Structural investigations of a lead(IV) tetraacetate-pyridine complex

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A 1:1 crystalline complex of lead(IV) tetraacetate and pyridine (LTA-py) has been prepared. The single-crystal X-ray structure, at 296 and 150 K, establishes the presence of a relatively short Pb–N bond (2.307 Å) within an intriguing seven-coordinate lead inner sphere consisting of the pyridine ligand and two bidentate and two monodentate acetate ligands. The pyridine occupies a surprising amount of the available coordination space and has induced a dramatic change in coordination compared to the four chelating acetate ligands found in lead tetraacetate (LTA). Thermal measurements (TGA/DSC) indicate the de-coordination of pyridine and its loss from the solid between 360 and 380 K.²⁰⁷Pb CP/MAS NMR spectroscopy also demonstrates the existence of the Pb-N bond through observation of ${}^{1}J({}^{207}\text{Pb},{}^{14}\text{N}) = 63 \text{ Hz}$ and a ${}^{207}\text{Pb}-{}^{14}\text{N}$ dipolar coupling constant, of 149 Hz. The solid-state ²⁰⁷Pb NMR parameters are used to give insight into the coordination environment of Pb(IV) in LTA-py. In solution, ligand exchange is rapid on chemical shift and J-coupling time scales. A ²⁰⁷Pb NMR study of the titration of an LTA solution by pyridine yields a stability constant for LTA-py of $K = 1.5 \text{ M}^{-1}$ and predicts it to have a ²⁰⁷Pb NMR chemical shift essentially identical to that observed by CP/MAS NMR in the solid state. This correlation between the solid state and solution indicates that the seven-coordinate LTA-py structure found in the crystalline state does persist in solution, and this could further explain why the addition of pyridine has such profound effects on lead(IV) carboxylate-mediated organic reactions. Simulations of exchange-broadened line shapes of ¹³C CP/MAS NMR spectra in the temperature regime above 280 K indicate local motion of the pyridine rings in the form of 180° jumps (activation energy 72.5 kJ mol⁻¹); these are first such ring flips reported for a coordinated pyridine ligand.

Introduction

Lead(IV) compounds have been shown to mediate both a wide range of oxidizing¹⁻⁵ and coupling processes.⁶⁻⁸ There is now considerable evidence that the latter processes occur by ligand coupling^{9,10} involving a reductive elimination at the lead atom^{11,12} rather than a radical or ionic mechanism.¹³ The ability to attenuate, enhance or otherwise modify the reactivity of metal cations by controlling their coordination environment is well known,^{14,15} and has recently been exploited extensively, for example, in asymmetric bond forming reactions (*e.g.* catalytic reduction,¹⁶ Sharpless allylic epoxidation,¹⁷ dihydroxylation¹⁸ and aminohydroxylation¹⁹). It has therefore been of interest to us to examine the effect of ligands on the reactions mediated by lead(IV) that have been investigated in our laboratory.^{20,21}

A recurring theme in the reactions of lead(IV) in much of the literature has been the influence of pyridine (py) in directing the course of a wide range of reactions, including oxidation and ligand coupling processes (vide supra). It has been widely speculated in the literature^{6,7,22,23} that pyridine acts as a σ -donor, thereby facilitating ligand exchange, particularly replacement of acetate by other enolic-type substrates, but no direct evidence has thus far been produced. For example, oxidations of alcohols by LTA are reported to occur in good yield only in neat pyridine; in other solvents such as benzene, competing reactions leading to a variety of products are predominant.²⁴ Furthermore, the rate of oxidation of lactic acid is found to be greatly increased by the presence of pyridine or 1,10-phenanthroline.²⁵ The kinetics of the oxidation of benzylic alcohols by lead(IV) acetate have been investigated,²⁶ and in the absence of pyridine the reaction is second order in the alcohol. However, with pyridine present, the reaction is first order in both the alcohol and pyridine; clearly the mechanism changes under these conditions. Similarly, the need for pyridine (or a similar nitrogen containing heterocyclic base) in cross-coupling reactions is also well known.⁶⁻⁸ Whilst it has been speculated that pyridine could be acting as a ligand, a base, or indeed both in these reactions, no direct evidence for its role has been established. However, indirect evidence for its role as a ligand has come from recent observations that pyridine catalyses ligand redistribution between aryllead triacetates and diaryllead diacetates,²⁷ and that it, along with other sp²-hybridized amines, effectively catalyzes lead(IV) mediated arylation reactions.28 That this coordinative effect could be put to valuable synthetic effect was recently indicated by Yamamoto and co-workers,22 who showed that useful enantiocontrol and conversion yields could be achieved in biaryl coupling reactions mediated by lead(IV) in the presence of chiral amines (e.g. brucine) although incorporation of such σ -donors within a ligand neither enhanced yields nor enantioselectivity in arylation reactions.^{29,30} Furthermore, the value of imine-containing lead(IV) ligands for enantioselective aziridination reactions has recently been demonstrated.³¹ Direct evidence for the existence of aryllead(IV)-pyridine and aryllead(IV)-acetonitrile adducts was recently established using ESI mass spectrometry.32

In the light of the obvious importance of pyridine, and more generally amine ligands in the chemistry of lead(IV), we were intrigued by a report of the isolation of a LTA–pyridine complex,³³ and present here a re-investigation of that work, including results from a detailed structural analysis of this complex using a combination of crystallographic, and solidstate and solution multinuclear NMR techniques.

