Synthesis and Structure of the Mixed Anion Sandwich Complex $\{[(C_5H_5)_9Pb_4]^-[(C_5H_5)_5Pb_2]^-[Li(12\text{-crown-}4)_2]^+{}_2\}$

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The title compound, $\{[(C_5H_5)_9Pb_4]^-[(C_5H_5)_5Pb_2]^-[Li(12\text{-crown-}4)_2]^+{}_2\}$ **1**, is synthesised by the reaction of $[(C_5H_5)_2Pb]$ and $[(C_5H_5)Li]$ and 12-crown-4 (3:1:2 equiv.), and is shown by X-ray diffraction to contain both a quintuple-decker and a triple-decker sandwich anion; in contrast, the corresponding reaction with $[(C_5H_5)_2Sn]$ (which possesses no such polymeric lattice of its own) in place of $[(C_5H_5)_2Pb]_\infty$ yields the simple 'paddlewheel' molecule $\{[(C_5H_5)_3Sn]^-[Li(12\text{-crown-}4)_2]^+\}$ **2**.

We have shown that nucleophilic addition of cyclopentadienyl anions (C_5H_5) to p-block metal cyclopentadienyl complexes [group 13, $(C_5H_5)Tl$; group 14, $(C_5H_5)_2E$ (E = Sn, Pb)] produces a range of mononuclear ion-separated and ion-paired complexes.[1–4] The $[(\eta^3\text{-}C_5H_5)_3Pb]^-$ anion contains a trigonal planar Pb centre and can be regarded as a segment of the polymeric lattice of $[(C_5H_5)_2Pb]_\infty$.[5] We recently reported that extended organometallic anions can be prepared by increasing the size of the counterions in these systems and by variation of the reaction stoichiometry. Thus, the reaction of $[(\eta^5\text{-}C_5H_5)Tl]_\infty$ with $(C_5H_5)Li$ and [12-crown-4] (2:1:2 monomer equiv.) produces $[(\eta^5\text{-}C_5H_5)Tl(\mu\text{-}C_5H_5)Tl(\eta^5\text{-}C_5H_5)]^-[Li(12\text{-crown-}4)_2]^+$ which is the second anion homologue of the 14e $[(\eta^5\text{-}C_5H_5)_2Tl]^-$ anion.[6]

We report here the outcome of the reaction of $[(C_5H_5)_2Pb]$ with $[(C_5H_5)Li]$ and 12-crown-4 (3:1:2 equiv.) in THF. Rather than containing the anticipated $[(C_5H_5)_7Pb_3]^-$ anion and a $[Li(12\text{-crown-}4)_2]^+$ cation, the product is the mixed-anion complex $\{[(C_5H_5)_9Pb_4]^-[(C_5H_5)_5Pb_2]^-[Li(12\text{-crown-}4)_2]^+{}_2\}$ **1** resulting from the adoption of a surprising isomeric alternative. In contrast, such extended anions do not appear to be possible for Sn, and an attempt to prepare related extended anions gives only the mononuclear anion complex $\{[(C_5H_5)_3Sn]^-[Li(12\text{-crown-}4)_2]^+\}$ **2**.†

A low-temperature X-ray crystallographic study was undertaken on **1**.‡ It contains two separate anions, $[(C_5H_5)_9Pb_4]^-$ and $[(C_5H_5)_5Pb_2]^-$, and two $[Li(12\text{-crown-}4)_2]^+$ cations (Fig. 1). Each of the anions has a crystallographic centre of inversion [at the centroids of (C_5H_5) *C* and (C_5H_5) *H*]. In both anions the (C_5H_5) ligands are roughly η^5-coordinated to their respective Pb centres. However, there are large variations in the $(C_5H_5)_{centroid}$–Pb distances in both, with the terminal $(C_5H_5)_{centroid}$ contacts to Pb (2.511–2.615 Å) being shorter than the $\mu\text{-}C_5H_5$ bridging distances (2.728–2.919 Å). The $Pb(\mu\text{-}C_5H_5)Pb$ bridges also exhibit varying degrees of distortion from linearity {the Pb–[μ-$(C_5H_5)_{centroid}$]–Pb angles ranging from 165.0 to 180.0°}. The planar geometries of all the Pb centres of **1** are similar to that observed in the ion-contacted and ion-separated $[(\eta^3\text{-}C_5H_5)_3Pb]^-$ anion, the first homologue of the Pb anions of **1**.[3]

