

Crystallization and X-ray structures of [NaYb(C₅H₅)₃] and Yb(C₅H₅)₂

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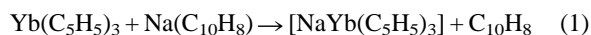
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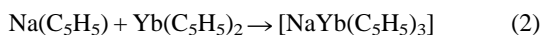
The complex [NaYb(C₅H₅)₃] (C₅H₅ = cyclopentadienyl), prepared from Yb(C₅H₅)₃ and sodium naphthalenide in tetrahydrofuran (thf) or from Yb(C₅H₅)₂ and Na(C₅H₅) in tetrahydrofuran and crystallized at ca. 400 °C (< 10⁻⁴ mm Hg), is a three-dimensional polymer in which $\mu\text{-}\eta^5\text{:}\eta^5\text{-C}_5\text{H}_5$ groups link sodium and ytterbium (each metal having a pseudo-triangular arrangement of C₅H₅ ligands); Yb(C₅H₅)₂, similarly crystallized, has a polymeric chain structure with one terminal and two bridging C₅H₅ ligands per ytterbium, and there is η^1 -bonding between adjacent chains.

No X-ray structure of an unsolvated [MLn^{II}Cp'₃] (M = alkali metal, Cp' = cyclopentadienyl or substituted cyclopentadienyl) complex has been reported,¹ and only one of a solvated analogue, viz. [NaSm(thf)($\mu\text{-}\eta^5\text{:}\eta^2\text{-C}_5\text{H}_4\text{Bu}^t$)₃] (thf = tetrahydrofuran).² Ions of the type Ln(C₅H₅)₃⁻ (Ln = Eu, Sm, Yb) have been detected electrochemically,^{3a} but only [KSm(C₅H₅)₃] has been isolated and in a form unsuitable for X-ray crystallography.^{3b} Similarly, X-ray characterized unsolvated bis(cyclopentadienyl)lanthanide(II) complexes are limited to the substituted cyclopentadienyls [Ln(C₅Me₅)₂] (Ln = Sm, Eu, Yb)⁴ and [Ln{C₅H₃(SiMe₃)₂-1,3}₂] (Ln = Eu, Yb).⁵ Structures of Ln(C₅H₅)₂ and [MLn(C₅H₅)₃] would be of great interest, especially as there is disagreement over the colour (red or green) of Yb(C₅H₅)₂,⁶ but crystallization of these compounds presents difficulties. They are perceived either as involatile or volatile with extreme difficulty [green Yb(C₅H₅)₂ is stated to sublime with decomposition at 400 °C (< 10⁻⁴ mmHg)],^{6b} they are insoluble in non-polar solvents, and are complexed by polar solvents. We now report that use of high-temperature sublimation has enabled the preparation of crystallographically characterizable green [NaYb(C₅H₅)₃] [perhaps accounting for green Yb(C₅H₅)₂] and red Yb(C₅H₅)₂.

Green [NaYb(C₅H₅)₃] has been obtained from the Yb(C₅H₅)₃/Na route previously reported to give green Yb(C₅H₅)₂.^{6b} After reaction of sodium naphthalenide, Na(C₁₀H₈), with Yb(C₅H₅)₃ in thf under argon, removal of naphthalene by sublimation (100 °C, 10⁻² mmHg), extraction with thf, followed by elimination of the solvent in vacuo (150 °C, 10⁻² mmHg) gave crystalline [NaYb(C₅H₅)₃] in high yield [eqn. (1)].



Single crystals of the bimetallic were obtained by sublimation (ca. 400 °C, < 40⁻⁴ mmHg). The compound was also prepared straightforwardly in high yield by reaction of Yb(C₅H₅)₂ with sodium cyclopentadienide in thf, and purified by sublimation under vacuum [eqn. (2)].



The identical nature of the two sublimed products and the unsublimed material was established by near and far[†] IR

spectra. The latter was highly characteristic and remarkably similar to that of Yb(C₅H₅)₃ suggesting that [NaYb(C₅H₅)₃] has a triangular arrangement of C₅H₅ ring centroids similar to that of Yb(C₅H₅)₃.⁷

The X-ray crystal structure of [NaYb(C₅H₅)₃] (Fig. 1)[‡] shows a highly symmetrical three-dimensional array of alternating sodium and ytterbium atoms bridged by $\mu\text{-}\eta^5\text{:}\eta^5\text{-C}_5\text{H}_5$ cyclopentadienyl groups with a near linear Na–Cp–Yb arrangement. There is a pseudo-triangular arrangement of three C₅H₅ ligands around both sodium and ytterbium. The Yb–C distances (av. 2.73 Å) are longer than those in Yb(C₅Me₅)₂ (av. 2.67 Å)^{4b} but shorter than in Yb(C₅H₅)₂, which is considered ten coordinate. Subtraction of an ionic radius for nine-coordinate Yb²⁺, extrapolated from Shannon's values,⁸ from Yb–C gives 1.53 Å (av.), rather shorter than the usual value, 1.64 ± 0.4 Å, for the cyclopentadienide ionic radius.⁹ The Na–Cp distance (2.58 Å) falls in the range typical for other crystallographically characterised cyclopentadienylsodium derivatives¹⁰ {e.g. 2.40 Å in Na(C₅Me₅)(py)₃ (py = pyridine)¹¹ and 2.65 Å in [Na(C₅H₅)(tmeda)]_n (tmeda = *N,N,N',N'*-tetramethylethylenediamine)¹²}.