Results

Preparation

The lead(IV) tetraacetate-pyridine complex (LTA-py) could be easily crystallized from a solution of lead(IV) tetraacetate and

Table 1 Selected bond lengths (Å) and angles (°) at 150 K

Ph1-N18	2 307(3)	C7–O8	1 206(4)
Pb1–O2	2.497(3)	C11-O10	1.263(4)
Pb1–O4	2.218(3)	C11-O12	1.265(4)
Pb1–O6	2.162(3)	C21–O20	1.297(4)
Pb1–O8	2.844(3)	C21–O22	1.232(4)
Pb1-O10	2.304(3)	C14-C15	1.367(3)
Pb1-O12	2.276(3)	C15-C16	1.375(3)
Pb1-O20	2.160(3)	C16-C17	1.392(3)
Pb1-O22	2.776(3)	C17–N18	1.342(3)
C3–O2	1.244(4)	N18-C19	1.339(3)
C3–O4	1.285(4)	C19-C14	1.397(3)
C7–O6	1.325(4)		
O2-Pb1-O4	55.0(1)	O20-C21-O22	121.1(2)
O6–Pb1–O8	50.4(1)	C14-C15-C16	119.0(3)
O10-Pb1-O12	57.0(1)	C15-C16-C17	119.7(3)
O20-Pb1-O22	51.1(1)	C16-C17-N18	120.6(3)
O2–C3–O4	120.1(2)	C17-N18-C19	120.3(3)
O6–C7–O8	122.5(2)	N18-C19-C14	120.6(3)
O10-C11-O12	119.7(2)	C19-C14-C15	119.8(3)

pyridine in dry acetonitrile. The yellow crystals are moisture sensitive, decomposing on contact with atmospheric moisture considerably more rapidly than lead(IV) tetraacetate itself, to give a brown powder, and hence were normally handled under a nitrogen or argon atmosphere. The complex is readily soluble in many non-protic organic solvents.

X-Ray structure analysis

The solid-state structure of the LTA–py complex was found by single-crystal X-ray diffraction at 150 K, and is shown in Fig. 1, with selected bond lengths and angles in Table 1. The presence of a lead-nitrogen bond, can be seen immediately, together with the large amount of 'coordination space' that the pyridine takes up. This lead–nitrogen bond, at 2.304(3) Å, is the shortest amongst the crystal structures of lead(IV) reported in the CCDB, and is of the same order as a lead–oxygen bond (*e.g.* Pb1–O10 2.302(3) Å), consistent with a strong coordination effect. It is also the first example of an uncharged but non-chelating N-ligand for lead(IV).



Fig. 1 Crystal structure of LTA-py with thermal ellipsoids.

It can be seen that the lead atom is seven coordinate, with only two of the acetate ligands bonding in a bidentate fashion. Of these, one is virtually symmetrically bound, with oxygen atoms almost equidistant from the lead atom (2.302(3), 2.277(3) Å), whereas the other shows significant distortion of

symmetry (2.218(3), 2.499(3) Å, $\Delta Pb-O = 0.281$ Å) and a significantly longer average Pb-O distance (by 0.066 Å). Even the more symmetrical chelate, which shows similar asymmetry in its binding ($\Delta Pb-O = 0.028$ Å) to lead(IV) tetraacetate³⁴ (LTA) ($\Delta Pb-O = 0.009-0.059$ Å), has a longer average Pb-O distance than those in LTA or lead tetra(o-benzoyl benzoate)35 by 0.015 Å. The other two acetate ligands are even more distorted, bonded to the lead atom through only one oxygen atom, with the other oxygen atom falling outside the van der Waals radius of the lead atom normally considered for bonding. The bonded Pb-O distances in these ligands are significantly shorter (2.160(3), 2.162(3) Å) than those in the chelating ligands (av. 2.324(3) Å). The distortion in the lead-oxygen bond lengths is also reflected in the oxygen-carbon bonds (C7-O6 is notably long at 1.328(5) Å), such that the acetate group is deformed by the mode of binding. Pictorial representations of the inner coordination sphere of the lead atom of LTA, and of the LTA-pyridine adduct are shown in Fig. 2. That of LTApy can be described as a distorted pentagonal bipyramidal coordination, with chelation across two edges of the pentagon, the two monodentate carboxylates being axial and the pyridine being the final vertex of the pentagon. Such an arrangement is expected for complexes of the type M(bidentate)₂(unidentate)₃ with low normalized bite, b < 1.2, for the chelate.³⁶ The pyridine ligand occupies a larger cone volume than any other ligand and interestingly the ring plane lies roughly in the approximate plane of the distorted pentagon. This structure is in contrast to that for



Fig. 2 Selected views of the coordination sphere of (a) LTA; (b) LTA–py showing all ligands and (c) LTA–py showing only bonds involving the lead(IV) cation.

the eight-coordinate LTA,³⁴ and other lead tetracarboxylates,³⁵ in which both oxygen atoms of each carboxylate are bonded to the lead atom, with a rather smaller variation in lead–oxygen bond lengths. The structure of this complex was also determined at 293 K, and except for the expected increase in the lattice dimensions and atomic displacement parameters, shows no discernable differences from the low-temperature structure.

An X-ray powder diffraction pattern of a bulk sample of the LTA-py complex was obtained and showed good correlation with that predicted from the single-crystal lattice parameters and atomic positions³⁷ suggesting that the single-crystal structure is indeed representative of the bulk sample.

