SUPPORTING INFORMATION

Europium(II) and Ytterbium(II) Cyclic Organohydroborates with Agostic Interactions

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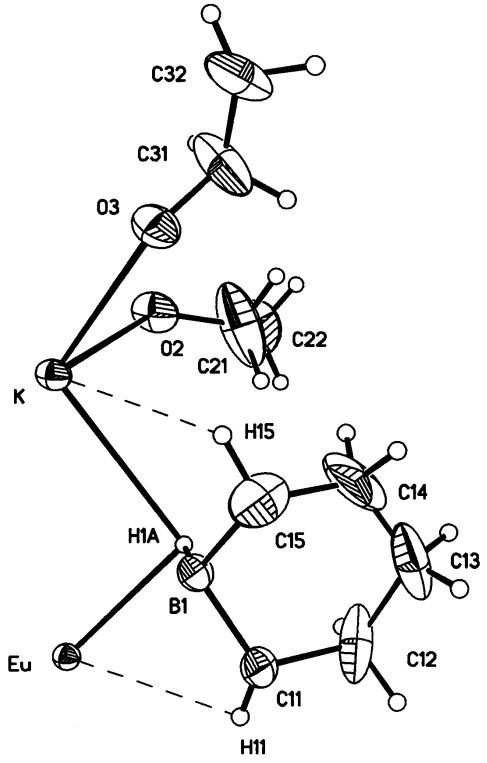
Table S1. Crystallographic data for complexes **3**, and **4**

	3	**4**
empirical formula	$C_{64}H_{64}O_8B_4Eu\ K_2$	$C_{64}H_{64}O_8B_4YbK_2$
fw	1299.06	1320.14
space group	P4(2)/nmc(No.137)	P4(2)/nmc(No.137)
a, Å	13.439(1)	13.3634(1)
b, Å	13.439(1)	13.3634(1)
c, Å	20.421(1)	20.2053(1)
α, deg	90	90
β, deg	90	90
γ, deg	90	90
V, Å^3	3688.2(4)	3608.27(4)
Z	2	2
D_{calcd}, g·cm^{-3}	1.170	1.215
T, °C	-33	-73
μ, mm^{-1}	1.009	1.458
R1 [$I > 2\sigma(I)$] [a]	0.0453	0.0510
wR2 (all data) [b]	0.1554	0.1784

[a] $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

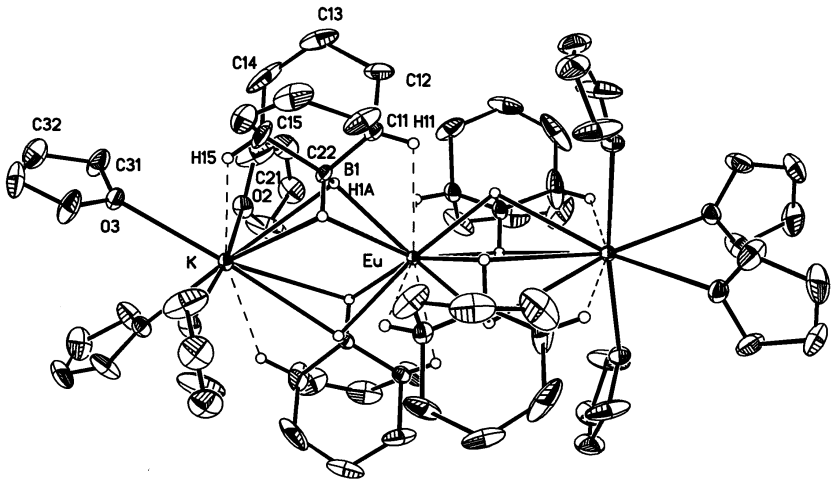
[b] $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

Figure S1. Molecular structure (10 % probability thermal ellipsoids) of the asymmetric unit of $\{K(THF)_4\}_2\{Eu\{(\mu\text{-}H)_2BC_8H_{14}\}_4\}$, **3.**



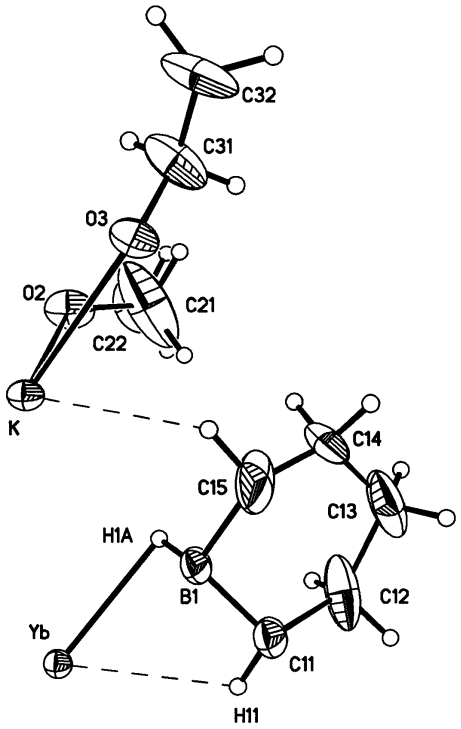
The Eu atom in **3** resides on a special position, (3/4, 1/4, 1/4). The asymmetric unit is comprised of 1/8 Eu atom, 1/4 K atom, a half of $\{(\mu\text{-}H)_2BC_8H_{14}\}_4\}$unit and one THF solvent.