Brick-red Yb(C₅H₅)₂ from desolvation of Yb(C₅H₅)₂(dme)^{6d} (dme = 1,2-dimethoxyethane) at 100 °C (10⁻³ to 4 × 10⁻⁵ mmHg) for 12 h and crystallized in low yield as red crystals by sublimation at 420 °C (4 × 10⁻⁵ mmHg) in a sealed tube, has a polymeric, C₅H₅-bridged, zigzag chain structure (Fig. 2)[‡] within the metal centres related by C₂ and C_i symmetry, and there are weak interchain C–Yb interactions. The X-ray data

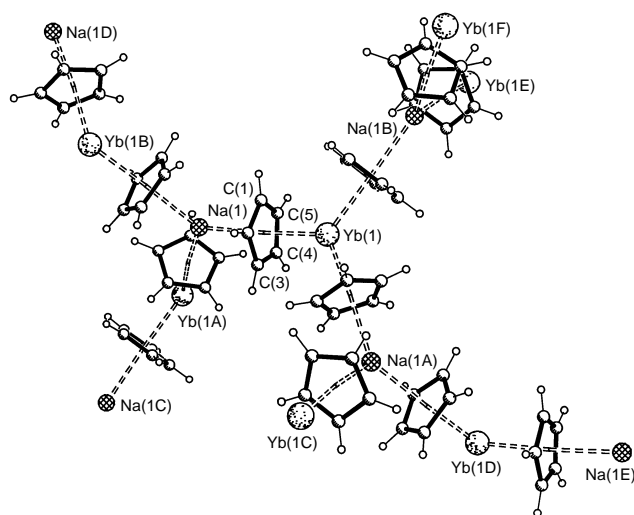


Fig. 1 Section from the packing diagram of [NaYb(C₅H₅)₃]. Selected bond lengths (Å) and angles (°): Yb(1)–C 2.73 (av.), Na–C 2.83 (av.), Yb–Cp 2.46, Na–Cp 2.58; Yb–Cp–Na 176. Cp represents the centroid of the C₅H₅ rings.

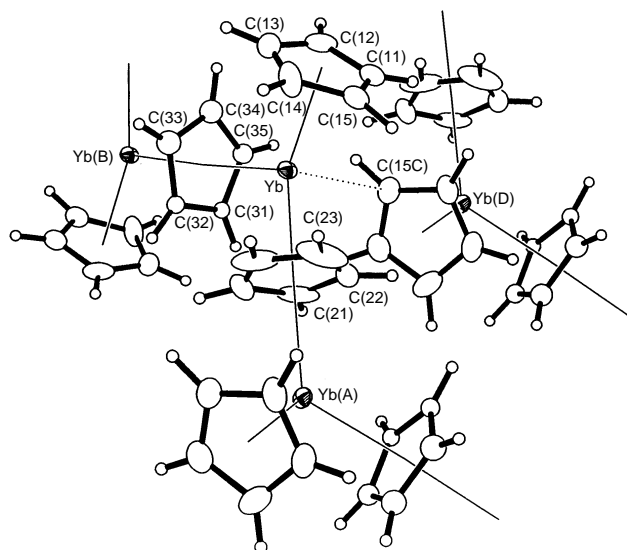


Fig. 2 Part of the polymeric structure of $\text{Yb}(\text{C}_5\text{H}_5)_2$ [C(31a)–C(35a) of the disordered ring omitted for clarity]. Selected bond lengths (Å) and angles ($^\circ$): $\text{C}_5\text{H}_5(1)$ [C(11)–C(15)], Yb–C 2.769 (av.); $\text{C}_5\text{H}_5(2)$ [C(21), C(22), C(23), C(23b), C(22b)], C(21)–Yb 2.692(4), C(22)–Yb 2.784(10), C(23)–Yb 2.967(12), C(23b)–Yb 2.957(12), C(22b)–Yb 2.821(10); $\text{C}_5\text{H}_5(3)$ [C(31)–C(35)], Yb–C 2.858 (av.); $\text{C}_5\text{H}_5(3')$, Yb–C 2.852 (av.); Cp–Yb–Cp 117.6 (av.), Yb–Cp(2)–Yb 164.3, Yb–Cp(3)–Yb 177.6 Inter-chain Yb–C(15c) 2.996.

