# $[\{Yb_6[\eta\text{-}C_5Me_4(SiMe_2Bu^t)]_6I_8\}\{Li(thf)_4\}_2]$: the spontaneous self-assembly of a hexanuclear ytterbium(II) octaiododianion

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**Reaction of 1 equiv. of LiCp$^s$ [Cp$^s$ = $C_5Me_4(SiMe_2Bu^t)$] with $YbI_2$ affords the novel half-sandwich polyatomic species $[\{Yb_6(\eta\text{-}Cp^s)_6I_8\}\{Li(thf)_4\}_2]$ 1; the molecular structures and solid- and solution-state $^{171}Yb$ NMR data for 1 and, for comparison, the dimeric half sandwich derivatives $[\{Yb(\eta\text{-}C_5Me_5)(\mu\text{-}I)L_n\}_2]$ (L = thf, $n$ = 2, 2; L = dme, $n$ = 1, 3) are presented.**

Recently, we reported the syntheses, characterisation and molecular structures of $[Sn(\eta\text{-}Cp^s)_2]$[1] and $[Pb(\eta\text{-}Cp^s)_2]$[2] in which the sterically demanding cyclopentadienyl ligands, $Cp^{s-}$, are parallel. The ligand has also been successful in permitting the isolation and structural characterisation of the half sandwich $Sn(\eta\text{-}Cp^s)Cl$ compound[3] and the novel polyatomic $[Sn_9(\eta\text{-}Cp^s)_6Cl_{12}]$ species.[4] Herein we report the product of the reaction of LiCp$^s$ with $YbI_2$ and, for comparison, the syntheses and molecular structures of $[\{Yb(\eta\text{-}C_5Me_5)(\mu\text{-}I)L_n\}_2]$, (L = thf, $n$ = 2, **2**; L = dme, $n$ = 1, **3**). Recently, iodofunctionalised alkyls,[5,6] aryloxides[7] and tris-pyrazolylborate[8,9] derivatives of $Yb^{II}$, employing sterically demanding ligands, have been reported. Compounds **2** and **3** were prepared either by the reaction of 1 equiv. of $NaC_5Me_5$ with $YbI_2$ or by the metathetical exchange between $[Yb(\eta\text{-}C_5Me_5)_2(thf)_2]$ and $YbI_2$ in thf. The molecular structures of **2** and **3** were determined and show both to be iodo-bridged dimers with the $^-C_5Me_5$ groups in a *trans* orientation, similar to the structure adopted by their Sm analogue (Fig. 1).[10] The reaction of 1 equiv. of LiCp$^s$ with $YbI_2$, however, did not produce a similar dimeric species but a polyatomic compound, $[\{Yb_6(\eta\text{-}Cp^s)_6I_8\}\{Li(thf)_4\}_2]$ **1**.† The molecular structure of **1** comprises two $Li^+$ cations, each tetrahedrally coordinated by four thf molecules, and a $[Yb_6(\eta\text{-}Cp^s)_6I_8]^{2-}$ dianion (Fig. 2).‡ This dianion may be viewed as an inverted version of the classic $M_6X_8$ structure adopted by many later transition-metal cluster ions such as $Mo_6Cl_8{}^{4+}$ in which each face of the $M_6$ octahedral core is bridged in a $\mu_3$-mode by a halide.[11] In **1**, however, the $M_6$ core expands beyond the $X_8$ cube. The I···I nearest neighbour distance (4.09 Å) is less than twice the van de Waals radius of I and similar to the weak intermolecular interactions observed for $I_3{}^-$ zintl ions in $\{[PI\{Fe(\eta\text{-}C_5H_4)(\eta\text{-}C_5H_5)\}_3][I_3]\}$ [4.139(1) Å].[12] By comparison, the I···I distances for **2** and **3** are *ca.* 4.23 and 4.33 Å, respectively. Each face of the $I_8$ cube of **1** is bridged, in a $\mu_4$-fashion, by a $Yb(\eta\text{-}Cp^s)$ moiety. The six Yb centres are each *ca.* 1.28 Å above their respective $I_4$ faces and separated by *ca.* 4.71 Å from their nearest neighbours. By comparison the Yb···Yb separations for **2** and **3** are *ca.* 4.68 and 4.47 Å, respectively. The coordination geometry about each Yb atom in **1**, **2** and **3** is that of a square-based pyramid, with an $I_4$ face comprising the basal plane for **1**, or for **2** and **3**, the bridging I and O atoms of the thf or dme. For all three compounds, the cyclopentadienyl ligand centroid occupies the final vertex. Despite the increased bulk of the $Cp^{s-}$ ligand, with respect to its $^-C_5Me_5$ analogue, the Yb–centroid distances are almost identical (Table 1). Interestingly, the shortest Yb–C distance is that of the Yb–C(1) 2.641(11) Å in **1**, which is the ring C atom bearing the $SiMe_2Bu^t$ substituent. These substituents are bent by some 14° out of the plane of the cyclopentadienyl rings and away from the Yb centres. Furthermore, each $Cp^{s-}$ is rotated by 90 and 180° with respect to the one located on adjacent or opposite faces of the

