

Observation of intermolecular ligand exchange in lead(IV) carboxylates by 1- and 2-D ^{207}Pb NMR spectroscopy

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Intermolecular ligand exchange, which is slow on the NMR timescale, has been observed for lead(IV) carboxylate species containing acetate and benzoate ligands by the use of ^{207}Pb NMR spectroscopy.

Lead(IV) reagents are widely used as oxidising agents in organic synthesis, being suitable for a variety of oxidative transformations,¹⁻⁴ and in more recent studies the usefulness of these compounds for the formation of carbon-carbon bonds has been amply demonstrated.⁵⁻⁷ The occurrence of ligand exchange in these transformations has been established, and widely used to explain the oxidative chemistry of lead(IV). We recently reported a convenient approach for the preparation of a wide variety of lead(IV) tetracarboxylates, and an examination of their reactivity.⁸ In that work, we initiated a detailed systematic investigation of such complexes using ^{207}Pb NMR spectroscopy and observed dynamic exchange effects in some cases. For example, although the chemical shift of a wide range of lead(IV) carboxylates lay in the range 1870 ± 25 ppm at 295 K, the linewidths at half-height were highly variable (typically 8–25 Hz, but as high as 100 Hz) and both linewidths and chemical shifts were temperature dependent.†

In this paper we describe work undertaken to study the behaviour of more complex systems, containing lead(IV) species derived from mixed ligands; in this case acetate and benzoate. We chose to observe the lead(IV) nucleus directly as this offers a sensitive probe of the lead(IV) environment and because ^{207}Pb is well suited to NMR observation; it has a nuclear spin of $\frac{1}{2}$, a natural abundance of 22.6% and nuclear receptivity that is 11.7 times that of ^{13}C .⁹⁻¹²

At 295 K the 104.4 MHz ^{207}Pb NMR spectra of lead(IV) tetraacetate and lead(IV) tetrabenzoate,‡ display single resonances at -1870.4 ($\nu_{\frac{1}{2}} = 2$ Hz) and -1887.8 ppm ($\nu_{\frac{1}{2}} = 18$ Hz), respectively§ [Fig. 1(a) and (b)]. Under similar conditions, a *ca.* 1:1 mixture of these produced a broader resonance at -1878.2 [$\nu_{\frac{1}{2}} = \text{ca. } 470$ Hz, Fig. 1(c)] consistent with exchange processes at a rate intermediate between 'fast' and 'slow' on the chemical shift timescale. On reducing the temperature of the system, the single broad resonance separates further until, at 225 K, five distinct resonances could be resolved [Fig. 1(c), (d) and (e) and Table 1; assignments were established as described below]. Increasing the temperature of this cold solution in stages back to 295 K showed these changes to be reversible, as expected for a system undergoing dynamic exchange. Clearly, at 225 K the exchange rates had reduced such that the processes were now slow on the NMR timescale.

Of the five resonances observed at 225 K, the outer two at

Table 1 Chemical shift assignments for the five resonances observed at 225 K^a

	δ_{Pb}
PbA ₄	-1885.2
PbA ₃ B	-1888.9
PbA ₂ B ₂	-1892.0
PbAB ₃	-1894.7
PbB ₄	-1896.8

^a The following abbreviations apply: PbA₄, lead(IV) tetraacetate; PbA₃B, lead(IV) triacetate monobenzoate; PbA₂B₂, lead(IV) diacetate dibenzoate; PbAB₃, lead(IV) monoacetate tribenzoate; PbB₄, lead(IV) tetrabenzoate.

Table 2 Relative % integrals of the five species observed at 225 K following the addition of benzoic acid to a solution of lead(IV) tetraacetate

	Equivalents of benzoic acid added					
	0	1	2	3	4	5
PbA ₄	100	40	15	5	2	0
PbA ₃ B	0	40	37	24	14	6
PbA ₂ B ₂	0	17	32	36	31	26
PbAB ₃	0	3	13	28	36	41
PbB ₄	0	0	3	7	17	27

-1885.2 ppm and -1896.8 ppm were identified as being due to the species PbA₄ and PbB₄, respectively, by comparison with the spectra of PbA₄ and PbB₄ alone; the chemical shift of PbA₄ at 225 K exactly matched that of the low-field resonance, whilst that of PbB₄ at 225 K matched that of the high-field resonance (spectra not shown). The remaining three resonances were identified by titration. Thus, addition of equivalents of benzoic acid into a solution of PbA₄ produced increases in the relative intensities of the high-field resonances, as summarised in Table 2. Conversely, additions of acetic acid to PbB₄ systematically increased the intensity of the low-field resonances. These data indicate the assignments shown in Table 1, and show a trend of decreasing lead(IV) chemical shift, as acetate ligands are replaced by benzoate ligands. In accordance with these observations, the spectra recorded at 225 K of compounds with mixed ligands, produced by direct synthesis using a modification of the literature procedure⁸ [using the required stoichiometric quantities of lead(IV) acetate and benzoic acid], also showed a distribution of resonance intensities that was dependent on the acetate:benzoate ratios. In synthesising these compounds, excess free acetic acid was removed by azeotroping with toluene and the acetate:benzoate ratios of the final solutions were readily determined by integration of proton spectra. These data were, therefore, indicative of an exchange process in which acetate ligands were substituted for benzoate ligands, and *vice-versa*, but gave no information on the number of exchanging

† More recent studies have indicated that the linewidth broadening is due, in some cases, to ligand exchange with residual lead(IV) tetraacetate.