Figure S2. Molecular structure (5 % probability thermal ellipsoids) of $\{K(THF)_4\}_2\{Eu\{(\mu\text{-}H)_2BC_8H_{14}\}_4\}$, **3.**



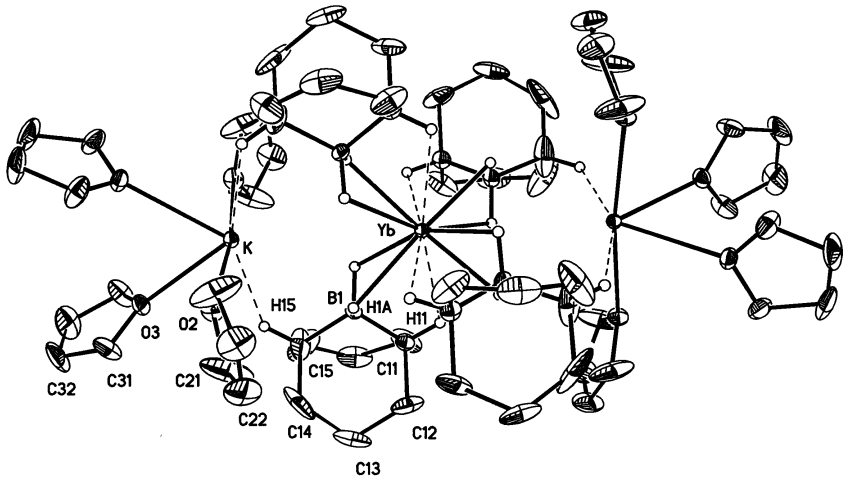
The remainder of **3** is generated by symmetry transformations through the Eu center. Symmetry transformations used to generate equivalent atoms: A(#1): $y + 1/2, -x + 1, -z + 1/2$; B(#2): $-y + 1, x - 1/2; -z + 1/2$; C(#3): $-x + 3/2, -y + 1/2, z$; D(#4): $x, -y + 1/2, z$; E(#5): $-x + 3/2, y, z$. The hydrogen atoms on THF solvent and on β-, and γ-position in $\{(\mu\text{-}H)_2BC_8H_{14}\}_4\}$ unit are omitted for clarity.

Figure S3. Molecular structure (10 % probability thermal ellipsoids) of the asymmetric unit of $\{K(THF)_4\}_2\{Yb\{(\mu\text{-}H)_2BC_8H_{14}\}_4\}$, **4.**



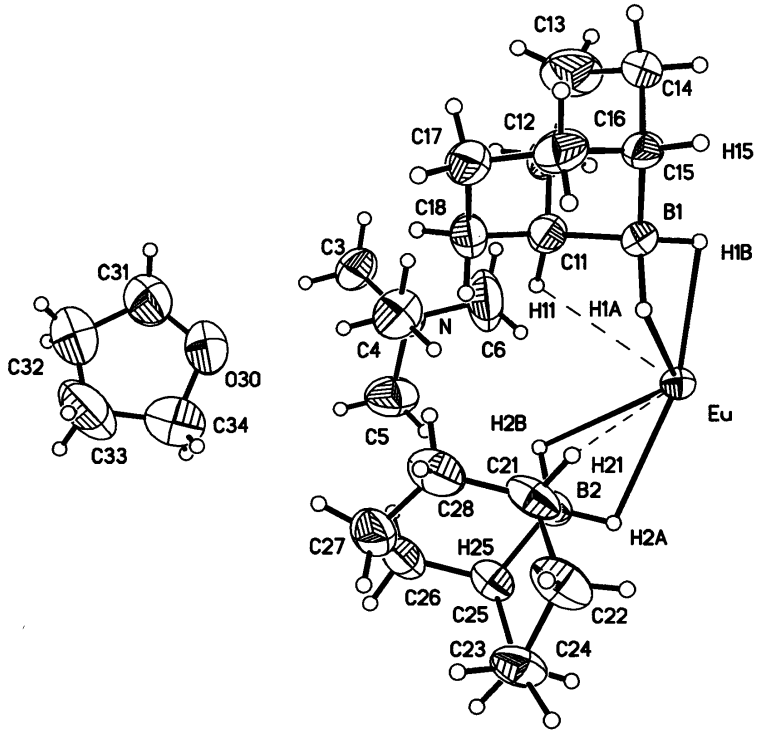
The Yb atom in **4** resides on a special position, (3/4, 1/4, 1/4). The asymmetric unit is comprised of 1/8 Yb atom, 1/4 K atom, a half of $\{(\mu\text{-}H)_2BC_8H_{14}\}_4\}$unit and one THF solvent.

