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Synthesis and structure of $[\mathrm{Cp_2PbCp^{\mathit{thf}}Na}]\cdot 0.5\mathrm{thf}$; implications to the control of dimensionality in p block metallocene anion systems ($\mathrm{Cp} = \mathrm{C_5H_5}$, $\mathrm{Cp^{\mathit{thf}}} = \{\mathrm{C_5H_4}\}\mathrm{CH_2C_4H_7O}$)

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The title compound $[\mathrm{Cp_2PbCp^{\mathit{thf}}Na}]\cdot 0.5\mathrm{thf}$ 1, obtained from the addition reaction of $\mathrm{Cp_2Pb}$ with $[\mathrm{Cp^{\mathit{thf}}Na\cdot thf}]$, provides the first opportunity to assess the structural impact of internal donation on aggregation within a p block metal cyclopentadienide anion system; the result being the adoption of an unusual polymeric sheet structure composed of $[\mathrm{Cp_2PbCp^{\mathit{thf}}Na}]_3$ rings.

The addition of alkali or alkaline earth metal cyclopentadienides to neutral Group 13 and 14 metallocenes furnishes a family of homologous sandwich anions of formulae $[\mathrm{Cp}_{x+1}\mathrm{E}_x]^-$ (E = Tl; $x = 1$ or 2) and $[\mathrm{Cp}_{2x+1}\mathrm{E}_x]^-$ (E = Sn, Pb; $x = 1$, 2 or 4).[1,2] Various studies indicate that the extent of aggregation of these anions depends on the solvation of the cations. In particular, encapsulation of alkali metal cations by crown ethers or cryptands gives ion-separated complexes in which larger anion chains are promoted on the grounds of lattice energy.[3] For example, reaction of $\mathrm{Cp_2Pb}$ with CpNa in the presence of the tridentate donor PMDETA [$= (\mathrm{Me_2NCH_2CH_2})_2\mathrm{NMe}$] produces the ion-paired complex $[\mathrm{CpPb(\mu\text{-}Cp)Na\cdot PMDETA}]$,[4a] whereas the reaction between $\mathrm{Cp_2Pb}$ and CpLi in the presence of 12-crown-4 gives the ion-separated complex $[\mathrm{Cp_5Pb_2}]^-[\mathrm{Cp_9Pb_4}]^-2[\mathrm{Li(12\text{-}crown\text{-}4)_2}]^+$ (containing two types of extended anions).[4b] Lattice energy considerations also appear to be crucial in the formation and selection of related alkali metal sandwich anions such as $[\mathrm{Cp_2Li}]^-$[5a] and $[\mathrm{Cp_3Cs_2}]^-$.[5b] Given the importance of cation solvation on the structures of these anions, we have recently initiated investigation of main group metal anions containing donor functionalised cyclopentadienide ligands. Our rationale being that the presence of *intramolecular* Lewis base solvation should result in the interdependence of cation solvation and the structure and nature of aggregation of the sandwich anions. These predictions are realised for the first time in the present study of $[\{\mathrm{Cp_2PbCp^{\mathit{thf}}Na}\}\cdot 0.5\mathrm{thf}]$ (**1**) ($\mathrm{Cp^{\mathit{thf}}} = \{\mathrm{C_5H_4}\}\mathrm{CH_2C_4H_7O}$).

Complex **1** was prepared by the reaction of $\mathrm{Cp_2Pb}$ with $[\mathrm{Cp^{\mathit{thf}}Na\cdot thf}]$[6] in toluene as solvent [eqn. (1)].† Despite the

$$[\mathrm{Cp^{\mathit{thf}}Na\cdot thf}] + \mathrm{Cp_2Pb} \xrightarrow{\text{toluene}} \underset{\mathbf{1}}{[\mathrm{Cp^{\mathit{thf}}Na(Cp_2Pb)}]\cdot 0.5\mathrm{thf}} \quad (1)$$

polymeric nature of **1** (as later revealed by X-ray diffraction) it is highly soluble in organic solvents such as toluene and thf.

