

Synthesis and Crystal Structure of a new Lanthanide Cyclooctatetraene Complex ($\eta^8\text{-C}_8\text{H}_8$)Er($\mu\text{-}\eta^8\text{-C}_8\text{H}_8$)K($\mu\text{-}\eta^8\text{-C}_8\text{H}_8$)Er($\mu\text{-}\eta^8\text{-C}_8\text{H}_8$)K(THF)₄

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The tetranuclear nearly-linear complex ($\eta^8\text{-C}_8\text{H}_8$)Er($\mu\text{-}\eta^8\text{-C}_8\text{H}_8$)K($\mu\text{-}\eta^8\text{-C}_8\text{H}_8$)Er($\mu\text{-}\eta^8\text{-C}_8\text{H}_8$)K(THF)₄ (THF=tetrahydrofuran) is first synthesised by the reaction of benzylcyclopentadienyl erbium dichloride ($\text{PhCH}_2\text{C}_5\text{H}_4$)ErCl₂·3THF with cyclooctatetraenyl potassium K₂C₈H₈ in 1 : 1 molar ratio in THF; a single crystal X-ray study has shown that the complex has the tetralayer-sandwich structure and that the adjacent Er³⁺ and K⁺ ions are bridged by η^8 -cyclooctatetraenyl group.

The cyclooctatetraenyl lanthanide derivatives were first synthesised by Hayes and Thomas¹ in 1969. From then on, many types of cyclooctatetraenyl complexes of the lanthanides have been synthesised.^{1-12,17,18} The cyclooctatetraenyl lanthanide complexes which have so far been characterised by single crystal X-ray determinations are listed as follows: [K(diglyme)][Ce(C₈H₈)₂],³ [Nd(C₈H₈)(THF)₂][Nd(C₈H₈)₂],⁵

[(C₈H₈)LnCl·2THF]₂ (Ln = Ce, Pr and Nd),¹¹ (C₈H₈)Lu[*o*-C₆H₄CH₂N(Me)₂],⁹ (C₈H₈)Yb·(C₅H₅N)₃·1/2C₅H₅N,¹⁸ (C₈H₈)Lu(C₅Me₅),¹⁷ (C₈H₈)Lu[C₅(CH₂Ph)],¹⁰ (C₈H₈)Pr(C₅H₅)·2THF and (C₈H₈)Pr(C₉H₇)·2THF,⁸ and (2,4-C₇H₁₁)Sm(C₈H₈)·THF.¹² The studies show that the cyclooctatetraene (COT) behaves as a (COT)²⁻ anion having ten π -electrons in these complexes and some of them have proved

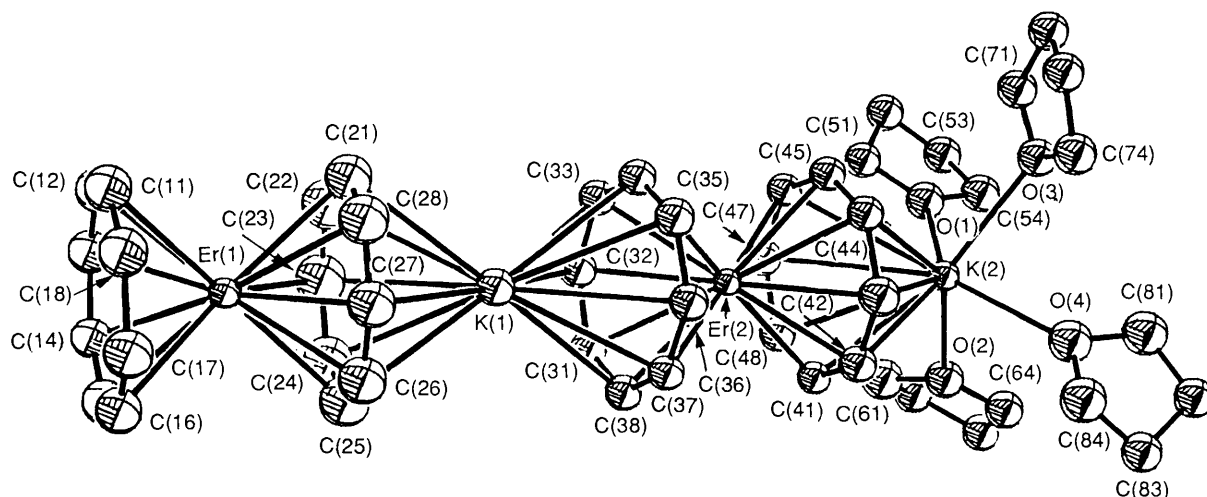
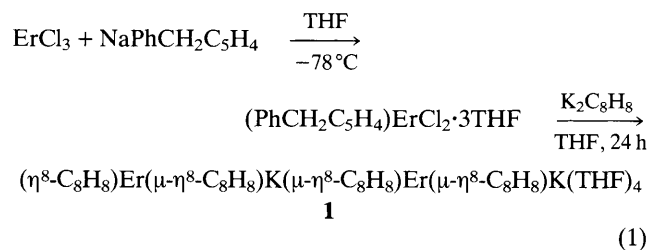