show the complex to be isostructural with $\text{Ca}(\text{C}_5\text{H}_5)_2$.¹³ Each ytterbium has three C_5H_5 ligands, (1)–(3), with $\text{C}_5\text{H}_5(1)$ essentially terminal (but η^1 -bound to the next chain), $\text{C}_5\text{H}_5(2)$ bridging on the two-fold axis, and μ - η^5 : η^5 - $\text{C}_5\text{H}_5(3)$ disordered about the inversion centre. $\text{C}_5\text{H}_5(2)$, reported as μ - η^3 : η^3 for $\text{Ca}(\text{C}_5\text{H}_5)_2$,¹³ has three shorter Yb–C distances [av. 2.77 Å, comparable with Yb–C of $\text{C}_5\text{H}_5(1)$] and two longer (av. 2.96 Å). Thus strong μ - η^3 : η^3 bonding of an allylic four-electron donor unit [C(21), C(22), C(22b)] is indicated, but the more distant C(23), C(23b) are sufficiently close to be μ - η^2 : η^2 bonded. The distances are comparable with those of formally seven-coordinate [$\text{Yb}(\text{C}_5\text{Me}_5)_2(\eta^2\text{-MeC}\equiv\text{CMe})$] [Yb–C > 2.85(1) Å],¹⁴ and Eu–C (av. 3.00 Å) of nine-coordinate [$\text{Eu}(\eta^6\text{-C}_6\text{Me}_6)(\text{AlCl}_4)_2$],¹⁵ when the potential formal ten coordination of $\text{Yb}(\text{C}_5\text{H}_5)_2$ is considered. They are marginally shorter than the interchain Yb– η^1 - C_5H_5 distance (2.996 Å), which is notably (> 0.1 Å) shorter than the interchain Ca– η^1 - C_5H_5 interaction of $\text{Ca}(\text{C}_5\text{H}_5)_2$ (Ca^{2+} and Yb^{2+} have similar ionic radii⁸). Interestingly, there is a close topological relationship between the structures of $\text{Yb}(\text{C}_5\text{H}_5)_2$ and $\text{Yb}(\text{C}_5\text{H}_4\text{Me})_2(\text{thf})$ ¹⁶ with the interchain Yb– η^1 - C_5H_5 linkage of $\text{Yb}(\text{C}_5\text{H}_5)_2$ replacing Yb–O of the latter.

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Footnotes

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† *FIR data*: [$\text{NaYb}(\text{C}_5\text{H}_5)_3$]; 260(sh) (Al), 240m (Al), 180vs (br) (e), 164(sh) (Al), 146(sh) (e), 109s (e) cm^{-1} . $\text{Yb}(\text{C}_5\text{H}_5)_2$: 252s(sh) (Al), 244vs, 230vs, 217vs (e), 168sh (Al), 150m (e), 109m (e) cm^{-1} .

‡ *Crystal data*: [$\text{NaYb}(\text{C}_5\text{H}_5)_3$]; $\text{C}_5\text{H}_5\text{Na}_{0.33}\text{Yb}_{0.33}$, cubic, space group $Pa\bar{3}$, $a = 14.238(2)$ Å, $U = 2886.2(6)$ Å³, $Z = 24$, $D_c = 1.801$ g cm^{-3} , $\mu = 6.485$ mm⁻¹, $F(000) = 1488$, crystal dimensions $0.4 \times 0.4 \times 0.05$ mm, 4117 reflections measured in the range of $5 < 2\theta < 45^\circ$, all 638 unique reflections and 40 restraints were used to refine 52 parameters; $g^1 = 0.0$, $g^2 = 42.95$. The refinement converged to $wR_2 = 0.170$ (all data) and $R_1 = 0.069$ [$F > 4\sigma(F)$] and a final residual electron density of $0.545/-0.914$ e Å⁻³.

$\text{Yb}(\text{C}_5\text{H}_5)_2$: $\text{C}_{10}\text{H}_{10}\text{Yb}$, $M = 303.22$, monoclinic, space group $C2/c$, $a = 13.908(5)$, $b = 8.571(3)$, $c = 15.325(8)$ Å, $\beta = 111.95(3)^\circ$, $U = 1694.3(12)$ Å³, $Z = 8$, $D_c = 2.38$ g cm^{-3} , $\mu = 10.50$ mm⁻¹, $F(000) = 1120$, $T = 293$ K. 1509 unique reflections were collected ($4 < 2\theta < 50^\circ$) with 1272 [$F_o \geq 4\sigma(F_o)$]; $R = 0.036$; $R_w = 0.037$, weighting scheme [$\sigma^2(F_o) + 0.0008$ $14(F_c)^2$]⁻¹. 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 182/413.

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