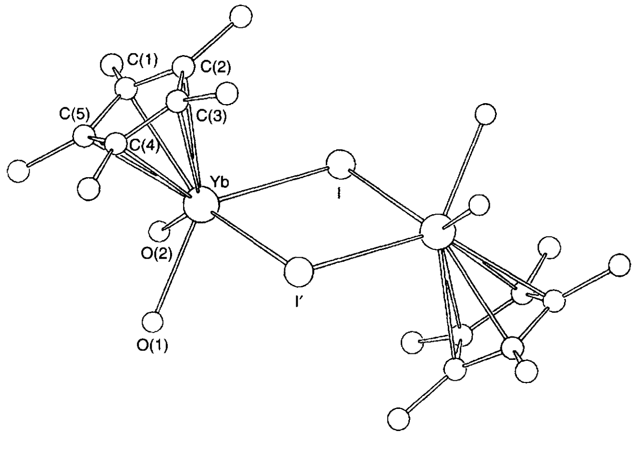

**Fig. 1** The molecular structure of **2** and **3** with the atom numbering scheme with selected bond lengths (Å) and angles (°): for **2**; Yb–Cp 2.414(9), Yb–I(1) 3.134(1), Yb–I(1′) 3.175(1), Yb–O(1) 2.437(11), Yb–O(2) 2.471(11); I(1)–Yb–I(1′) 84.17(3), O(1)–Yb–O(2) 75.9(5). For **3**; Yb–Cp 2.38(2), Yb–I(1) 3.120(2), Yb–I(1′) 3.102(2), Yb–O(1) 2.44(2), Yb–O(2) 2.42(2); I(1)–Yb–I(1′) 88.28(5), O(1)–Yb–O(2) 65.0(6). Cp denotes the centroid of the ring C(1)–C(5) and O(1) and O(2) are the oxygen atoms of thf and dme respectively.