Figure 4. Molecular structure (5 % probability thermal ellipsoids) of $\{K(THF)_4\}_2\{Yb\{(\mu\text{-}H)_2BC_8H_{14}\}_4\}$, **4.**



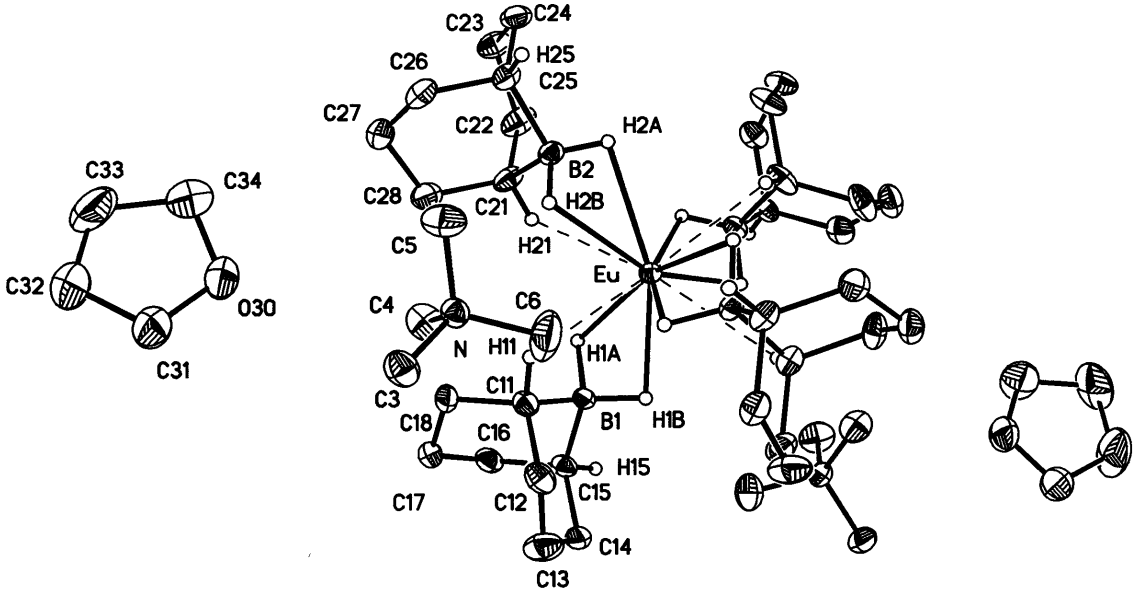
The remainder of **4** is generated by symmetry transformations through the Yb center. Symmetry transformations used to generate equivalent atoms: A(#1): $y + 1/2, -x +1, -z +1/2$; B(#2): $-y +1, x - 1/2; -z + 1/2$; C(#3): $-x +3/2, -y +1/2, z$; D(#4): $x, -y + 1/2, z$; E(#5): $-x +3/2, y, z$. The hydrogen atoms on THF solvent and on β-, and γ-position in $\{(\mu\text{-}H)_2BC_8H_{14}\}_4\}$ unit are omitted for clarity.

Figure 5. Molecular structure (50 % probability thermal ellipsoids) of the asymmetric unit of $[NMe_4]_2[Eu\{(\mu\text{-}H)_2BC_8H_{14}\}_4]\cdot 2THF$, **5·2THF.**



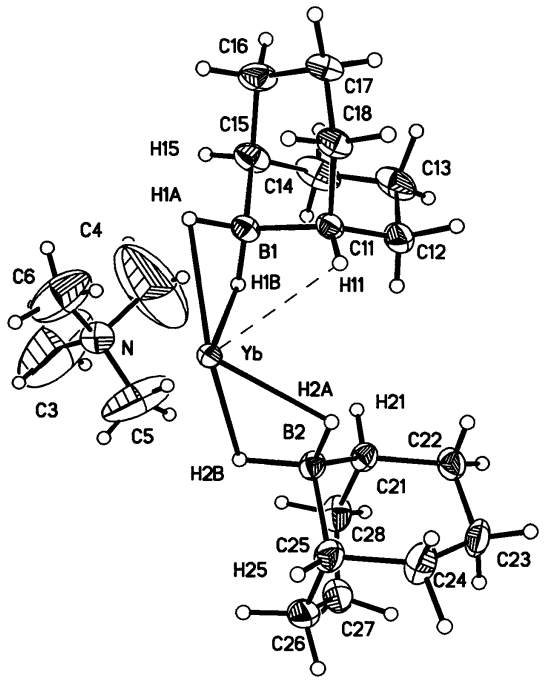
The Eu atom in **5** is resides on a special position, (0, 1/2, *z*). The asymmetric unit is comprised of a half of Eu atom, two $\{(\mu\text{-}H)_2BC_8H_{14}\}$units, one THF solvent and one cation $[NMe_4]^+$.