Thermal measurements

TGA and DSC were performed on LTA-py in a flowing nitrogen gas atmosphere from 293 to 473 K with a temperature ramp of 2 °C min⁻¹. Several features of interest are observed in the DSC and relate to two specific regions of mass loss (Fig. 3). The first distinct region of mass loss between 70 and 110 °C may be split into two processes by observation of two separate endotherms in the DSC. The first and smaller endotherm is attributed to loss of residual solvent,³⁸ the second (from 87 to 110 °C) represents a relative 15% mass loss, which is consistent with the loss of all the pyridine from the LTA-py complex. Between 120 and 165 °C, a further relative mass loss of 22% occurs, which may be compared to the expected mass loss of 26.5% for the complete loss of two acetate groups (LTA decomposing to lead(II) diaacetate (LDA)). The DSC exotherm which accompanies this mass loss has a distinct shoulder to it, perhaps suggesting two separate processes. Beyond 165 °C a further endotherm is detected in a region of only slow mass loss.



Fig. 3 Combined TGA and DSC of LTA-py, performed under a flow of dry nitrogen gas.

Solution NMR

In chloroform solution the ¹H and ¹³C NMR spectra of the LTA–pyridine complex are identical to those of an equimolar solution of LTA and pyridine. The ¹³C NMR spectrum, for example, shows only very slight deshielding of the acetate carbon atoms compared to LTA (see Table 2). In the ¹³C NMR spectrum of LTA at low temperatures (225 K), carbon–lead *J*-couplings (²*J*(¹³C,²⁰⁷Pb) = 131 Hz, ³*J*(¹³C,²⁰⁷Pb) = 141 Hz) can be observed in satellites for the acetate carbon atoms;³⁹ these are not observed at higher temperatures due to a higher rate of intermolecular exchange of the acetate ligands. In the ¹³C NMR spectra of LTA–py these couplings are not seen at all, suggesting that the rate of acetate exchange is increased by the presence of the pyridine.

Further evidence for this phenomenon arises from an investigation of the ²⁰⁷Pb NMR spectroscopy of these compounds. We have previously shown⁴⁰ that in a mixture of LTA (PbA₄) and benzoic acid (B), the rate of exchange of the carboxylate ligands (PbA₄ \rightleftharpoons PbA₃B \rightleftharpoons PbA₂B₂ *etc.*) is rapid at room temperature, but by cooling the solution to 225 K, five distinct ²⁰⁷Pb NMR resonances, one for each species, can be observed. Upon the addition of pyridine, even at low temperatures, only a single very broad resonance is observed (Fig. 4). This suggests that the rate

Table 2 ¹³C NMR Chemical shifts and $J({}^{13}C, {}^{207}Pb)$ for LTA and LTA-py

	Solution δ (ppm)		CP/MAS δ (ppm) [J/Hz]		
	LTA	LTA-py ^a	LTA	LTA-py	
CO ₂ CH ₂	18.3	18.1	17.0 [75]	16.7 [73]	
2 - 3			18.1 [71]	20.1 [48]	
				21.4 (2) [46]	
CO_2CH_3	180.0	180.0	182.1 [56]	173.5 [59]	
			183.4 [65]	176.6 [67]	
				178.7 98	
				180.0 [73]	
				128.4	
Pyridine		124.0		129.4	
		136.7		142.3	
				145.6	
		149.1		147.6	

^a For a 1 : 1 solution mixture of LTA and pyridine.



Fig. 4 Solution ²⁰⁷Pb NMR data for (a) a 1 : 1 mixture of LTA and B in CDCl₃; and (b) LTA–py in CDCl₃.

of exchange of these carboxylates is increased. In contrast, the addition of pyridine to LTA alone decreases the ²⁰⁷Pb shielding but does not significantly broaden the ²⁰⁷Pb NMR resonance.

The ²⁰⁷Pb NMR chemical shift was recorded as pyridine was titrated into a solution of LTA. From these chemical shifts the binding constant of the pyridine to the lead atom was calculated by means of the Associate program,⁴¹ assuming a 1 : 1 binding model. This was found to be 1.5 (± 0.1) M⁻¹, with a good fit of the data, as demonstrated in Fig. 5. This indicates a weakly bound species in solution, which is consistent with the other observations. Extrapolating the observed chemical shifts allows the solution chemical shift of the LTA–py complex to be predicted to be –1855.0 ppm, a downfield shift of 18 ppm from



Fig. 5 ^{207}Pb NMR Binding curve, determined by titration of LTA with py in CDCl_3.

	LTA	LTA-py	
$egin{array}{c} \delta_{ m iso} \ \delta_{ m i1} \ \delta_{ m 22} \ \delta_{ m 33} \ \kappa_{\delta} \ arOmega \end{array}$	-1872.7 -1692 -1938 -1988 0.66 296	-1854.9 -1729 -1862 -1973 0.09 244	

LTA, which is still not a large change compared to the known ²⁰⁷Pb chemical shift range of over 6000 ppm.⁴²

²⁰⁷Pb CP/MAS NMR

The ²⁰⁷Pb CP/MAS NMR of LTA-py shows apparently three isotropic resonances of approximately equal intensity at -1853.3, -1854.9 and -1856.3 ppm (all with their associated spinning sidebands) (Fig. 6). These are different from the single resonance manifold recorded for LTA (Fig. 6), both in isotropic and anisotropic (obtained from an analysis of the sideband intensities through the Herzfeld-Berger method⁴³) chemical shifts (Table 3). The pattern of these three peaks is highly reproducible between samples; the same peak envelope is seen in each sideband, and the pattern is conserved throughout the temperature range of 213-330 K, with merely a slight (ca. 10 ppm) upfield shift in the isotropic resonance observed as the temperature is increased through this range. The average chemical shift at 296 K, -1854.9 ppm, is essentially identical to the shift predicted for the LTA-py complex by ²⁰⁷Pb solution NMR, -1855.0 ppm.



