

COMMUNICATION

PREPARATION AND STRUCTURAL CHARACTERIZATION OF A FUNCTIONALIZED TRIGONAL ORGANOERBIUM CLUSTER WITH TWO BRIDGING HYDROXYL GROUPS AND A μ_3 -OXO GROUP

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Abstract—Traces of water in the reaction involving ErCl_3 with $\text{Ph}_2\text{PC}_5\text{H}_4\text{Na}$ resulted in the formation of the novel complex $[\{(\text{Ph}_2\text{PC}_5\text{H}_4)_2\text{Er}\}_3(\mu_3\text{-O})(\mu\text{-OH})_2]^- [\text{Na}(\text{DME})_3]^+$ (**1**) (DME, dimethoxyethane), which has been characterized by elemental analysis, IR, ^{31}P NMR and X-ray single crystal structure analysis.

The tendency towards higher coordination numbers and the strong oxophilicity of lanthanide elements result in the preferential formation of

organolanthanide oxo-complexes.^{1–8} Most of these oxo-complexes are tetranuclear^{3,4,6,8} or pentanuclear;^{2,5} trinuclear organolanthanide oxo-complexes are very rare.¹ Herein, we report a novel trinuclear organoerbium oxo-complex with an unusual $\text{Er}_3(\text{O})(\text{OH})_2$ core.

We found that anhydrous ytterbium trichloride reacts with $\text{Ph}_2\text{PC}_5\text{H}_4\text{Na}$ in tetrahydrofuran at 60°C under dinitrogen to produce an organoytterbium complex.⁹ In contrast, traces of water in the reaction mixture of ErCl_3 with $\text{Ph}_2\text{PC}_5\text{H}_4\text{Na}$ using the same procedure result in the formation of a new organoerbium cluster with hydroxyl groups and the oxo ion, $[\{(\text{Ph}_2\text{PC}_5\text{H}_4)_2\text{Er}\}_3(\mu_3\text{-O})(\mu\text{-OH})_2]^- [\text{Na}(\text{DME})_3]^+$ (**1**) in approximately 50% yield based on the amount of $\text{Ph}_2\text{PC}_5\text{H}_4\text{Na}$.[†] We have determined the crystal and molecular structure of **1** by X-ray diffraction technique and revealed that complex **1** exists as discrete cation and anion pairs.[‡] The anion shown in Fig. 1, with some important bond parameters shown in Table 1, is comprised of three bis[(diphenylphosphino)cyclopentadienyl] erbium units arranged in a triangular array. Two sides of the triangle are bridged by hydroxyl groups. An oxo ion was positioned in the centre of the triangle forming a new pattern of metal–oxygen core, see Fig. 2. A similar metal–hydrogen core was

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† IR (KBr, cm^{-1}): 3068 m, 3051 m, 1584 m, 1519 m, 1472 m, 1434 s, 1347 m, 1180 m, 1155 w, 1118 m, 1089 m, 1064 m, 1026 m, 994 m, 893 m, 741 s, 696 s, 591 w, 562 m, 535 w and 503 s. $^{31}\text{P}\{^1\text{H}\}$ NMR (THF, 85% H_3PO_4 , ext): -14.50 and -16.37 ppm. Found: C, 58.7; H, 5.1; P, 7.4. Calc for $\text{C}_{114}\text{H}_{116}\text{P}_6\text{Er}_3\text{O}_9\text{Na}$: C, 58.5; H, 5.0; P, 7.9%.

‡ Crystal data: $\text{C}_{114}\text{H}_{116}\text{O}_9\text{P}_6\text{NaEr}_3$, $M = 2340.92$, monoclinic, space group $P2_1/c$ (no. 14), $a = 22.893(9)$, $b = 17.235(6)$, $c = 29.610(10)$ Å, $\beta = 101.96(4)^\circ$, $U = 11427(6)$ Å³, $Z = 4$, $D_c = 1.361$ g cm⁻³, $F(000) = 4708$, Mo- K_α radiation, $\lambda = 0.71073$ Å, μ (Mo- K_α) = 23.18 cm⁻¹. Off-pink block $0.24 \times 0.34 \times 0.36$ mm, 15541 data measured at 293 K on an AFC7R diffractometer ($4.0^\circ < 2\theta < 45.0^\circ$), absorption-corrected, 7503 observed [$I > 3\sigma(I)$]. Structure solved by direct methods (SIR88)¹⁰ and Fourier difference techniques, refined by full-matrix least-squares analysis (Er, P, Na, O on the anion anisotropic) to $R = 0.075$, $R_w = 0.093$, $w = 4F_o^2/[\sigma^2(F_o^2)]$; program used *teXsan*.¹¹ Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

