Preparation and Crystal Structure of the Mixed-valence ($Yb^{III,II}$) Tetranuclear Complex, $(Me_5C_5)_6Yb_4(\mu\text{-}F)_4$

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Silver fluoride and $(Me_5C_5)_2Yb$ in toluene give the novel, tetranuclear, mixed-valence complex $(Me_5C_5)_6Yb_4(\mu\text{-}F)_4$ as shown by single crystal *X*-ray crystallography.

Binary transition-metal fluorides form a wide range of interesting solid-state structures.[1] It is generally observed that those compounds in oxidation state less than six form M–F–M bridge bonds. These bridge bonds have been likened to the bridge bonding in aluminium alkyls with the important difference that a bridging methyl group has one σ-orbital and an electron for bonding and fluorine has two σ-orbitals, two π-orbitals, and seven electrons for bonding.[2] The three-centre-bond model can be used to describe bridge bonding in d- and f-transition metal alkyls and fluorides and as such is a unifying and predictive principle in synthetic and structural organometallic and inorganic chemistry.[2,4] With this analogy in mind we decided to try to prepare $(Me_5C_5)_2YbF$ since $(Me_5C_5)_2LuMe$ is a molecule which has a terminal methyl group and a methyl group that bridges the two lanthanoid centres in a near-linear fashion, the Lu–C(Me)–Lu angle being 170(4)°, and the ytterbium methyl is thought to have a similar structure, $(Me_5C_5)_4Yb_2(Me)(\mu\text{-}Me)$.[3] The pentamethylcyclopentadienyl ligand is crucial for giving the unusual bridging methyl since $(H_5C_5)_4Yb_2(\mu\text{-}Me)_2$ has two normal bridge bonds in which the Yb–C(Me)–Yb angle is 86.5(5)°.[4]

We have used silver(I) salts to oxidize $(Me_5C_5)_2Yb(L)$ to $(Me_5C_5)_2Yb(L)(X)$, where L is a Lewis base[5] and others have used silver(II) salts to oxidize $(H_5C_5)_2Yb(L)_2$.[6] Hence reaction of base-free $(Me_5C_5)_2Yb$[7] with AgF in hydrocarbons was a rational synthetic route to the target molecule.

Stirring $(Me_5C_5)_2Yb$ (0.30 g) with one or up to four molar equivalents of AgF in toluene for 8 h yielded a red solution and silver metal. Crystallization of the red solution yielded brown blocks and red needles. The brown blocks, the identity of which is currently under study, may be converted into the red needles (total yield, 0.08 g) by heating in toluene. The red needles do not melt up to 350 °C, do not give an understandable mass spectrum, and are not soluble enough in aromatic solvents to give a satisfactory ^1H n.m.r. spectrum; they were shown by single crystal *X*-ray crystallography to be of the

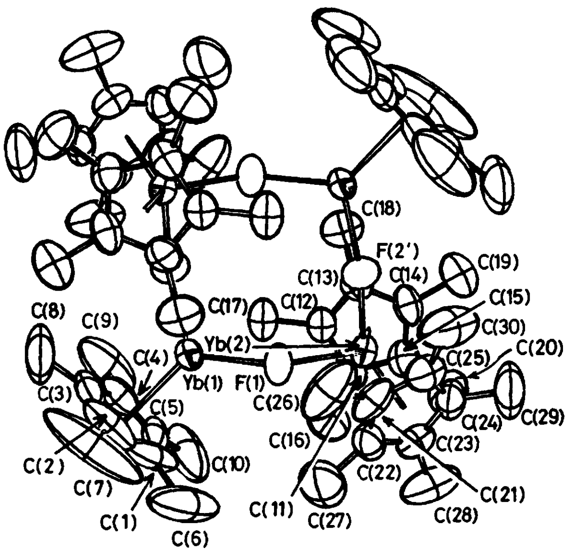

Figure 1. ORTEP view of $(Me_5C_5)_6Yb_4(\mu\text{-}F)_4$. The averaged Yb(2)–$Me_5C_5$ ring centroid and the Yb(1)–Me_5C_5 ring centroid distances are 2.33 and 2.39 Å, respectively.

tetranuclear complex $(Me_5C_5)_6Yb_4(\mu\text{-}F)_4(PhMe)_2$ when crystallized from toluene (Figure 1).†

The structure consists of two trivalent ytterbium fragments, $(Me_5C_5)_2YbF$, and two divalent ytterbium fragments, $(Me_5C_5)YbF$, connected by way of near-linear bridging fluorides, Yb(2)F(2)Yb(1) 160.0(2)° and Yb(2)F(1)Yb(1) 157.3(2)°. The molecule has idealized C_{2h} symmetry, the inversion centre being located in the centre of the Yb_4F_4 ring. The eight-membered Yb_4F_4 ring is non-planar; the dihedral angle formed by intersection of the plane defined by F(1)F(1')F(2)F(2') and Yb(2)F(1)F(2) is 26.1°. In addition Yb(1) and Yb(1') are out of the plane defined by F(1)F(1')F(2)F(2') by −0.056 and −0.056 Å, respectively, and Yb(2) and Yb(2') are out of this plane by +0.65 and −0.65 Å, respectively.