‡ For convenience, the lead(IV) carboxylates will be referred to as PbA_nB_n in the remainder of the text, where A and B represent acetate and benzoate ligands, respectively.

§ Chemical shifts are referenced to 80% Me₄Pb in toluene. The reference ^{207}Pb frequency for Me₄Pb was calculated¹² from the ^1H frequency of Me₄Si at 100.000 MHz, for which, at the same magnetic field strength, Me₄Pb resonates at 20.920 597 MHz.^{11,12}

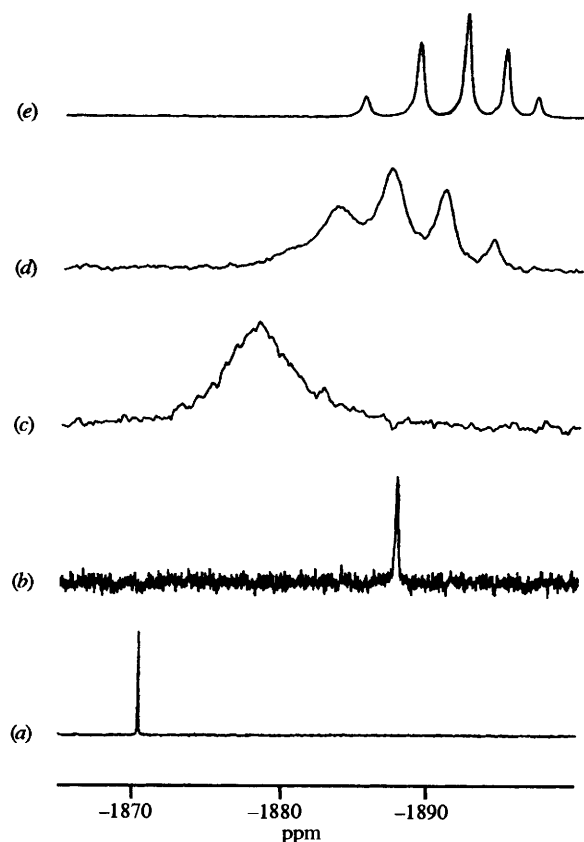


Fig. 1 104.4 MHz ^{207}Pb NMR spectra: (a) 450 mmol dm^{-3} lead(IV) tetraacetate at 295 K; (b) 300 mmol dm^{-3} lead(IV) tetrabenzoate at 295 K; (c) a ca. 1:1 mix (500 mmol dm^{-3} each) of lead(IV) tetraacetate and lead(IV) tetrabenzoate at 295 K; (d) as (c) but recorded at 260 K; (e) as (c) but recorded at 225 K. All samples were prepared in CDCl_3 in 5 mm diameter tubes. Spectra were recorded on a Bruker AMX500 equipped with a broadband probe and are referenced externally to Me_4Pb . Typically, 32 K real data points were acquired for a 10.6 KHz spectral width. Exponential window functions corresponding to a line-broadening of 2 Hz for spectra (a) and (b), and of 20 Hz for (c)–(e) were applied prior to Fourier transformation. Spectra recorded at 52.2 MHz (now shown) were obtained on a Bruker AM250 instrument with a 10 mm broadband probe.

ligands in any exchange encounter. In order to gain further insights into this, we made use of 2D exchange spectroscopy (EXSY)^{13,14} in which cross-peaks correlate species that are undergoing a mutual magnetisation exchange process.¶ The separation of the five resonances at 225 K was sufficient at both 52.2 MHz and at 104.4 MHz, to allow cross-peaks to be resolved (Fig. 2). In our initial studies, performed at 52.2 MHz, 2 equiv. of benzoic acid were added to lead(IV) tetraacetate (170 mmol dm^{-3}) such that a population of all five species could be observed. EXSY spectra were recorded with mixing times (τ_m) of 5, 10, 20 and 50 ms. Spectra with a τ_m of 5 and 10 ms displayed cross-peaks between adjacent resonances only, that is resonances i to $i \pm 1$, whereas those with a τ_m of 20 or 50 ms displayed additional peaks due to i to $i \pm 2$ exchanges. The $i, i \pm 2$ peaks have been observed only after a significant build-up of $i, i \pm 1$ cross-peak intensity in all cases, suggesting these arise from a two-step transfer process. Higher quality data have also been obtained at 104.4 MHz for which EXSY spectra

¶ The EXSY experiment is, in essence, similar to the NOESY experiment, so cross-peaks can, in principle, arise from the nuclear Overhauser mechanism, although these would not be anticipated in these systems.