Figure 6. Molecular structure (25 % probability thermal ellipsoids) of $[NMe_4]_2[Eu\{(\mu\text{-}H)_2BC_8H_{14}\}_4]\cdot 2THF$, **5·2THF.**



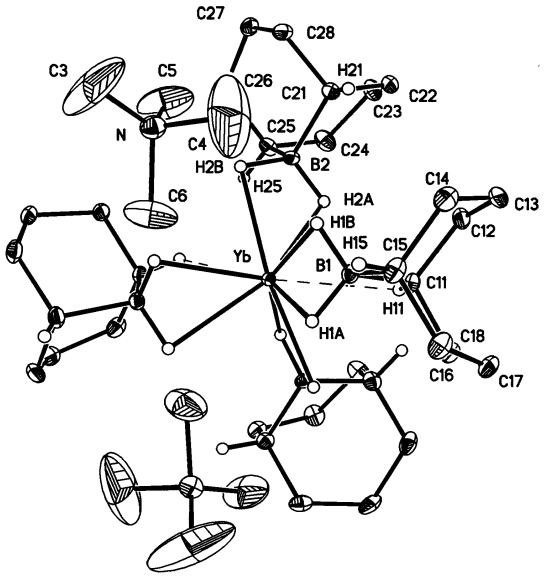
The remainder of **5·2THF** is generated by inversion through the Eu center. Symmetry transformation used to generate equivalent atoms: *-x, -y* + 1, *z*. Hydrogen atoms on solvents THF, cation NMe_4, and β- and γ-position in the $\{(\mu\text{-}H)_2BC_8H_{14}\}$unit are omitted for clarity.

Figure 7. Molecular structure (50 % probability thermal ellipsoids) of the asymmetric unit of $[NMe_4]_2[Yb\{(\mu\text{-}H)_2BC_8H_{14}\}_4]$, **6.**



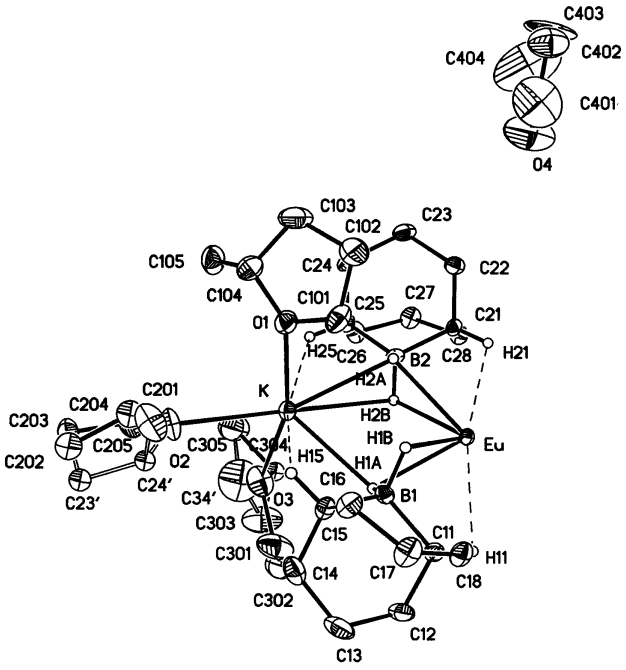
The Yb atom in **6** is resides on a special position, (1/2, *y*, 3/4). The asymmetric unit is comprised of a half of Yb atom, two $\{(\mu\text{-}H)_2BC_8H_{14}\}$units, and one cation $[NMe_4]^+$.

Figure 8. Molecular structure (25 % probability thermal ellipsoids) of $[NMe_4]_2[Yb\{(\mu\text{-}H)_2BC_8H_{14}\}_4]$, **6.**



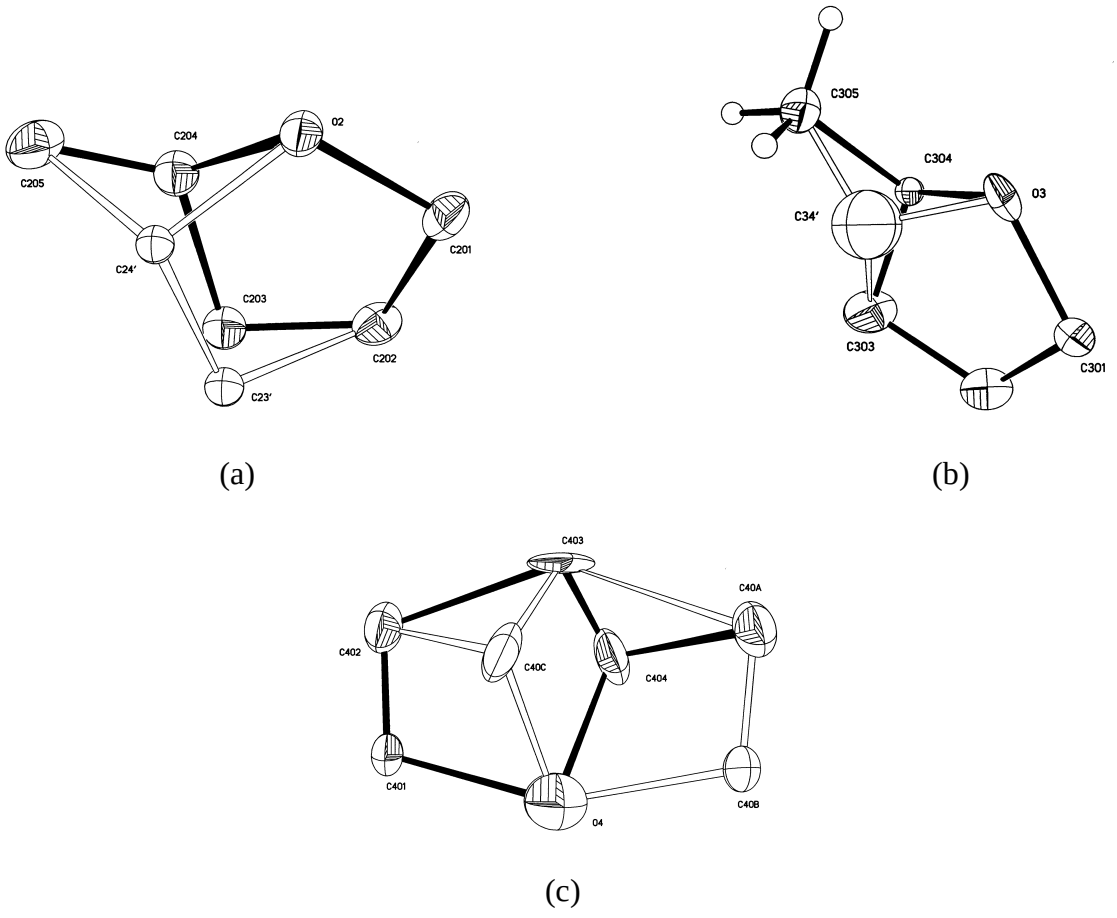
The remainder of **6** is generated by inversion through the Yb center. Symmetry transformation used to generate equivalent atoms: $-x + 1,\ y,\ -z + 3/2$. Hydrogen atoms on cation NMe_4, and β- and γ-position in the $\{(\mu\text{-}H)_2BC_8H_{14}\}$unit are omitted for clarity.