Examination of the pattern of $(C_5H_5)_{centroid}$–Pb distances in the $[(C_5H_5)_9Pb_4]^-$ anion shows that this can be rationalised as a $[(C_5H_5)_5Pb_2]^-$ anion which is loosely complexed by two terminal $(C_5H_5)_2Pb$ units [*i.e.* $(C_5H_5)_2Pb\cdots\{(C_5H_5)_5Pb_2\}^-\cdots Pb(C_5H_5)_2$]. Thus, the $(C_5H_5)_{centroid}$–Pb contacts between the terminal $(C_5H_5)_2Pb$ units and the central $[(C_5H_5)_5Pb_2]^-$ fragment of the $[(C_5H_5)_9Pb_4]^-$ anion [(C_5H_5)*F,F′*-Pb(3,3a) 2.919 Å] are far longer than the other (μ-C_5H_5)–Pb interactions [(C_5H_5)*F,F′*–Pb(2,2a) 2.698 Å and (C_5H_5)*H*–Pb(2,2a) 2.728 Å]. The result of the attachment of the terminal $(C_5H_5)_2Pb$ units to this $[(C_5H_5)_5Pb_2]^-$ moiety has been to pull the (C_5H_5)*F,F′* ligands away from their interactions with Pb(2,2a) and, by way of compensation, to strengthen the interactions between the other (C_5H_5) ligands [(C_5H_5)*G,G′* and (C_5H_5)*H*] and Pb(2,2a). As a result, these $(C_5H_5)_{centroid}$–Pb distances are significantly shorter than the corresponding distances in the separate $[(C_5H_5)_5Pb_2]^-$ anion of **1**. This structural relationship between the two anions of **1** may give some insight into the reasons for the formation of these two anions as opposed to two $[(C_5H_5)_7Pb_3]^-$ anions.

The structural interpretation of the two anions of **1**, discussed above, provides a possible interpretation for the solid-state MAS-NMR behaviour of the complex.§ Two similar resonances (δ −5270 ± 10, −5180 ± 10) and one more distinct resonance (δ −4740) are observed in the ^{207}Pb spectrum at +25 °C (*ca.* 1:1:1), which can be assigned to the similar environments of Pb(1,1a) and Pb(2,2a) and to the more distinct environment of Pb(3,3a), respectively. Irrespective of the temperature (+25 to 100 °C), the ^{13}C spectrum shows only three (C_5H_5) resonances. Although there are a number of possible interpretations for this behaviour, this may stem from the two terminal and $\mu\text{-}C_5H_5$ environments of the separate $[(C_5H_5)_5Pb_2]^-$ anion being very similar to the corresponding environments in the central $[(C_5H_5)_5Pb_2]^-$ fragment of the $[(C_5H_5)_9Pb_4]^-$ anion, so producing two signals. A third (C_5H_5) resonance would then arise from the loosely bonded $(C_5H_5)_2Pb$ units of the latter.

It is interesting to note that, whereas the two anions of **1** can be seen as fragments of the polymeric lattice of $[(C_5H_5)_2Pb]_\infty$, the corresponding reaction with $[(C_5H_5)_2Sn]$, which is a