Low-temperature X-ray crystallography ‡ reveals that **1** has an elaborate polymeric structure composed of identical $[\mathrm{Cp^{\mathit{thf}}Na\{PbCp_2\}}]$ crystallographic units. In addition there is a half molecule of thf within the lattice. Fig. 1 shows the way in which the polymer structure is propagated, by bridging of the Pb and Na centres by the Cp and $\mathrm{Cp^{\mathit{thf}}}$ ligands. By relation to the structures of the ion-paired and ion-separated complexes $[\mathrm{Cp_2Pb(\mu\text{-}Cp)Na\cdot PMDETA}]$ and $2[\mathrm{Cp_3Pb}]^-\cdot[\mathrm{Mg(thf)_6}]^{2+}$,[4] the arrangement in **1** can be regarded as resulting from the association of $\mathrm{Na^+}$ cations with $[(\mathrm{Cp^{\mathit{thf}}})\mathrm{Cp_2Pb}]^-$ anions. Indeed, the nearly planar geometry of the Pb centre within the $[(\mathrm{Cp^{\mathit{thf}}})\mathrm{Cp_2Pb}]^-$ fragments (Pb only *ca.* 0.10 Å out of the plane of the three Cp centroids) and the almost symmetrical coordination of the Pb centre $\{\mathrm{Cp(A)_{centroid}}$ 2.65 Å [Pb–C range 2.925(9)–3.00(1) Å], $\mathrm{Cp(B)_{centroid}}$ 2.70 Å [range 2.85(1)–3.07(1) Å], $\mathrm{Cp^{\mathit{thf}}_{centroid}}$ 2.62 Å [range 2.86(1)–2.91(1) Å]$\}$ are akin to that in the ion-separated $[\mathrm{Cp_3Pb}]^-$ anion.[4a] Significantly also, the bond lengths involved in the Na–$\mathrm{Cp^{\mathit{thf}}}$ interaction $\{\mathrm{Cp^{\mathit{thf}}_{centroid}}$–Na(1) 2.78 Å [2.80(1)–3.21(1) Å][7]$\}$ are on average longer than those involved between this ligand and Pb(1).