Figure 9. Molecular structure (25 % probability thermal ellipsoids) of the asymmetric unit of $\{K(MeTHF)_3\}_2\{Eu\{(\mu\text{-}H)_2BC_8H_{14}\}_4\}\cdot MeTHF$, **7·MeTHF.**



The Eu atom in **7·MTHF** is resides on a special position, (1/2, *y*, 3/4). The asymmetric unit is comprised of Eu on an inversion center, one K atom, two $\{(\mu\text{-}H)_2BC_8H_{14}\}$units, three coordinated MeTHF solvent ligands, and a half of free MeTHF ligand. Inversion through the Eu center generates the remainder of molecule. Symmetry transformation used to generate equivalent atoms: $-x+1$, y, $-z+3/2$. Hydrogen atoms on solvents MeTHF, and on β- and γ- position in $\{(\mu\text{-}H)_2BC_8H_{14}\}$unit are omitted for clarity. The free MeTHF solvent and two coordinated MeTHF solvents are disordered.

Figure 10. Molecular structure (10 % probability thermal ellipsoids) showing the disorderd MeTHF solvent ligands and free MeTHF solvnt in **7·MeTHF**.

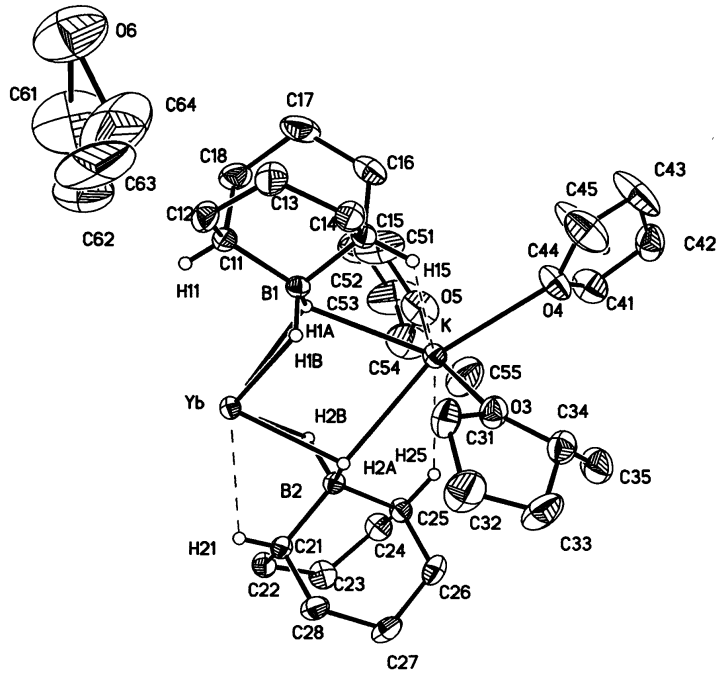


(a) (b)

(c)

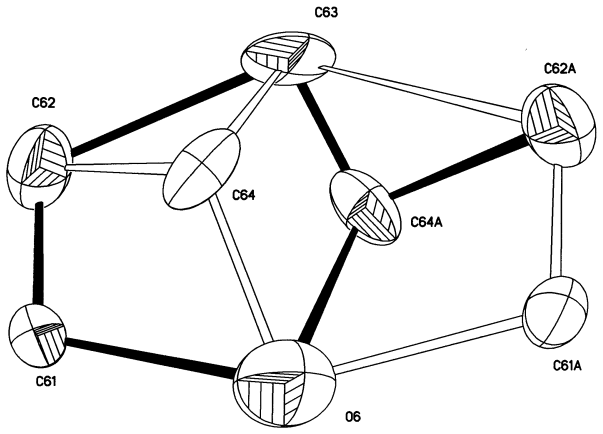
The α-, and β-carbon in coordinated MeHTF solvents in **7·MeTHF** is disordered (Figure (a), (b)). These atoms were treated by splitting the MeTHF ring (C203, C204, and C304). The following site occupancy factors were determined: C203, C204, C304, 0.43; and C23', C24', C34', 0.57. The free MeTHF solvent in **7·MeTHF** is disordered (Figure (c)). The carbon atoms adopt two sets of alternate orientation that are related by rotation. The site occupancy factors of two sets are 50%. Two sets are represented by solid line and open line, respectively. Positions of hydrogen atoms on the disordered solvent ligands were not calculated.