Fig. 6 ²⁰⁷Pb CP/MAS NMR spectra of (a) LTA and (b) LTA–py at a MAS rate of 2.5 Hz. *iso* indicates the region of the isotropic resonances, the profile of which is also shown in expanded form for LTA–py.

J-Coupling of ²⁰⁷Pb to ¹⁴N (I = 1) should result in a 1 : 1 : 1 triplet of the sort recently reported in the ${}^{207}Pb{}^{1}H$ solution NMR spectra of trisaryllead amide compounds where the slow quadrupolar relaxation rates allow the measurement of ${}^{1}J({}^{207}Pb, {}^{14}N) = 224$ Hz for ${}^{\prime}Bu_{3}PbNH_{2}$ and 265 Hz for ^tBuPbN(H)SiMe₃.⁴⁴ If the triplet of lines in the ²⁰⁷Pb CP/MAS NMR spectrum of LTA-py reflects such a scalar coupling, it is clearly smaller in value than the lead amide examples and the spectrum is distorted by a further interaction such that the intra-triplet peak separations are not symmetrical. The spectral distortion reflects a residual dipolar coupling between ²⁰⁷Pb and ¹⁴N which is not removed by MAS. Such residual dipolar couplings are commonly observed in ¹³C CP/MAS spectra of carbon atoms directly bonded to nitrogen atoms.45 Resonance patterns similar to that observed in our LTA-py spectrum and shown to be due to scalar coupling and residual dipolar coupling to ¹⁴N have been observed in the ²⁹Si MAS NMR spectra of silicon-nitrogen ceramics containing locally tetrahedral SiNO₃ units.^{46,47} The ²⁰⁷Pb resonance profile for LTApy was simulated using the computer program WSolids.48 Using the Pb-N bond distance of 2.30 Å obtained from the singlecrystal determination a 207Pb-14N dipolar coupling constant of 148.7 Hz is calculated. This, together with ${}^{1}J({}^{207}\text{Pb},{}^{14}\text{N}) = 63$ Hz, with J-anisotropy $\Delta_J \approx 0$ Hz, an axial quadrupolar coupling constant for ¹⁴N of ≈ -1.0 MHz with coincident dipolar and quadrupolar tensor frames at ¹⁴N, and appropriate linebroadening (both Gaussian and Lorentzian functions) yields an excellent simulation, shown together with the experimental profile in Fig. 7. An identical simulation was generated from a simpler procedure which models the system simply in terms of the *J*-coupling (J = 63 Hz) and a residual dipolar coupling ($\delta =$ 3 Hz). The precedent from ²⁹Si MAS NMR and the excellent fit of the simulations to the experimental ²⁰⁷Pb CP/MAS NMR spectrum of the LTA-py indicates that it is reasonable to suggest that the three resonances observed in the ²⁰⁷Pb CP/MAS NMR spectrum are caused by a scalar coupling and a residual dipolar coupling to the 14N nucleus of the bound py ligand. This confirms the very real nature of the lead-nitrogen bond in this complex and is the first report of $J(^{207}\text{Pb},^{14}\text{N})$ in the solid state and also the first observation of residual dipolar coupling in ²⁰⁷Pb MAS NMR.



Fig. 7 (a) Isotropic region of the ²⁰⁷Pb CP/MAS NMR spectrum of the LTA–py complex; and (b) simulated spectrum with scalar coupling $J(^{207}\text{Pb},^{14}\text{N}) = 63$ Hz and residual dipolar coupling, d = 3 Hz. An identical simulation is produced with $J(^{207}\text{Pb},^{14}\text{N}) = 63$ Hz, dipolar coupling of D = 148.7 Hz (calculated from Pb–N = 2.307 Å) and ¹⁴N quadrupolar coupling constant of $\chi = -1.0$ MHz with coincident dipolar and quadrupolar tensor orientations.

CSA analysis of the integrated intensities of the pattern of the spinning sidebands observed at several MAS rates was performed using the Herzfeld–Berger method and the resultant principle values of the CSA tensor, along with those of LTA, are given in Table 3. The most notable feature of the LTA– py CSA tensor is that the anisotropy is small and the skew is close to zero, indicative of an essentially spherical distribution of electron density around the lead atom. This is very different from the general pattern for lead tetracarboxylates which have axial or close to axial CSA tensors. The span of the CSA is, however, within the range typical for lead tetracarboxylates.⁴⁹

¹³C CP/MAS NMR

The structures of both LTA and the LTA–py complex were further investigated by ¹³C CP/MAS NMR spectroscopy at ambient temperature. The spectrum of LTA (Fig. 8(a)) shows two resonances for each of the distinct acetate carbon atoms. This is interpreted as reflecting the presence of two independent molecules of LTA in the asymmetric unit of the X-ray crystal structure.³⁴ Although in principle each of the independent carbon atoms should give rise to a separate carbon resonance it is assumed that because the acetate ligands within each molecule



Fig. 8 ¹³C CP/MAS NMR data of (a) LTA and (b) LTA-py recorded at MAS rate = 3 Hz (* indicates spinning side bands).

type, although crystallographically independent, are so similar they are not distinguished through ¹³C NMR chemical shifts.

