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Metallacarborane Complexes That Incorporate the Lanthanides. Synthesis, Molecular Structure, and Spectroscopic Characterization of Dicarbollide Complexes of Samarium and Ytterbium

by

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The interaction of $Na_2[nido\text{-}7,8\text{-}C_2B_9H_{11}]$ (1) with LnI_2 (Ln = Sm, Yb) in THF affords a complex with the composition $Ln(C_2B_9H_{11})(THF)_4$ (Ln = Sm (2), Yb (3)). Both these complexes have been fully characterized by spectroscopic techniques, and the molecular structure of the DMF derivative of 3 has been established by a single-crystal X-ray diffraction study. The DMF derivative, $Yb(C_2B_9H_{11})(DMF)_4$ (3b), crystallizes in the orthorhombic space group *Pbca* with a = 10.208 (1) Å, b = 17.005 (3) Å, c = 31.627 (5) Å, V = 5479 Å^3, and Z = 8. Data were collected on a modified Picker FACS-1 diffractometer at 25 °C using Mo Kα radiation, to a maximum 2θ = 50°, giving 4841 unique reflections, and the structure was solved by statistical methods. The final discrepancy index was R = 0.082, R_w = 0.084 for 1424 independent reflections with $I > 2\sigma(I)$. The dicarbollide ligand is η^5-bound to the Yb ion, and four DMF molecules are coordinated to Yb through the oxygen atoms. Complex 2 is fluxional in solution. The fluxionality of complex 2 in solution has been monitored by variable-temperature ^{11}B NMR spectroscopy, and a dynamic process involving the Sm^{2+} ion and the dicarbollide ligand has been proposed. The reaction of *closo*-1,1,1,1-$(THF)_4$-1,2,3-$LnC_2B_9H_{11}$ (Ln = Sm (2), Yb (3)) with $[PPN]^+[closo\text{-}3,1,2\text{-}TlC_2B_9H_{11}]^-$ in THF produces [3,3-$(THF)_2$-*commo*-3,3′-Ln(3,1,2-$LnC_2B_9H_{11})_2$]$^-$[PPN]$^+$ (Ln = Sm (4), Yb (5)), which has been characterized spectroscopically. The molecular structure of 4 has been established by an X-ray diffraction study. The complex 4 crystallizes in the triclinic space group $P\bar{1}$ with a = 8.9374 (3) Å, b = 17.8703 (6) Å, c = 18.4989 (7) Å, α = 107.5402 (9)°, β = 91.085 (1)°, γ = 90.705 (1)°, V = 2816 Å^3, and Z = 2. Data were collected at 25 °C on a diffractometer equipped with a small Huber circle, using Mo Kα radiation, to

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Mark J. Manning, Carolyn B. Knobler, Rajesh Khattar, and M. Frederick Hawthorne*

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The interaction of $Na_2[nido\text{-}7,8\text{-}C_2B_9H_{11}]$ (**1**) with LnI_2 (Ln = Sm, Yb) in THF affords a complex with the composition $Ln(C_2B_9H_{11})(THF)_4$ (Ln = Sm (**2**), Yb (**3**)). Both these complexes have been fully characterized by spectroscopic techniques, and the molecular structure of the DMF derivative of **3** has been established by a single-crystal X-ray diffraction study. The DMF derivative, $Yb(C_2B_9H_{11})(DMF)_4$ (**3b**), crystallizes in the orthorhombic space group *Pbca* with a = 10.208 (1) Å, b = 17.005 (3) Å, c = 31.627 (5) Å, V = 5479 Å^3, and Z = 8. Data were collected on a modified Picker FACS-1 diffractometer at 25 °C using Mo Kα radiation, to a maximum 2θ = 50°, giving 4841 unique reflections, and the structure was solved by statistical methods. The final discrepancy index was R = 0.082, R_w = 0.084 for 1424 independent reflections with $I > 2\sigma(I)$. The dicarbollide ligand is η^5-bound to the Yb ion, and four DMF molecules are coordinated to Yb through the oxygen atoms. Complex **2** is fluxional in solution. The fluxionality of complex **2** in solution has been monitored by variable-temperature ^{11}B NMR spectroscopy, and a dynamic process involving the Sm^{2+} ion and the dicarbollide ligand has been proposed. The reaction of *closo*-1,1,1,1-$(THF)_4$-1,2,3-$LnC_2B_9H_{11}$ (Ln = Sm (**2**), Yb (**3**)) with $[PPN]^+[closo\text{-}3,1,2\text{-}TlC_2B_9H_{11}]^-$ in THF produces [3,3-$(THF)_2$-*commo*-3,3′-Ln(3,1,2-$LnC_2B_9H_{11})_2]^-[PPN]^+$ (Ln = Sm (**4**), Yb (**5**)), which has been characterized spectroscopically. The molecular structure of **4** has been established by an X-ray diffraction study. The complex **4** crystallizes in the triclinic space group $P\bar{1}$ with a = 8.9374 (3) Å, b = 17.8703 (6) Å, c = 18.4989 (7) Å, α = 107.5402 (9)°, β = 91.085 (1)°, γ = 90.705 (1)°, V = 2816 Å^3, and Z = 2. Data were collected at 25 °C on a diffractometer equipped with a small Huber circle, using Mo Kα radiation, to a maximum of 2θ = 45°, giving 7358 unique reflections, and the structure was solved by a combination of conventional Patterson, Fourier, and full-matrix least-squares techniques. The final discrepancy index was R = 0.053, R_w = 0.065 for 5324 independent reflections with $I > 3\sigma(I)$. Both the dicarbollide ligands are η^5-bound to the Sm ion in a nonparallel or bent fashion, and the coordination sphere about the Sm is completed by two THF molecules. The coordination geometry of **4** can be best described as a distorted tetrahedron. This is the first structurally authenticated example of a bis(dicarbollide)lanthanide complex. The structure of **4** is compared with related bis(cyclopentadienyl)lanthanides.

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