Figure 11. Molecular structure (25 % probability thermal ellipsoids) of the asymmetric unit of $\{K(MeTHF)_3\}_2\{Yb\{(\mu\text{-}H)_2BC_8H_{14}\}_4\}\cdot MeTHF$, **8·MeTHF.**



The Yb atom in **8·MeTHF** is resides on a special position, (1, *y*, 5/4). The asymmetric unit is comprised of Yb on an inversion center, one K atom, two $\{(\mu\text{-}H)_2BC_8H_{14}\}$units, three coordinated MeTHF solvent ligands, and a half of free MeTHF ligand. Inversion through the Yb center generates the remainder of molecule. Symmetry transformations used to generate equivalent atoms: $-x + 2,\ y, -z + 5/2$ and $-x + 1,\ y, -z + 5/2$. Hydrogen atoms on solvents MeTHF, and on β- and γ- position in $\{(\mu\text{-}H)_2BC_8H_{14}\}$unit are omitted for clarity. The free MeTHF solvent is disordered.

Figure 12. Molecular structure (10 % probability thermal ellipsoids) showing the disorderd free THF solvent in **8**·**MeTHF**.



The free MeTHF solvent in **8**·**MeTHF** is disordered. The carbon atoms adopt two sets of alternate orientation that are related by rotation. The site occupancy factors of two sets are 50%. Two sets are represented by solid line and open line, respectively. Positions of hydrogen atoms on the disordered solvent ligands were not calculated.

Figure 13. Solid-state (KBr) IR spectra of $\{K(THF)_4\}_2\{Eu\{(\mu\text{-}H)_2BC_8H_{14}\}_4\}$, **3**.

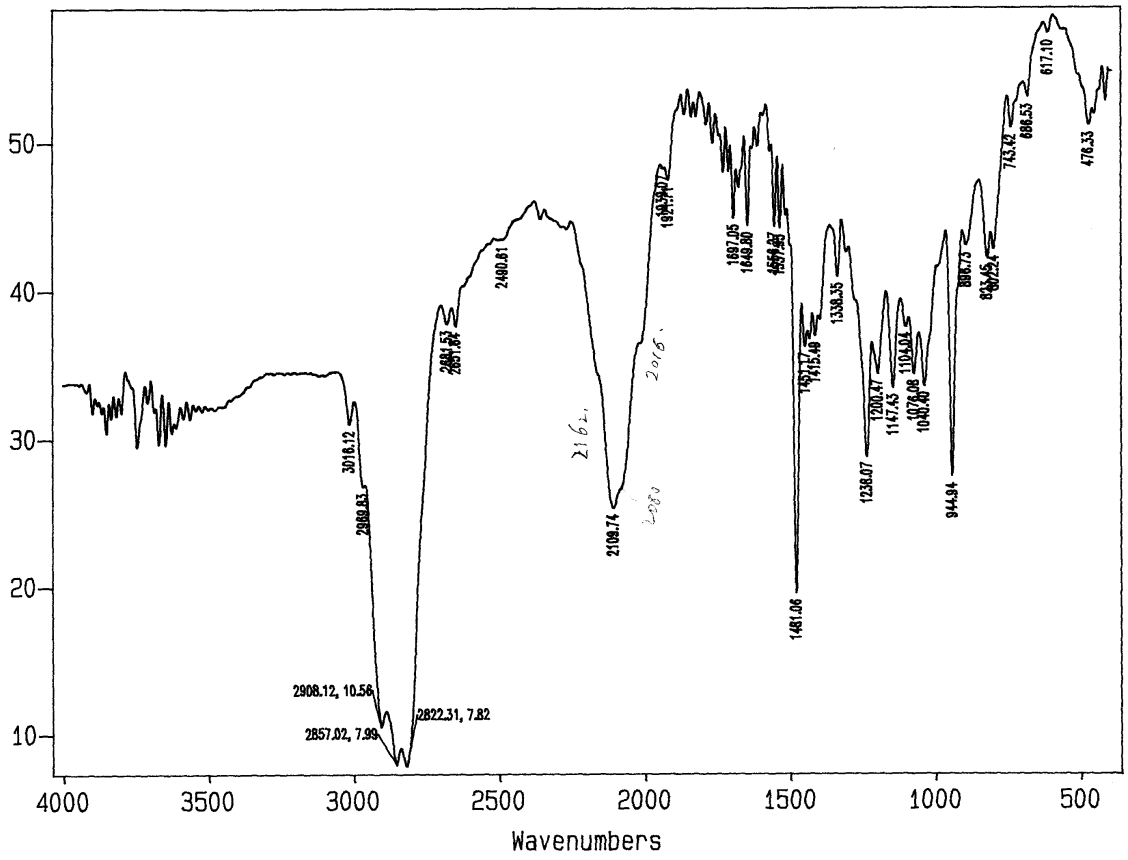


Figure 14. Solid-state (KBr) IR spectra of $\{K(THF)_4\}_2\{Yb\{(\mu\text{-}H)_2BC_8H_{14}\}_4\}$, **4**.