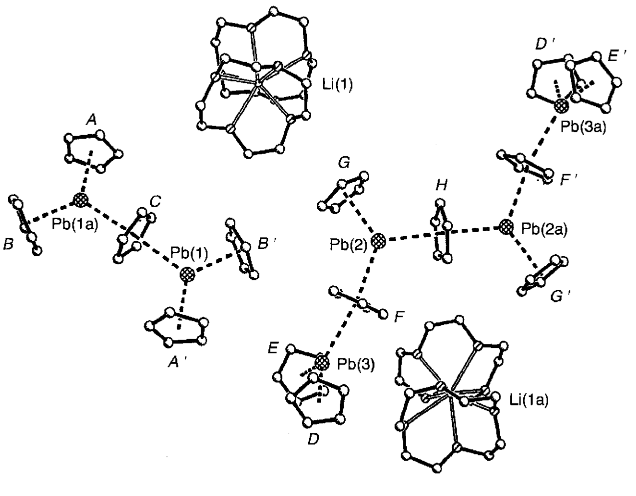

Fig. 1 The unit cell of **1**. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°) for the $(C_5H_5)_5Pb_2^-$ anion: (C_5H_5)*A*—Pb(1) 2.612, (C_5H_5)*B*–Pb(1) 2.543, (C_5H_5)*C*–Pb(1) 2.861, (C_5H_5)*A*–Pb(1)–(C_5H_5)*B* 123.9, (C_5H_5)*A*–Pb(1)–(C_5H_5)*C* 120.4, (C_5H_5)*B*–Pb(1)–(C_5H_5)*C* 115.0, sum of $(C_5H_5)_{centroid}$–Pb(1)–$(C_5H_5)_{centroid}$ 359.3, Pb(1)–(C_5H_5)*C*–Pb(1a) 180.0; for the $(C_5H_5)_9Pb_4^-$ anion: (C_5H_5)*D*–Pb(3) 2.565, (C_5H_5)*E*–Pb(3) 2.554, (C_5H_5)*F*–Pb(3) 2.919, (C_5H_5)*F*–Pb(2) 2.698 (C_5H_5)*G*–Pb(2) 2.511, (C_5H_5)*H*–Pb(2) 2.728, (C_5H_5)*D*–Pb(3)–(C_5H_5)*E* 127.7, (C_5H_5)*F*–Pb(3)–(C_5H_5)*D* 113.0, (C_5H_5)*F*–Pb(3)–(C_5H_5)*E* 119.3, sum of $(C_5H_5)_{centroid}$–Pb(3)–$(C_5H_5)_{centroid}$ 360.0, (C_5H_5)*G*–Pb(2)–(C_5H_5)*F* 124.8, (C_5H_5)*H*–Pb(2)–(C_5H_5)*F* 117.4 (C_5H_5)*G*–Pb(2)–(C_5H_5)*H* 115.8, sum of $(C_5H_5)_{centroid}$–Pb(2)–$(C_5H_5)_{centroid}$ 358.0, Pb(3)–(C_5H_5)*F*–Pb(2) 165.0, Pb(2)–(C_5H_5)*H*–Pb(2a) 180.0; for the $[Li(12\text{-crown-}4)_2]^+$ cation: av. Li–O 2.37.

monomer in the solid state[7] and which possesses no polymeric lattice akin to $[(C_5H_5)_2Pb]_\infty$, yields only $[(C_5H_5)_3Sn]^-[Li(12\text{-crown-}4)_2]^+$ **2**, as confirmed by X-ray crystallography.[8] The ability to form extended anion homologues, such as those observed in **1** and in $[(\eta^5\text{-}C_5H_5)Tl(\mu\text{-}C_5H_5)Tl(\eta^5\text{-}C_5H_5)]^-[Li(12\text{-crown-}4)_2]^+$, therefore mirrors the behaviour of the parent cyclopentadienyl complexes in the solid state.

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Footnotes

† Synthesis of **1**: $[(C_5H_5)_2Pb]$ (1.101 g, 3.0 mmol) in THF (10 ml) was added to a freshly prepared solution of $[(C_5H_5)Li]$ (1.0 mol l^{-1} in THF; 1 ml, 1.0 mmol) under argon at *ca.* 0 °C. An orange solution was produced. To this was added 12-crown-4 (0.35 g, 2 mmol) and the resulting solution was filtered (porosity 3, Celite). The solution was reduced under vacuum (*ca.* 10 ml), resulting in the formation of an orange precipitate which redissolved on warming. Storage at −20 °C (24 h) gave orange blocks of **1**; yield 1.02 g, 71%; mp 170 °C; the phase purity of **1** was also confirmed by differential scanning calorimetry (DSC); IR (Nujol), ν/cm^{-1} 3068 [C–H, C_5H_5]; ^1H NMR ($[^2H_8]$THF), δ 5.65 [70H, (C_5H_5)], 3.57 (64H, 12-crown-4); satisfactory elemental analyses (C, H) were obtained for **1**.