The spectrum for the LTA-py complex (Fig. 8(b)) has four distinct carboxylate carbon resonances and three methyl carbon resonances, with one almost twice as intense as the others. Thus the four crystallographically distinct acetate groups in LTApy are distinguished by ¹³C NMR spectroscopy. Five slightly broader resonances in the aromatic region of the spectrum are assigned to the py carbon atoms and attribution to the carbons o-, m- and p- to the nitrogen atom is made partially by comparison with typical spectra of py and its adducts, and also by the observation that the peaks at 145.6 and 147.6 ppm are the broadest and so can be assigned to C17 and C19 (o- to nitrogen), since they have the largest residual dipolar coupling to ¹⁴N. There is evidence of ²⁰⁷Pb coupling satellites of each of the resonances associated with the acetate groups in both LTA and LTA-py. ¹³C NMR chemical shifts and coupling constants are collected in Table 2.

A spectrum taken at 213 K showed no appreciable difference to that recorded at room temperature. Heating of the LTA– py complex in the range 262 to 337 K, however, causes a dramatic change in the pyridine peaks of the ¹³C CP/MAS NMR spectrum. On increase in temperature, pairs of resonances attributed to C17/C19 (145.6 and 147.6 ppm) and C14/C16 (128.4 and 129.4 ppm) were observed to first broaden and then coalesce in a pairwise fashion (Fig. 9). The resonance assigned to C15 (142.3 ppm) broadens only very slightly, whilst the resonances for the acetate groups remain essentially unchanged. On cooling, the spectral changes are fully reversible and there is no hysteresis observed.

These observations suggest a local dynamic process of an activated 180° ring flip motion of the py about the N–C15 axis, which is slow on the NMR exchange-broadening time scale at room temperature, but at higher temperatures is of a greater rate, causing coalescence of first the C17 and C19 resonances and then the C14 and C16 resonances through pairwise exchange. The ¹³C CP/MAS NMR spectra between 305 and 337 K were further analysed by modelling, using the gNMR program, ⁵⁰ the spectral line shapes of the py carbon atoms on the above assumption of exchange, in order to obtain rates for the dynamic process at each temperature, as shown in Fig. 9. The exchange data are shown on an Arrhenius plot in Fig. 10. Fitting to the rate data from 308 to 337 K yields an activation barrier of $E_a = 72.5$ kJ mol⁻¹ with a pre-exponential factor of $A = 1.5 \times 10^{14}$ s⁻¹. The py ring flip process is expected to significantly average the ¹³C CSAs and

the ${}^{13}C{}^{-1}H$ dipolar couplings from their static values. Therefore, on raising the temperature, regions of spectral broadening are expected when the rate of exchange reaches the order of the MAS rate⁵¹ and then subsequently the frequency of the proton-decoupling field.⁵² The projected rates of exchange beyond 337 K are such that a MAS-broadening effect is likely, and since the simulation process assumes only an exchange-broadening effect, it will underestimate the true rate of exchange; spectra above 337 K were omitted from the analysis for this reason.

Discussion

The evidence in the crystalline state for the existence of a coordinative complex LTA-py containing a Pb-N bond is overwhelming. Specifically the single-crystal X-ray structure shows a Pb-N bond distance of 2.307 Å, and ²⁰⁷Pb CP/MAS NMR shows ${}^{1}J({}^{207}\text{Pb},{}^{14}\text{N}) = 63$ Hz and a residual dipolar coupling constant consistent with the X-ray bond length. The conclusion that a Pb-N bond is formed in solution relies on more circumstantial evidence. Firstly, it is to be noted that the crystalline material is obtained directly from solution, but this does not prove that the association between Pb(IV) and py is specific outside of the crystalline environment. NMR studies in solution indicate that exchange of py and acetate between the lead coordination sphere and bulk solution is rapid on the NMR time scales determined by chemical shift differences and coupling constants. Indeed, that J-coupling (13C, 207Pb) is observed at low temperature for acetate carbons in LTA, but not LTA-py (1 : 1) solutions, indicates that the rate of ligand exchange at Pb(IV) is accelerated by the presence of py. Observation of ²⁰⁷Pb NMR as LTA is titrated by py provides the crucial piece of evidence for an LTA-py complex in solution. Although the derived binding constant of 1.5 M⁻¹ is not in itself convincing as to a specific $Pb \cdots N$ interaction, the fact that the ²⁰⁷Pb NMR shift for the LTA-py complex is predicted from the titration to be -1855.0 ppm as compared to the measured shift in the solid-state ²⁰⁷Pb CP/MAS NMR spectrum at -1854.9 ppm is highly significant. Because the solid-state NMR is consistent both with the unequivocal evidence from X-ray crystallography and with the solution NMR data, it acts as a bridge between the solid state and solution, allowing us to postulate that the LTA-py complex exists in solution in a form substantially unaltered from its manifestation in the crystalline solid. Hence, also in solution, the addition of the py ligand has a profound influence on the coordination sphere of the lead atom, and it is perhaps therefore not surprising that LTA when dissolved in py has a very different reactivity than when dissolved in a noncoordinating solvent, and this offers insight into the observation that py catalysis is often required in a wide range of reactions of lead(IV).