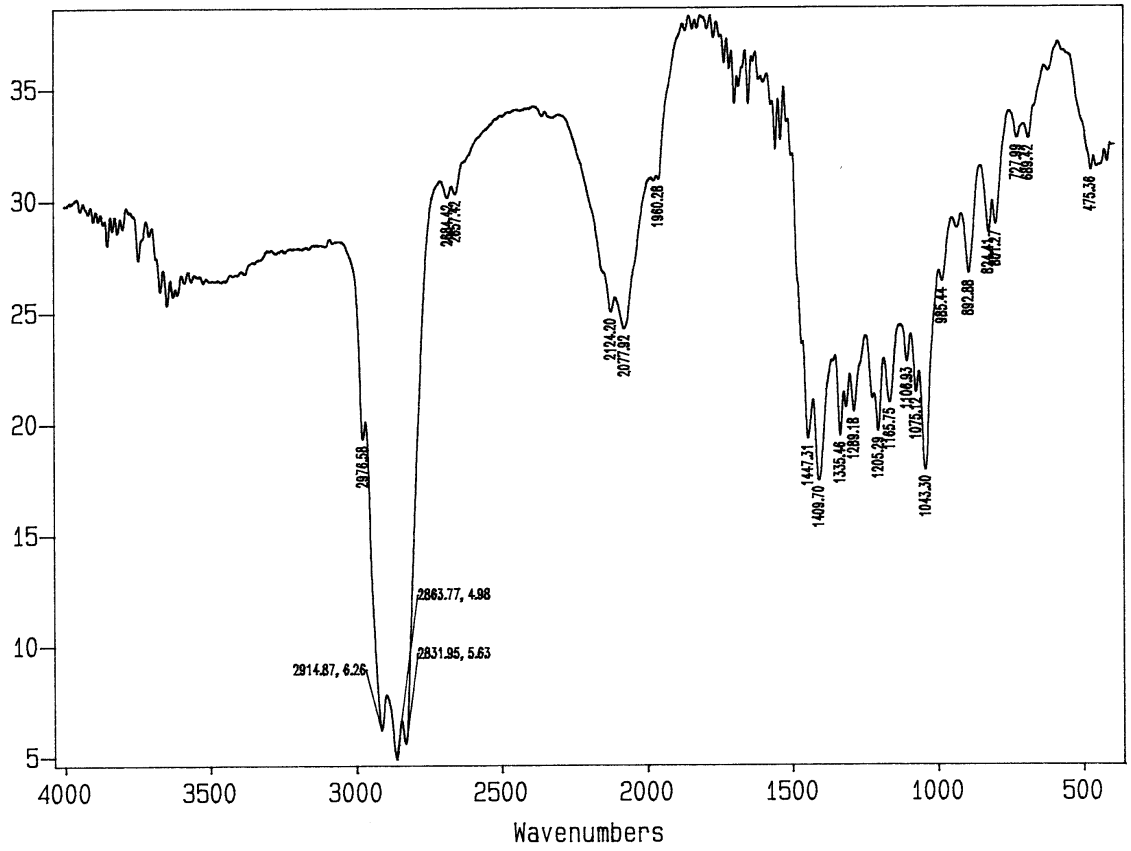


Figure 15. Solid-state (KBr) IR spectra of $[NMe_4]_2[Eu\{(\mu\text{-}H)_2BC_8H_{14}\}_4]$, **5**.