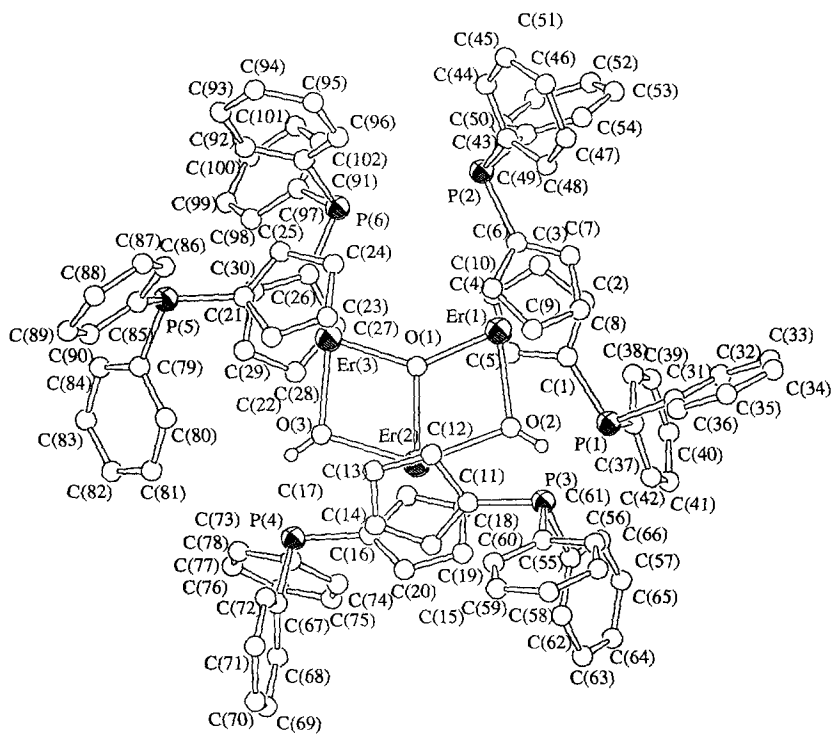


Fig. 1. A perspective view of the structure of $\{[(\text{Ph}_2\text{PC}_5\text{H}_4)_2\text{Er}]_3(\mu_3\text{-O})(\mu\text{-OH})_2\}^-$ anion.

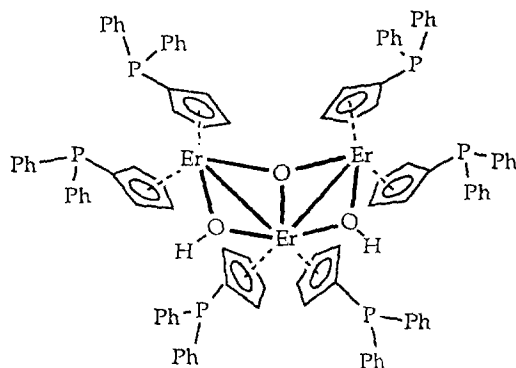


Fig. 2. Chemical drawing of $\{[(\text{Ph}_2\text{PC}_5\text{H}_4)_2\text{Er}]_3(\mu_3\text{-O})(\mu\text{-OH})_2\}^-$ with $\text{Er}_3(\text{O})(\text{OH})_2$ core highlighted.

Table 1. Selected bond lengths (Å) and bond angles (°) in **1**

Er(1)—Er(2)	3.635(3)	Er(2)—Er(3)	3.563(2)	Er(1)—Er(3)	3.930(2)
Er(1)—O(1)	2.07(2)	Er(2)—O(1)	2.27(2)	Er(3)—O(1)	2.14(2)
Er(1)—O(2)	2.26(2)	Er(2)—O(2)	2.31(2)	Er(2)—O(3)	2.31(2)
Er(3)—O(3)	2.22(2)	Er(1)—C _{av.} (1–5)	2.70(2)	Er(1)—C _{av.} (6–9)	2.69(2)
Er(2)—C _{av.} (11–15)	2.72(3)	Er(2)—C _{av.} (16–20)	2.77(2)	Er(3)—C _{av.} (21–25)	2.70(2)
Er(3)—C _{av.} (26–30)	2.72(2)				
O(1)—Er(1)—O(2)	72.7(8)	O(1)—Er(2)—O(2)	68.3(6)	O(1)—Er(2)—O(3)	72.0(7)
O(2)—Er(2)—O(3)	140.2(7)	O(1)—Er(3)—O(3)	76.3(7)	Er(1)—O(1)—Er(2)	113.6(9)
Er(2)—O(1)—Er(3)	107.8(8)	Er(1)—O(1)—Er(3)	138(1)	Er(1)—O(2)—Er(2)	105.3(8)
Er(2)—O(3)—Er(3)	103.8(8)				

observed in an organolanthanide hydride cluster of $[(C_5H_5)_2Lu]_3(\mu_3-H)(\mu-H)_2$.¹² In the cluster anion, Er(1) and Er(3) have coordination numbers of eight while Er(2) is nine coordinated if we consider Cp is equivalent to three terminal ligands. The six atoms, [Er(1), Er(2), Er(3), O(1), O(2) and O(3)], are almost coplanar with maximum deviation of 0.10 Å. The distance of erbium–oxo bonds with average value of 2.16(2) Å is significantly shorter than that of Er–O(OH) [av. Er–O(OH), 2.28(2) Å]. The distance of oxo–erbium bonds in **1** is also shorter than that of the corresponding bonds in tetranuclear and pentanuclear organolanthanide oxo-complexes. For instance, the mean distance of oxo-erbium bonds in $[(C_5H_9C_5H_4)_3Er_4(\mu-Cl)_6(\mu_3-Cl)(\mu_4-O)(THF)_3]$ is 2.26 Å.⁸ In essence, complex **1** was functionalized by the dangling phosphorus atoms which are expected to coordinate to transition metals. In this respect, complex **1** should be a good precursor for the preparation of larger heteronuclear clusters.

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