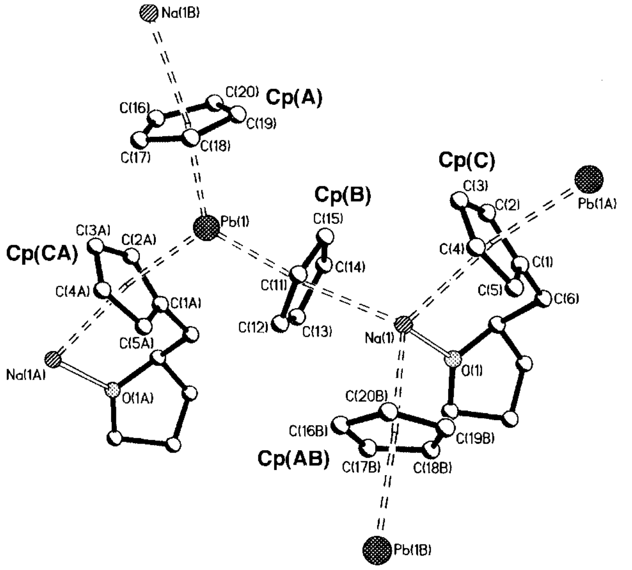

Fig. 1 The propagation of the $\mathrm{Na^+}$ and $[\mathrm{PbCp_2Cp^{\mathit{thf}}}]^-$ ions in **1** into a polymeric structure. H-atoms and the lattice-bound thf molecules have been omitted for clarity. Key bond lengths (Å) and angles (°); Na(1)–C(1) 2.98(1), Na(1)–C(2) 3.21(1), Na(1)–C(3) 3.19(1), Na(1)–C(4) 2.94(1), Na(1)–C(5) 2.80(1), $\mathrm{Cp(C)_{centroid}}\cdots$Na(1) 2.78, Na(1)–O(1) 2.30(1), Na(1)–C(11) 2.67(2), Na(1)–C(12) 2.89(1), Na(1)–C(13) 3.07(1), Na(1)–C(14) 3.12(1), Na(1)–C(15) 2.85(1), $\mathrm{Cp(B)_{centroid}}\cdots$Na(1) 2.68, Na(1)–C(16A) 3.06(1), Na(1)–C(17A) 2.93(1), Na(1)–C(18A) 2.94(1), Na(1)–C(19A) 3.07(1), Na(1)–C(20A) 3.14(1), $\mathrm{Cp(AB)_{centroid}}\cdots$Na(1) 2.78, Pb(1)–C(11) 2.88(1), Pb(1)–C(12) 2.98(1), Pb(1)–C(13) 3.07(1), Pb(1)–C(14) 2.99(1), Pb(1)–C(15) 2.85(1), $\mathrm{Cp(B)_{centroid}}\cdots$Pb(1) 2.70, Pb(1)–C(16) 2.848(9), Pb(1)–C(17) 2.825(9), Pb(1)–C(18) 2.92(1), Pb(1)–C(19) 3.00(1), Pb(1)–C(20) 2.96(1), $\mathrm{Cp(A)_{centroid}}\cdots$Pb(1) 2.65, Pb(1)–C(1B) 2.90(1), Pb(1)–C(2B) 2.91(1), Pb(1)–C(3B) 2.88(1), Pb(1)–C(4B) 2.86(1), Pb(1)–C(5B) 2.88(1), $\mathrm{Cp(CA)_{centroid}}\cdots$Na(1) 2.62; Cp(C)⋯Na(1)⋯Cp(B) 116.9, Cp(C)⋯Na(1)⋯Cp(AB) 119.1, Cp(B)⋯Na(1)⋯Cp(AB) 115.5, Na(1)⋯Cp(B)⋯Pb(1) 161.6, Cp(B)⋯Pb(1)⋯Cp(A) 121.4, Cp(B)⋯Pb(1)⋯Cp(CA) 116.7, Cp(A)⋯Pb(1)⋯Cp(CA) 121.1, Na(1A)⋯Cp(CA)⋯Pb(1) 170.5, Na(1B)⋯Cp(A)⋯Pb(1) 168.0.

Fig. 2 shows the way in which the monomer units of **1** build into a honeycomb, sheet structure composed of $[\mathrm{Cp^{\mathit{thf}}Na(Cp_2Pb)}]_3$ rings. The non-planarity of these rings results in a zigzag cross-section for the parallel sheets of **1** in the crystal lattice, with uncoordinated thf molecules residing in the cavity created by the eclipsed $[\mathrm{Cp^{\mathit{thf}}Na(Cp_2Pb)}]_3$ rings of adjacent

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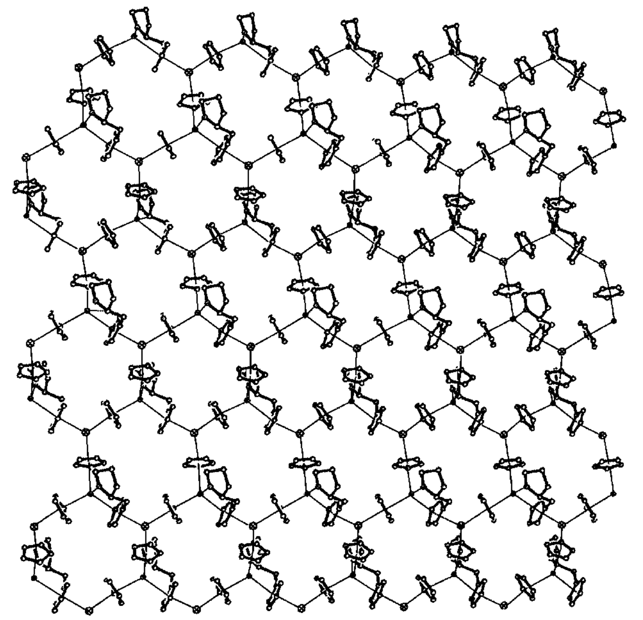

Fig. 2 Honeycomb lattice arrangement of **1** (viewed along the *b*-axis).