‡ *Crystal data*: for **1**: $C_{102}H_{134}Li_2O_{16}Pb_6$, $M = 2873.11$, triclinic, space group $P\bar{1}$, $a = 9.038(2)$, $b = 15.914(3)$, $c = 18.487(4)$ Å, $\alpha = 73.97(3)$, $\beta = 85.96(3)$, $\gamma = 79.21(3)°$, $V = 2522.0(9)$ Å^3, $Z = 1$, $D_c = 1.892$ Mg m^{-3}, $\lambda = 0.71073$ Å, $T = -120$ °C, $\mu(\text{Mo-K}\alpha) = 10.039$ mm^{-1}. Data were collected on a Siemens-Stoe AED diffractometer using an oil-coated rapidly-cooled crystal of dimensions $0.3 \times 0.2 \times 0.2$ mm in an oil drop[9] by the θ/ω method ($7.20 \leqslant 2\theta \leqslant 45.00°$). Of a total of 6839 collected reflections, 6568 were independent ($R_{int} = 0.0570$). The data was corrected for absorption by a semi-empirical method based on ψ-scans. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2[10] to final values of $R1$ $[F > 4\sigma(F)] = 0.0502$ and $wR2 = 0.1197$ and $R1 = 0.0670$ and $wR2 = 0.1418$ (all data) $\{R1 = \Sigma|F_o - F_c|/\Sigma F_o$ and $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}\}$, largest peak and hole in the final difference map 1.701 and − 1.422 e Å^{-3}. $(C_5H_5)C$ and $(C_5H_5)H$ are disordered about their centres of inversion. They were refined with distance constraints (with 50% occupancy over the two disordered sites). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ Solid-state MAS-NMR spectra of **1** (Chemagnetics CMX 400): ^{207}Pb NMR {+25 °C, 83.224 MHz, 10 kHz MAS [90° pulse width (2.5 μs); recycle delay, 5 s]}: δ −5270 ± 10, −5180 ± 10, −4740 ± 10 (relative to liquid $PbMe_4$). The large chemical shift anisotropy typical of ^{207}Pb results in large numbers of spinning sidebands. A rough measurement of the anisotropy was made by measuring the width of the sideband pattern, giving *ca.* 60, 90 and 90 kHz, respectively, for the signals listed above. ^{13}C NMR {+25 to −100 °C, 100.57 MHz, 4 kHz MAS [CP (cross polarisation)/^1H decoupled (decoupling field, 111 kHz), 90° pulse width (2.25 μs); contact time, 10 ms; recycle delay, 3 s]}: δ 115.0 ± 0.1, 113.8 ± 0.1, 112.1 ± 0.1 [(C_5H_5) ligands], 67.4 (12-crown-4) (relative to Me_4Si). Estimated anisotropies were *ca.* 15 kHz for all the (C_5H_5) ligand signals, suggesting that the (C_5H_5) ligands are spinning rapidly about their approximate C_5 axes. The relative intensities of the (C_5H_5) ligand signals showed some temperature dependence.

References

1 M. G. Davidson, D. Stalke and D. S. Wright, *Angew. Chem.*, 1992, **104**, 1265; *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1226.
2 A. J. Edwards, M. A. Paver, P. R. Raithby, C. A. Russell, A. Steiner, D. Stalke and D. S. Wright, *J. Chem. Soc., Dalton Trans.*, 1993, 1465.
3 D. A. Armstrong, M. G. Davidson, D. Moncrieff, C. A. Russell, D. Stalke, A. Steiner and D. S. Wright, *Organometallics*, submitted.
4 D. R. Armstrong, R. Herbst-Irmer, A. Kuhn, D. Moncrieff, M. A. Paver, C. A. Russell, D. Stalke, A. Steiner and D. S. Wright, *Angew. Chem.*, 1993, **105**, 1807; *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1774.
5 J. C. Panattoni, G. Bombieri and U. Croatto, *Acta Crystallogr.*, 1966, **21**, 823.
6 D. R. Armstrong, D. Moncrieff, M. A. Paver, P. R. Raithby, M.-A. Rennie, C. A. Russell and D. S. Wright, *J. Chem. Soc., Chem. Commun.*, 1995, 927.
7 J. L. Atwood, W. E. Hunter, A. H. Cowley, R. A. Jones and C. A. Stewart, *J. Chem. Soc., Chem. Commun.*, 1986, 925.
8 M. Lopez, M. A. Paver, P. R. Raithby, M.-A. Rennie, C. A. Russell and D. S. Wright, unpublished results.
9 T. Kottke and D. Stalke, *J. Appl. Crystallogr.*, 1993, **26**, 615.
10 G. M. Sheldrick, SHELXL-93, Göttingen, 1993.