Comparison of the nature of the coordination of Pb(IV) in LTA and LTA-py is of great interest. In LTA, Pb(IV) has a distorted dodecahedral PbO₈ inner coordination sphere in which all the acetate groups are chelating, with each acetate in the two molecules found in the crystallographic asymmetric unit having slight, but different, asymmetry in their chelation. LTA-py has a single molecule in the asymmetric unit with an unusual and intriguing geometry. Two of the acetate ligands are chelating, one similar to those in LTA though less tightly bound, the other more considerably distorted. The other two acetate ligands are clearly monodentate. Together with the coordination of the py molecule this leads to a distorted pentagonal-bipyramidal PbO₆N inner coordination sphere. Since the py ring is observed to lie in an approximate plane with the two bidentate acetate ligands (Fig. 2) there is no obvious steric reason why the monodentate acetate ligands could not chelate; the reason that they do not must be electronic in origin.

²⁰⁷Pb NMR in the solid state can offer some insight into the electronic environment of the Pb atoms and to the reasons for this interesting structure. The ²⁰⁷Pb NMR isotropic shift



Fig. 9 Region of ¹³C CP/MAS NMR spectra of LTA–py, showing the pyridine peaks at a range of temperatures indicated from 296 to 328 K, and the corresponding fit to the exchange model of pyridine ring flips at the temperature specified.

of LTA-py is, at -1854.9 ppm, just 16.5 ppm downfield of LTA. In the context of an overall range of ²⁰⁷Pb NMR shifts of ca. 6000 ppm and of a range of observed shifts for 20 lead(IV) tetracarboxylates of -1816.5 to -2137.0 ppm,⁴⁰ the average shielding of the 207Pb nucleus in LTA and LTA-py can be considered to be virtually identical (though note that in the preceding argument the difference is considered significant and reproducible in respect of proving that the LTA-py complex persists in solution). This suggests that the combined donor power of the two bidentate acetates, two monodentate acetates and py ligand in LTA-py is effectively the same as that of the four bidentate acetates in LTA. This offers a potential explanation for the unusual Pb coordination environment in LTA-it would seem to be unnecessary for the two monodentate acetate ligands to become bidentate, because the Pb(IV) atom is already receiving the optimum amount of electron donation. Presumably the electron density created by the alternative mono-capped square antiprismatic nine-coordinate geometry around Pb, in a structure where all the acetate ligands remained chelating, could not be tolerated, even by Pb(IV).

Because the ideal coordination sphere of Pb in LTA–py would have only C_{2v} point symmetry, in comparison with the D_{2d} symmetry approximated by lead tetracarboxylates, there is no expectation of an axial shielding tensor, so the skew of the ²⁰⁷Pb NMR CSA, $\kappa_6 = 0.09$, found for LTA–py is indicative of the changed geometry. The span of the ²⁰⁷Pb NMR CSA, $\Omega =$ 244 ppm is within the range of 187–449 ppm found for lead tetracarboxylates,⁴⁰ but may be placed in the context of spans of over 2000 ppm reported for some other lead compounds. Clearly, despite initial appearances, the distorted pentagonalbipyramidal PbO₆N coordination environment of the Pb in LTA–py provides as uniform an electron distribution around the ²⁰⁷Pb nucleus as does the slightly distorted PbO₈ dodecahedron around Pb in LTA.

The observation of a local dynamic motion, namely the 180° flips of the py ring, is also interesting. Similar flip-type motions are well-known for a variety of phenyl groups in solids,⁵³ but reports of activated dynamic processes of py rings within solids are restricted to inclusion and intercalation compounds in which it is a guest molecule⁵⁴⁻⁵⁷ and when adsorbed on surfaces,^{58,59} in



Fig. 10 Arrhenius plot $(\ln(\text{rate}) vs 1/T)$ for pyridine ring flip exchange data.

all of which cases the dynamics are not confined to a simple flip motion. The simple 180° ring flip does not, of course, lead to equilibrium positional disorder within the crystal and is hence essentially "diffraction-invisible". The localized electron density seen in the X-ray structure at 293 K confirms that the exchange motion detected by ¹³C CP/MAS NMR is indeed a flipping process rather than a continuous rotation. This is the first example of such a motion for a coordinated py molecule in the solid state and is the first full analysis of a flip motion for a ring bonded to Pb(IV).

That the py ring in this complex is unique in demonstrating ring flips under conditions where many other py coordination complexes do not⁶⁰ can almost certainly be rationalized through its unusual structure. All the previously studied py coordination complexes would be expected to have significant intramolecular and intermolecular steric barriers to a ring flip process. As we have previously remarked, the py ring occupies a large volume of the Pb(IV) coordination sphere, and because the axial acetate ligands are mono- not bi-dentate, we would expect little, if any, intramolecular steric barrier to the ring flip process. Here, as in the many reported examples of phenyl ring flips, it would appear that the barrier to the flip motion is determined primarily by intermolecular steric factors. It is far more likely that part of a neighboring molecule can move away for a sufficient time to allow a ring flip to occur than it is for part of another ligand in the same coordination sphere to do so. It seems that in the other py coordination complexes studied the intermolecular barrier to ring flips proves prohibitive.

It is probably also significant that we observe de-coordination and loss of py from the solid on heating to 360 K, only 25 K above the maximum of the temperature range in which ring flips are studied by CP/MAS NMR spectroscopy. Presumably the loss of the py molecules is presaged by some rearrangement within the complex, and most particularly one might expect the Pb– N bond to lengthen with increasing temperature, and that the crystal should become less dense prior to the de-coordination of py above *ca.* 360 K. Such behavior must have an effect in regard to the rate of py ring flips and means that caution should be observed in respect of the Arrhenius analysis as the activation barrier to ring flips might be expected not to be independent of temperature.