layers. The Na···Pb separation between neighbouring metal centres within the ring units is *ca.* 5.4 Å (the Na···Pb separation across the rings being *ca.* 10.6 Å). Cyclic main group metallocenes are extremely rare, the π-bonded hexamers $[Cp_2Pb]_6$[8] and $[\{1,3\text{-}(Me_3Si)_2C_5H_3\}Tl]_6$[9] and the σ,π-bonded heterometallics $[\{Au(C_5H_4PPh_2)_2\}Tl]_2$[10] and $[\{C_5H_4PPh_2\}\text{-}Na\cdot(MeOCH_2)_2]_2$[11] being among the very few structurally characterised examples. In the most closely related complex $[Na(YbCp)_3]$, which contains similar $[Cp_3Na]$ and $[Cp_3Yb]$ fragments to those of **1**, a complicated three-dimensional polymer structure results as a consequence of the planes of the metal–Cp_3 units being mutually perpendicular within the interlocking $Cp_2Na(\mu\text{-}Cp)YbCp_2$ fragments.[12] Although the same Cp–metal connectivity is present in **1**, the intramolecular coordination of the Na^+ cation by the Cp^{thf} ligand [2.30(1) Å[13]] results in disruption of the ligand–metal bonding [C–Na range 2.80(1)–3.21(1) Å[7,13]] and in the adoption of a pseudo-tetrahedral (rather than planar) geometry for Na (in which the metal centre is *ca.* 0.35 Å above the plane of the surrounding ligand centroids). Intramolecular ligand coordination and the resulting modification in the Na^+ geometry provides the principal reason for the very different supramolecular architecture of **1** compared to $[Na(YbCp)_3]$, and an important insight into how specific structural modification of related arrangements may be achieved in the future.

We are investigating a range of alkali metal complexes containing related $[(Cp^y)_xCp_{3-x}Pb]^-$ anions (Cp^y = donor functionalised Cp ligands) in order to uncover the ways in which supramolecular arrangements like that observed in **1** can be controlled by modifying the coordination spheres of the alkali metal cations.

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Notes and references

† Synthesis of **1**: a solution of Cp_2Pb (0.51 g, 1.50 mmol) in toluene (20 ml) was added to a stirred suspension of [Cp^{thf}Na·thf] (0.26 g, 1.50 mmol) in toluene (50 ml) at 0 °C. The resulting yellow solution was warmed to room temperature and stirred (2 h), after which time a yellow precipitate had formed. This was heated into solution and the reaction filtered while hot. Storage at −15 °C (24 h) afforded yellow crystals of **1** (0.50 g, 60%). Decomp. 109 °C to brown oil. IR (Nujol, NaCl), ν_{max}/cm^{-1} 3065 (C–H str. C_5H_4 and C_5H_5), 1260 and 1092 (C–O str., Cp^{thf}/thf). ^1H NMR (400.129 MHz, +25 °C, benzene-d_6), δ 5.97 (s, 5H, C_5H_5), 5.78 (s, 4H, C_5H_4), 3.57 (m, 2H, overlapping thf CH_2O), 3.43 (m, 2H, Cp^{thf} CH_2O), 3.29 (m, 1H, Cp^{thf} CHO), 2.68 (m, 2H, Cp^{thf} $-CH_2-$), 1.7–1.4 (m, 6H, overlapping thf and Cp^{thf} $-CH_2CH_2-$). Satisfactory elemental analysis (C, H) were obtained for **1**.

‡ Crystal data for **1**: $C_{22.50}H_{28}NaO_{1.50}Pb$, $M = 552.23$, monoclinic, space group $P2_1/n$, $Z = 4$, $a = 9.1145(8)$, $b = 15.798(2)$, $c = 15.0060(10)$ Å, $\beta = 92.230(5)°$, $V = 2159.1(4)$ Å^3, μ(Mo-Kα) = 1.700 mm^{-1}, $T = 150(2)$ K. Data were collected on a Nonius Kappa CCD diffractometer. Of a total of 10002 reflections collected, 2798 were independent ($R_{int} = 0.053$). The structure was solved by direct methods and refined by full-matrix least squares on F^2.[14] $R1 = 0.067$ [$I > 4\sigma(I)$], $wR2 = 0.195$. The light atoms (C and O) are poorly resolved and the refinement made extensive use of common, isotropic temperature factors and bond length restraints for these atoms (22 restraints in all).

CCDC reference number 186/2026.

See http://www.rsc.org/suppdata/dt/b0/b004608f/ for crystallographic files in .cif format.

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