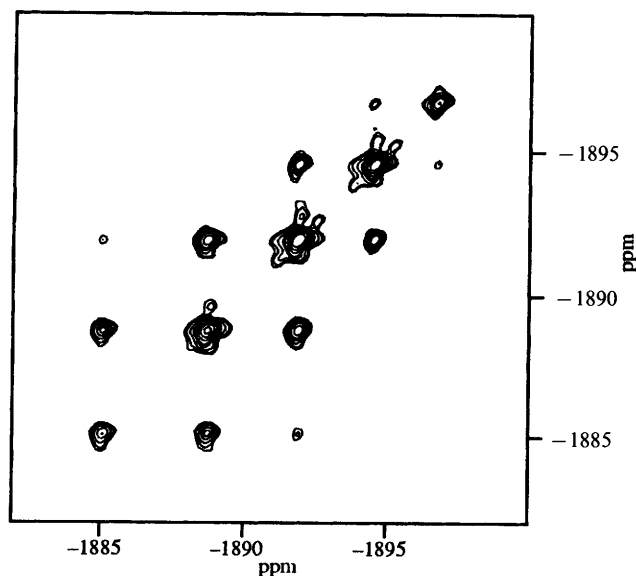


Fig. 2 104.4 MHz phase-sensitive ^{207}Pb EXSY spectrum of a ca. 1:1 mixture of lead(IV) tetraacetate and lead(IV) tetrabenzoate at 225 K [as for Fig. 1(e)]. The pulse sequence was $\text{D1}-90^\circ-t_1-90^\circ-\tau_m-90^\circ-t_2$. 512 Data points were collected in t_2 for 256 t_1 increments of 248 scans each with spectral widths of 3 kHz. D1 was 800 ms and τ_m (the mixing time for magnetisation exchange) was 25 ms, giving a total acquisition time of 17 h. Phase-sensitive detection in t_1 was afforded by time proportional phase incrementations (TPPI). Free induction decays were processed with an exponential function (10 Hz line-broadening) in both dimensions prior to Fourier transformation and F_2 spectra were subject to 5th order polynomial baseline correction prior to transformation of the t_1 data.

Table 3 Approximate linewidths for the five resonances of a 1:1 mixture of PbA_4 and PbB_4 at 260 K. Line-widths were obtained by deconvolution of the experimental data to five Lorentzian lineshapes with the half-height linewidths stated below

	$\nu_{1/2}/\text{Hz}$
PbA_4	350
PbA_3B	280
PbA_2B_2	190
PbAB_3	100
PbB_4	40

have been recorded on 1:1 mixtures of lead(IV) tetraacetate and tetrabenzoate. Conclusions drawn from the lower-field work were supported by the higher-field results, and suggest the exchange process involves only a 1:1 swap of ligands. The exchange equilibria are summarised in Scheme 1.



Scheme 1

Qualitative differences in rates for the exchange processes can be seen in the 1D variable-temperature experiments. In Fig. 1(d), the five resonances, although not fully resolved, can just be distinguished. It is apparent that the linewidths for the lower-field resonances are significantly greater than those of the higher-field signals, as summarised in Table 3. This suggests the rate processes for the species containing higher numbers of acetate ligands are faster than those with more benzoate ligands surrounding lead(IV). Similar results are seen in the 2D EXSY spectra where the build-up of cross-peak intensity is faster between low-field resonances than between those at high-field. For example, in the 25 ms EXSY spectrum shown in Fig. 2 there is considerable cross-peak intensity between PbA_4 : PbA_3B although there exists little between PbAB_3 : PbB_4 . Furthermore,

cross-peaks between $PbA_4:PbA_2B_2$ indicative of a two-step transfer process are of similar intensity to those of the single-step $PbAB_3:PbB_4$ process. These observations also suggest relatively faster exchange processes for those species containing a greater number of acetate ligands. It is suggested that these differences are due, in part at least, to steric factors involving the addition of the relatively bulky benzoate ligands around the lead atom.

The results from this qualitative ^{207}Pb NMR study show that a mixture of lead(IV) tetraacetate and lead(IV) tetrabenzoate exists as five distinct species in solution, and present the first direct spectroscopic evidence for ligand exchange in these lead(IV) systems. Whilst exchange phenomena had been investigated using ^{119}Sn EXSY for tin compounds,¹⁵⁻¹⁷ analogous studies on lead(IV) systems have not been previously reported, although ligand exchange in lead(IV) systems has been established from isotopic exchange reactions.¹⁸ It is our intention to use these NMR techniques for the investigation of the behaviour of lead(IV) carboxylates in solution, with the ultimate aim to apply this information to the design and construction of new complexes with modified reactivity. An examination of the exchange behaviour for a variety of ligand systems, and of the implications for reactivity, is underway, and will be reported in due course.

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