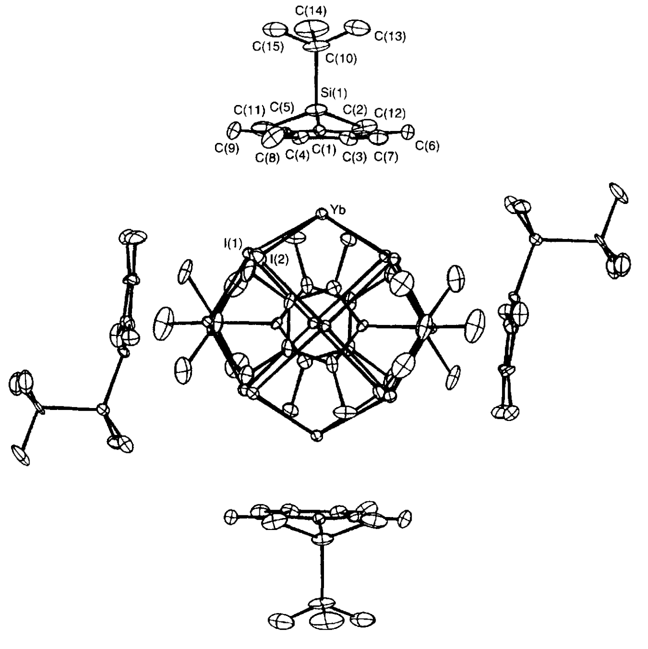

**Fig. 2** The molecular structure of **1** and atom numbering scheme with selected bond lengths (Å) and angles (°): Yb–Cp 2.379(11), Yb–I(1) 3.193(1), Yb–I(2) 3.130(1); Cp–Yb–I(1) 110.01(2), Cp–Yb–I(2) 109.69(4). Cp denotes the centroid of the ring C(1)–C(5).

$Yb_6$ octahedron respectively. The following featues of **1** are noteworthy. (*i*) The dianion $[Yb_6(\eta\text{-}Cp^s)_6I_8]^{2-}$ is the first example of an Ln polynuclear species comprised solely of $Ln^{II}$ centres. (*ii*) This dianion is also the first example of a polynuclear Ln system which does not contain an interstitial atom or molecule.§ (*iii*) It is also the first example of an Ln–I containing polynuclear species and the largest polynuclear Yb species reported to date.¶ The $M_6$ motif has been previously observed in the distorted octahedral $[\{Sm(\eta\text{-}C_5Me_5)\}_6Se_{11}]$.[13] (*iv*) The solid-state $^{171}Yb$ $\delta_{iso}$ for **1** compares well with that for **2** and **3** (Table 2). A comparison of the solid- and solution-state $^{171}Yb$ NMR data of **1**, however, does not support the retention of its structure in thf solution. The nature of this species and the mechanism of the spontaneous self-assembly of **1** during the benzene extraction step in its synthesis, instead of the formation of dimeric species such as **2** and **3**, is under investigation.||

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## Footnotes

† *Synthesis of* $[\{Yb_6(\eta\text{-}Cp^s)_6I_8\}\{Li(thf)_4\}_2]$ **1**: to a Schlenk tube charged with a slurry of $YbI_2$ (1.56 g, 3.64 mmol) in thf (40 ml) was added, over a 2 min period with stirring, $LiCp^s$ (0.84 g, 3.64 mmol) dissolved in thf (40 ml). An immediate change from green to brown was observed. After 24 h stirring, the thf was removed *in vacuo* and the product extracted with benzene (50 ml), giving rise to an intensely orange solution. Removal of the benzene *in vacuo* or recrystallisation from benzene afforded **1** as an orange powder or deep orange needles respectively. Yield 73.3% (1.80 g, 0.44 mmol). $^{13}C\{^1H\}$ NMR (100.61 MHz, 20% $C_6D_6$ in thf), δ 122.52, 117.88, 106.28, 27.33, 20.27, 15.02, 11.83, –0.66; $^{29}Si\{^1H\}$ NMR (79.49 MHz, 20% $C_6D_6$ in thf), δ −4.91; $^{171}Yb\{^1H\}$ NMR (70.02 MHz, 20% $C_6D_6$ in thf), δ 471, 451; $^7Li$ MAS NMR (155.46 MHz), δ −1; $^{13}C\{^1H\}$ CP MAS NMR (100.61 MHz), δ 126, 123, 122, 109, 72 (thf), 30 (thf), 27, 23, 17, 2; $^{29}Si\{^1H\}$ CP MAS NMR (79.49 MHz), δ −3; $^{171}Yb\{^1H\}$ CP MAS NMR (70.02 MHz), δ 211. Elemental analysis [found (calc.)] for $C_{122}H_{226}I_8Li_2O_8Si_6Yb_6$: C 36.01 (36.12), H 5.76 (5.61%).

