo groups have been suggested to derive from hydrolysis by water produced by the esterification reaction between the acid and liberated alcohol [36]. Polynuclear species have also been detected by various spectroscopic techniques in solutions of Ti(OEt)₄ which have reacted with acetylacetone [30]. Such considerations make it impossible to conclude from synthetic experiments alone that oxo groups derived from PbO are found in the final Pb-Ti complexes but the experiments at least show that the oxide can be a useful reagent in the synthesis of mixed Pb-Ti derivatives as an alternative to the use of preformed lead carboxylates.

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