Fig. 1 Molecular structure of (C₈H₈)₄Er₂K₂(THF)₄ with thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles (°) are as follows: K(2)–O(1) 2.699(6), K(2)–O(2) 2.695(9), K(2)–O(3) 2.695(8), K(2)–O(4) 2.697(7), Er(1)–cent(1) 1.831, Er(1)–cent(2) 1.925, K(1)–cent(2) 2.504, K(1)–cent(3) 2.548, Er(2)–cent(3) 1.870, Er(2)–cent(4) 1.860, K(2)–cent(4) 2.640, Er(1)–K(1) 4.428, K(1)–Er(2) 4.418, Er(2)–K(2) 4.499, Er(1)–Er(2) 8.809, K(1)–K(2) 8.916, cent(1)–cent(2) 3.756, cent(2)–cent(3) 5.034, cent(3)–cent(4) 3.729, Er(1)–K(1)–Er(2) 169.6, K(1)–Er(2)–K(2) 179.4, cent(1)–Er(1)–cent(2) 178.0, cent(2)–K(1)–cent(3) 170.6, cent(3)–Er(2)–cent(4) 177.9, cent(4)–K(2)–O(1) 114.0, cent(4)–K(2)–O(2) 114.3, cent(4)–K(2)–O(3) 111.1, cent(4)–K(2)–O(4) 113.8 (cent = centroid of cyclooctatetraenyl ring).

to be sandwich complexes analogous to ferrocene. Here, we report the synthesis and crystal structure of a novel type of cyclooctatetraenyl lanthanide-alkali metal complex $(\eta^8\text{-C}_8\text{H}_8)\text{Er}(\mu\text{-}\eta^8\text{-C}_8\text{H}_8)\text{K}(\mu\text{-}\eta^8\text{-C}_8\text{H}_8)\text{Er}(\mu\text{-}\eta^8\text{-C}_8\text{H}_8)\text{K}(\text{THF})_4$ **1**.

The complex **1** was synthesised by the reaction of $(\text{PhCH}_2\text{C}_5\text{H}_4)\text{ErCl}_3\cdot 3\text{THF}$ ¹³ with $\text{K}_2\text{C}_8\text{H}_8$ at 1:1 molar ratio in THF as shown in eqn. (1). After the centrifugation and concentration of the THF solution, orange-yellow block crystals of **1** crystallised from the solution in a refrigerator in 35% yield.†



Single crystal X-ray analysis established the structure of **1** (Fig. 1).‡ The complex has a tetranuclear nearly-linear structure, and the adjacent Er^{3+} and K^+ ions are bridged by η^8 -cyclooctatetraenyl group. The relative positions of four metals are illustrated by the angles $\text{Er}(1)\text{-K}(1)\text{-Er}(2)$ 169.6° and $\text{K}(1)\text{-Er}(2)\text{-K}(2)$ 179.4° . The complex has a tetralayer sandwich structure in which $\text{Er}(1)$, $\text{Er}(2)$ and $\text{K}(1)$ are all bonded to two cyclooctatetraenyls, each with the eight carbons of an eight-membered ring, and the coordination number of each metal is 10. Only one side of $\text{K}(2)$ is symmetrically coordinated to the COT ring, the other side is bonded to the four oxygen atoms of the four THFs, the coordination number of $\text{K}(2)$ is 9. Plane $\text{COT}(1)$ is somewhat parallel to $\text{COT}(2)$, and $\text{COT}(3)$ to $\text{COT}(4)$, as illustrated by

† Selected spectroscopic data: IR (KBr) ν/cm^{-1} , 402m, 628s, 673s, 774sh, 800s, 905m, 1047m, 1130w, 1220w, 1374m, 1517sh, 1596s, 2871m, 2951m, 3003s; $^1\text{H NMR}$ ($[\text{C}_8\text{H}_8\text{THF}]$, 400 MHz): δ 5.2, 5.3, 5.4, 5.5, 5.6, 5.7, 5.8, 6.0; $^{13}\text{C NMR}$ ($[\text{C}_8\text{H}_8\text{THF}]$, 400 MHz): δ 126.719, 127.496, 132.861, 135.969.