‡ *Crystal data* for **1**, **2** and **3**: for all three compounds, crystallographic measurements were made on an Enraf-Nonius CAD4 diffractometer using Mo-Kα radiation, $\lambda = 0.71073$ Å. The structure was solved by direct methods and refined on $F^2$ by a full-matrix least-squares procedure. For **1**: $C_{122}H_{226}I_8Li_2O_8Si_6Yb_6$, $T = 173(2)$ K. Specimen 0.4 × 0.3 × 0.3 mm, $M = 4056.9$, trigonal, space group $P\bar{3}c1$, $a = 17.974(3)$, $c = 26.955(5)$ Å, $U = 7542(13)$ Å$^3$, $D_c = 1.79$ g cm$^{-3}$, $Z = 2$. For reflections with $2 < \theta < 22°$, $R(F) = 0.042$ for 2364 observed reflections $[I > 2\sigma(I)]$ and $wR(F^2) = 0.098$ for all 3092 reflections. For **2**: $C_{36}H_{62}I_2O_4Yb_2$, $T = 173(2)$ K. Specimen 0.4 × 0.4 × 0.2 mm, $M = 1158.7$, monoclinic, space group $P2_1/n$ (non-standard no. 14), $a = 12.274(4)$, $b = 13.208(5)$, $c = 13.466(2)$ Å, $\beta = 110.87(2)°$, $U = 2039.8(11)$ Å$^3$, $D_c = 1.89$ g cm$^{-3}$, $Z = 2$. For reflections with $2 < \theta < 25°$, $R(F) = 0.052$ for 2979 observed reflections $[I > 2\sigma(I)]$ and $wR(F^2) = 0.171$ for all 3588 reflections. For **3**: $C_{28}H_{50}I_2O_4Yb_2$, $T = 173(2)$ K. Specimen 0.3 × 0.2 × 0.1 mm, $M = 1050.6$, orthorhombic, space group *Pbca* (no. 61), $a = 13.760(4)$, $b = 15.953(5)$, $c = 15.883(4)$ Å, $U = 3487(2)$ Å$^3$, $D_c = 2.00$ g cm$^{-3}$, $Z = 4$. For reflections with $2 < \theta < 25°$, $R(F) = 0.070$ for 1897 observed reflections $[I > 2\sigma(I)]$ and $wR(F^2) = 0.257$ for all 3055 reflections. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/250.

§ The necessity for interstitial atoms in order to stabilise such clusters has been recently discussed.[20]

¶ The reaction of $[Yb(\eta\text{-}C_5Me_5)_2F(L)]$ ($L = Et_2O$ or thf) with perfluoroalkenes affords the pentanuclear $Yb^{III}$ complex $[Yb_5(\eta\text{-}C_5Me_5)_6(\mu^4\text{-}F)(\mu^3\text{-}F)_2(\mu\text{-}F)_6]$.[14]

|| Attempts to prepare the $C_5Me_5$ analogue of **1** from the reaction of 1 equiv. of $Li(C_5Me_5)$ with $YbI_2$ in thf resulted in a $^{171}Yb$ resonance at δ 403. This resonance is not consistent with the formation of the dimeric **2** though no crystalline product has been isolated to date.

**Table 1** Selected structural data for $Yb^{II}$-containing compounds

| Compound | Yb–I/Å | Yb–$Cp^a$/Å | Ref. |
|---|---|---|---|
| **1** | 3.130–3.193 | 2.379(11) | This work |
| **2** | 3.134(1), 3.175(1) | 2.414(9) | This work |
| **3** | 3.102(2), 3.120(2) | 2.38(2) | This work |
| $[YbI_2(thf)_4]$ | 3.103(1) | | 19 |

**Table 2** Solid- and solution-state $^{171}Yb$ NMR chemical shift data for selected $Yb^{II}$ derivatives

| Compound | $\delta_{iso}$ | δ | Ref. |
|---|---|---|---|
| **1** | 211 | 471,451 | This work |
| **2** | 235 | 250 | This work |
| **3** | 360 | 375 | This work |
| $[Yb(\eta\text{-}C_5Me_5)_2(thf)_2]$ | 24 | 0 | 15, 16($\delta_{iso}$) |
| $YbI_2$ | 369 | — | 17 |
| $[YbI_2(thf)_4]$ | 443 | 456 | 18, 17($\delta_{iso}$) |

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