Conclusions

We have prepared a complex of lead tetraacetate and py; complexes of this type have become of greater synthetic interest in recent years, although their chemistry has developed in an empirical fashion. The structure reported here represents the first hard evidence towards the development of a mechanistic approach to this class of reagent. The X-ray crystal structure indicates a Pb-N bond of 2.307 Å and an intriguing sevencoordination of the Pb(IV). Solid-state ²⁰⁷Pb CP/MAS NMR studies act as a bridge to the solution NMR measurements, showing that this structure of the complex persists in solution, despite a relatively rapid rate of ligand exchange. The structure of this product is totally unexpected; that lead tetracetate might associate with pyridine seems at first glance to unremarkable, but that the neutral N-donor pyridine ligand should displace two O-donor atoms from two chelating and charged acetate ligands from the Pb(IV) coordination sphere is unprecedented. Analysis of the solid-state ²⁰⁷Pb NMR spectra suggests that the driving rationale for the coordination environment of Pb(IV) is for it, in all cases, to receive from the combination of ligands a similar electron density in as symmetrical a distribution as possible; the huge structural diversity and apparent adaptability of known Pb(IV) environments seems to have masked this simple principle. All these apparently dissimilar environments achieve essentially the same result for the lead atom: Pb(IV) controls its electronic distribution and the ligands must adapt, hence the potentially interesting modifications in their chemistry. It seems clear that when pyridine is added to solutions for the enhancement of the exploitation of lead(IV) carboxylate-assisted organic reactions, it can act as a ligand to Pb(IV) with a profound effect on the coordination sphere of the lead atom, and not just as a Brønsted base. The coordination structure, geometry and local pyridine ring dynamics of the crystalline LTA-py coordination compound are of great intrinsic interest too, offering insight into the delicate balance of forces involved in the construction of these compounds. The link between the solid state and solution provided by the 207Pb NMR is possibly the most compelling example to date of using NMR to show that a relatively weakly bound and labile complex in solution has as a highly defined and unforeseen structure that is identical to that determined crystallographically.

Experimental

Preparation of the complex

Lead tetraacetate (4 mmol, 1.77 g) was dissolved in acetonitrile (15 ml) at room temperature under an inert argon atmosphere. Upon the addition of pyridine (20 mmol, 1.56 ml) the solution turned to a deep red color, and a yellow crystalline solid started to precipitate. Precipitation was completed by standing at 4 °C for 4 days. The supernatant liquid was then decanted and the crystals washed with cold hexane under an argon atmosphere and dried *in vacuo*, to yield the lead(IV) tetraacetate–pyridine (LTA–py) complex (1.49 g, 72%). Elemental analysis: C, 28.9; H, 3.00; N, 2.50; Pb, 38.7%. C₁₃H₁₇NO₃Pb requires C, 29.9; H, 3.28; N, 2.68; Pb, 39.66%.⁶¹

Solution NMR spectroscopy

Broadband proton-decoupled ¹³C NMR spectra at 125 MHz were recorded at 300 K on a Bruker AM500 spectrometer with a 5 mm broadband probe. Broadband proton-decoupled ²⁰⁷Pb NMR spectra in solution were recorded at 52.2 MHz on a Bruker AM250 spectrometer with a 10 mm broadband probe, at a temperature of 295 K unless otherwise stated. The spectra were referenced externally to 80% Me₄Pb in toluene, whereby the reference frequency of this standard was calculated⁶² from Ξ (²⁰⁷Pb) = 20.920597 MHz^{62,63} (when the ¹H NMR frequency of Me₄Si is 100.000 MHz). For each sample about 64 scans were required to obtain a satisfactory signal-to-noise ratio.

Solid-state CP/MAS NMR spectroscopy

¹³C and ²⁰⁷Pb CP/MAS NMR spectra were acquired, at 50.32 and 41.868 MHz respectively, on a Bruker MSL200

spectrometer, with a multinuclear, proton-enhanced, double bearing magic angle sample spinning probe, using a dry nitrogen gas supply. Inside an inert atmosphere box, approximately 250 mg of sample was packed into 7 mm zirconia rotors with Kel-F caps. MAS was performed at typical rates of 2-3 kHz. A single contact spin-locked cross polarization (CP) sequence⁶⁴ was used with alternate cycle spin-temperature inversion⁶⁵ and flip-back of ¹H magnetization.⁶⁶ The ¹H rf field strength was 55 kHz (a 90⁶ pulse length of $4.5 \,\mu$ s). Free induction decays were defined by 2 K data points over a spectral width of 20 kHz for ¹³C spectra and 30 kHz for ²⁰⁷Pb and were zero filled to 16 K data points before Fourier transformation. For ¹³C NMR experiments, typically 500 transients, with a contact time of 2 ms and a relaxation delay of 5 s, were recorded for each spectrum. ¹³C NMR chemical shifts are reported on the scale with respect to TMS = 0 ppm and were referenced externally to the upfield resonance of adamantane at 29.5 ppm.⁶⁷ For ²⁰⁷Pb NMR experiments, typically 120 transients, with a contact time of 5 ms and a relaxation delay of 10 s, were recorded for each spectrum. ²⁰⁷Pb NMR chemical shifts were referenced externally to a 1 M aqueous solution of lead nitrate at 298 K as 0 ppm.42 Temperature measurement and regulation of the bearing gas were controlled with a Bruker B-TV1000 unit equipped with a copper-constantan thermocouple and digital reference. Temperature calibration was achieved both with the samarium ethanoate tetrahydrate Curie Law ¹³C NMR chemical shift thermometer,68 previously set against the phase transitions of D-camphor, cobaltocenium hexafluorophosphate and 1,4-diazobicyclo[2.2.2]octane, and with the samarium stannate (Sm₂Sn₂O₇) Curie Law ¹¹⁹Sn NMR chemical shift thermometer.⁶⁹ The sample was allowed to equilibrate at each new temperature for ca. 20 min before spectral acquisition. Nonquaternary suppression (NQS) dipolar dephasing experiments,70 using delays of 20-200 µs, were carried out with the pulse sequence of Alemany et al.71 Chemical Shift Anisotropy (CSA) calculations were performed on integrated intensities of the sidebands and analyzed with the Herzfeld-Berger method using the HBA routine of the WSolids computer program.48 The CSA tensors are reported following the suggestions of Harris⁷² with $\delta_{11} > \delta_{22} > \delta_{33}$ along with the span, $\Omega = \delta_{11} - \delta_{33}$, and the skew, $\kappa_{\delta} = 3(\delta_{\rm iso} - \delta_{22})/\Omega.$