‡ Crystal data: $\text{C}_{48}\text{H}_{64}\text{O}_4\text{Er}_2\text{K}_2$, $M = 1117.85$, triclinic, space group $P\bar{1}$, $a = 12.432(3)$, $b = 12.913(4)$, $c = 16.735(7)$ Å, $\alpha = 107.45(3)$, $\beta = 98.38(3)$, $\gamma = 111.41(2)^\circ$, $V = 2285.4(13)$ Å³, $Z = 2$, $\mu(\text{Mo-K}\alpha) = 40.1$ cm^{-1} , $D_c = 1.62$ g cm^{-3} , $F(000) = 1116$. Scan type $\theta\text{-}2\theta$, 8269 unique reflections were measured to $2\theta_{\text{max}} 50^\circ$ under dry and cold nitrogen atmosphere (-80°C), 6335 reflections with $F^2 > 3\sigma(F^2)$ were used in the refinement, $R = 0.0535$, $R_w = 0.0549$. All crystallographic measurements were made on an Nicolet R3m/E four-circle diffractometer using graphite-monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71069$ Å). The intensities were corrected for Lorentz-polarization factors but not for absorption. The structure was solved by Patterson and Fourier methods, all non-hydrogen atoms were refined anisotropically by full-matrix least-squares analysis and hydrogen atoms were introduced at theoretical positions. All calculations were carried out on a Eclipse S/140 computer. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

the following dihedral angles: $\text{COT}(1)\text{-COT}(2)$ 2.1 , $\text{COT}(3)\text{-COT}(4)$ 2.3 and $\text{COT}(2)\text{-COT}(3)$ 168.1° .

In complex **1**, the $\text{Er}(1)$ and $\text{Er}(2)\text{-C}(\eta^8)$ bond lengths range from 2.569(14)–2.660(19) Å, which is comparable with $\text{Er-C}(\eta^5)$ [2.629(15)–2.654(13) Å] reported for $(\eta^5\text{-C}_5\text{H}_5)_2\text{Er}(\mu\text{-CH}_3)_2\text{Li}(\text{tmeda})$,¹⁴ (tmeda = tetramethylethylenediamine). The $\text{K}(1)\text{-C}(\eta^8)$ bond lengths range from 3.024(16)–3.153(10) Å and $\text{K}(2)\text{-C}(\eta^8)$ 3.130(12)–3.284(13) Å, which are comparable with the values of $[\text{K}(\text{diglyme})][\text{Ce}(\text{C}_8\text{H}_8)_2]$ [3.062(12)–3.236(7) Å]³ and $(2,4\text{-C}_7\text{H}_{11})\text{K}(\text{tmeda})$ [3.069(7)–3.276(7) Å],¹⁵ but slightly larger than that of $\text{C}_8\text{H}_8\text{K}_2\cdot(\text{THF})_3$ [2.936(6)–3.029(7) Å].¹⁶ These bond lengths show that the $\text{K-C}(\eta^8)$ bond in complex **1** has a somewhat higher ionic character than that in $\text{C}_8\text{H}_8\text{K}_2\cdot(\text{THF})_3$, as is the case in $(2,4\text{-C}_7\text{H}_{11})\text{K}(\text{tmeda})$ and $[\text{K}(\text{diglyme})][\text{Ce}(\text{C}_8\text{H}_8)_2]$.

We have also investigated the reaction of $(\text{PhCH}_2\text{C}_5\text{H}_4)\text{YbCl}\cdot 3\text{THF}$ with $\text{K}_2\text{C}_8\text{H}_8$, which gave a complex with a similar structure to that of **1**, $(\eta^8\text{-C}_8\text{H}_8)\text{Yb}(\mu\text{-}\eta^8\text{-C}_8\text{H}_8)\text{K}(\mu\text{-}\eta^8\text{-C}_8\text{H}_8)\text{Yb}(\mu\text{-}\eta^8\text{-C}_8\text{H}_8)\text{K}(\text{THF})_4$; its X-ray structure is currently under investigation. We have been unable to isolate this type of complex for the early and middle lanthanides.

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