The co-ordination of Yb(2) is distorted tetrahedral, defining the Me_5C_5 ring centroid as occupying one co-ordination site. The averaged Me_5C_5 ring centroid–Yb(2)–Me_5C_5 ring centroid angle is 138.4°, the averaged Me_5C_5 ring centroid–Yb(2)–F angle is 104.3°, and the F(2)–Yb(2)–F(1) angle is 91.9°. The co-ordination of Yb(1) is near-trigonal planar, the averaged Me_5C_5 ring centroid–Yb–F angle is 127.1° and the F(2)–Yb(1)–F(1) angle is 105.9(1)°. Alternatively, the two $(Me_5C_5)_2Yb(2)F_2$ tetrahedra and the two $(Me_5C_5)Yb(1)F_2$ trigonal planar units are fused so that they share common vertices. The four fluoride atoms are at the corners of a rectangle with F(1)F(2') and F(1)F(2) being 3.061(5) and 3.544(5) Å, respectively, and F(1)F(2)F(1') and F(2)F(1)F(2') being 90.20(5) and 8^{0}.88(5)°, respectively.

The average oxidation state of the ytterbium atoms in the tetranuclear complex is 2.5. The Yb(2) atoms are most reasonably described as being trivalent with a co-ordination number of eight, defining a Me_5C_5 group as occupying three co-ordination sites, and the Yb(1) atoms being divalent with co-ordination number five since the radius of Yb^{III} in eight-co-ordination is nearly the same as that of Yb^{II} in five-co-ordination.[8] Thus the averaged Yb(2)–C and Yb(1)–C distances are 2.62 ± 0.02 and 2.65 ± 0.02 Å, respectively, and the averaged Yb(2)–F and Yb(1)–F distances are 2.129 ± 0.002 and 2.220 ± 0.001 Å, respectively. Not surprisingly, Yb(1), in an attempt to increase its co-ordination number, has two close Yb · · · C (17,18) contact distances of 3.124(7) and 3.232(7) Å, respectively. All other intra- and inter-molecular contacts are >3.6 Å.

Variable temperature magnetic susceptibility studies are consistent with the $Yb^{II,III}$ mixed-valence formulation with non-interacting spins, *i.e.*, a class I or trapped-valence complex, even though the near-linear Yb–F–Yb angles provide the correct π-symmetry orbitals for such magnetic exchange.[9] Powdered samples follow Curie–Weiss behaviour and the shape of the plot of χ_m^{-1} *vs.* T/K is as expected for isolated Yb^{III} paramagnets, $\mu_{eff.} = 3.67\ \mu_B$ (per Yb^{III}) and $\theta = -3$ K from 7 to 35 K and $\mu_{eff.} = 4.95\ \mu_B$ and $\theta = -37$ K from 80 to 280 K at a field strength of 5 kG (1 G = 10^{-4} T). The magnetic susceptibility is highly anisotropic since measurement of χ_m on randomly orientated crystals gives $\mu_{eff.} = 3.87\ \mu_B$ (per Yb^{III}) and $\theta = -2$ K from 7 to 30 K and $\mu_{eff.} = 6.06\ \mu_B$ and $\theta = -64$ K from 80 to 200 K. The anisotropy in the magnetic moment is not unusual in lanthanoid magnetism.[10]

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† *Crystal data:* $C_{74}H_{106}F_4Yb_4$, M = 1763.96, monoclinic, space group $C2/c$, a = 26.805(3), b = 10.285(1), c = 24.621(2) Å, β = 104.53(1)°, U = 6570(2) Å^3, D_c = 1.78 g cm^{-3}, Mo-K_α radiation, R = 0.71073 Å, μ(Mo-K_α) = 56.8 cm^{-1}. The structure was solved by a combination of Patterson and Fourier methods and refined using 3305 unique reflections [$F_o^2 > 3\sigma(F_o^2)$] measured on a CAD4 diffractometer ($2\theta_{max.}$ 45°). An analytical absorption correction was applied to the data, all non-hydrogen atoms were refined anisotropically, and the hydrogen atoms on the Me_5C_5-rings on Yb(1) were located, included in the structure factor calculations with isotropic thermal parameters, but were not refined. The hydrogen atoms on the Me_5C_5-ring on Yb(2) were not located. The toluene of solvation was disordered and the disorder was modelled with two half-occupancy molecules related by a crystallographic two-fold axis of symmetry. The R value is 0.027 for 329 variables. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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