To obtain the exchange rates for the pyridine ring flips, the ¹³C CP/MAS NMR spectral line shapes were modeled using the *gNMR* program.⁵⁰ The chemical shifts and Gaussian and Lorentzian line widths of the pyridine carbon peaks were simulated from the room temperature spectrum, which is in the low-temperature limiting region of the exchange broadening timescale. The rates of exchange at higher temperatures were then fitted iteratively to the experimental data assuming a twofold exchange model between C17 and C19, and between C14 and C16. Rate data from the exchange broadening simulations were used to determine Arrhenius parameters. The isotropic ²⁰⁷Pb CP/MAS NMR resonance was simulated using the *WSolids* computer program⁴⁸ to fit the chemical shift, line width, $J(^{207}\text{Pb},^{14}\text{N})$ and the residual dipolar coupling constant $D(^{207}\text{Pb},^{14}\text{N})$. The residual dipolar coupling constant was calculated from the value of the Pb–N bond distance obtained from the X-ray crystal structure and also independently obtained by fitting the spectrum using the assumptions of an axial quadrupolar coupling and similar orientation of the dipolar and quadrupolar tensor frames.⁷³

Thermal measurements

Simultaneous thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on a Stanton Redcroft STA 785 Thermal Analyzer. The dry powdered sample (20 mg) was loaded into a platinum crucible and heated under a flow of dry nitrogen at a rate of 2 °C min⁻¹; data points were recorded at 5 s intervals. Calibration of the DSC was against the solid-state transition of KNO₃ (taking due note of the particular properties of this change^{74,75} and against the fusion of naphthalene).

Powder X-ray diffraction

The sample was sealed in a 0.3 mm soda-glass capillary tube. Powder diffraction patterns were collected using a Siemens D5000 diffractometer operating in transmission geometry using monochromatic Cu-K α_1 radiation ($\lambda = 1.54056$ Å). Data was collected for $5 \le 2\theta \le 50^\circ$ in steps of 0.02°. The X-ray powder pattern was simulated from the single-crystal X-ray parameters using the *CrystalDiffract* computer program.³⁷

Single-crystal X-ray diffraction

For the low-temperature determination a crystal of the LTApy complex was selected and mounted on a nylon fibre using a drop of perfluoropolyether oil. It was then rapidly cooled to 150 K in a stream of cold nitrogen using an Oxford Cryosystems CRYOSTREAM cooling system. The crystal for the ambient temperature determination was mounted using silicone grease in a Lindemann capillary. The data were collected on an Enraf-Nonius DIP2020 image-plate diffractometer using graphitemonochromated Mo-K α radiation ($\lambda = 0.71070$ Å). The images were processed using the DENZO and SCALEPACK suite of programs.76 Data were corrected for Lorentz and polarization effects and a partial absorption correction applied by multi-frame scaling of the image-plate data using equivalent reflections. Selected crystal data, data collection and refinement parameters are given in Table 4. The structure was solved by direct methods using the SIR92 program,77 and refined using fullmatrix least squares procedures, based on F, with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were placed in calculated positions during the final

Tab	ole 4	Crystal	data,	data co	llection	and	refinement	parameters
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	At 150 K	At 293 K	
Crystal formula	$C_{13}H_{17}PbNO_8$	$C_{13}H_{17}PbNO_8$	
Crystal dimensions/mm	Pale yellow, $0.3 \times 0.3 \times 0.3$	Pale yellow, $0.35 \times 0.25 \times 0.25$	
Symmetry	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	
a/Å	8.971(1)	9.103(1)	
b/Å	13.870(1)	14.036(1)	
c/Å	12.950(1)	13.122(1)	
$V/Å^3, Z$	1611.14, 4	1676.49, 4	
β/°	90.901(3)	90.625(2)	
Measured reflections	5921	12572	
Independent reflections	2783	3452	
Reflections with $I > 3\sigma(I)$	2415	2759	
Parameters refined	209	209	
Final $\Delta \rho / e \text{ Å}^{-3}$	-1.03, 1.22	-1.86, 1.52	
Final \vec{R} and \vec{R}_{w}	0.0242, 0.0273	0.0295, 0.0372	

cycles of refinement. A three-parameter Chebychev weighting scheme⁷⁸ was applied. All crystallographic calculations were performed using the CRYSTALS program.⁷⁹ Neutral atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B).

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See http://dx.doi.org/10.1039/b506366c for crystallographic data in CIF or other electronic format.

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