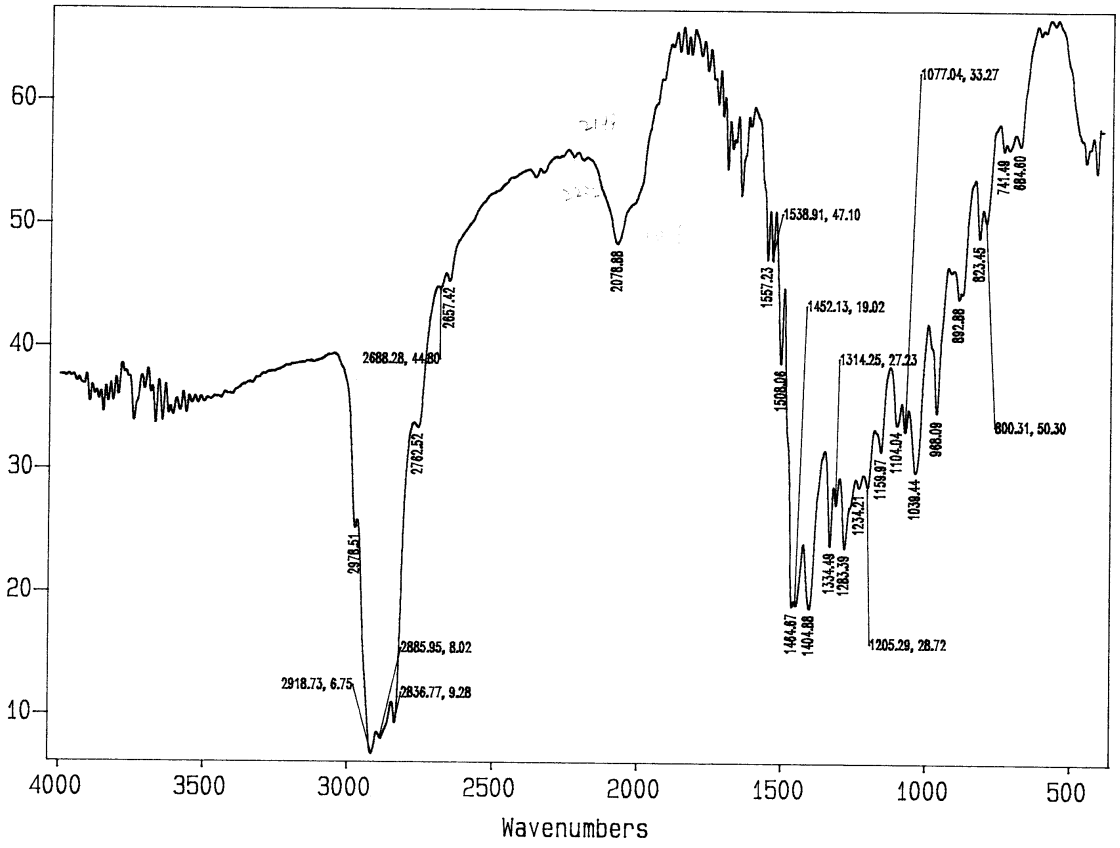


Figure 16. Solid-state (KBr) IR spectra of $[NMe_4]_2[Yb\{(\mu\text{-}H)_2BC_8H_{14}\}_4]$, **6.**

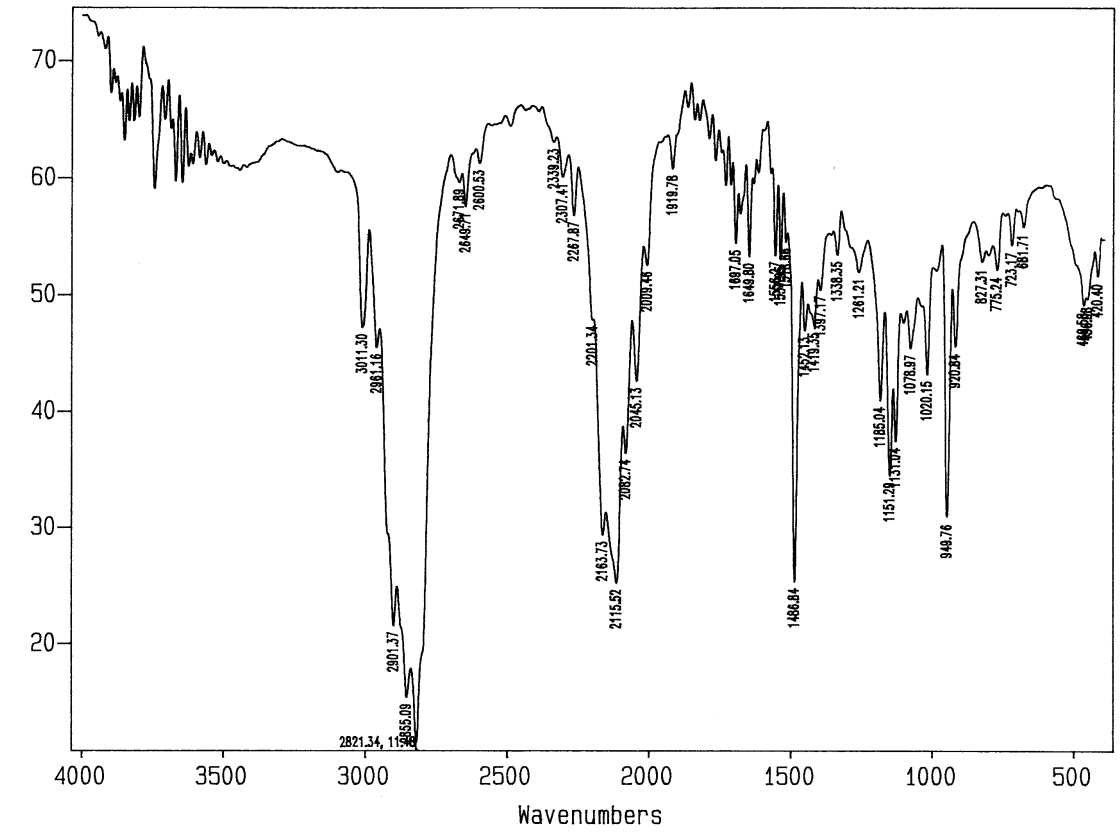


Figure 17. Solid-state (KBr) IR spectra of $\{K(MeTHF)_3\}_2\{Eu\{(\mu\text{-}H)_2BC_8H_{14}\}_4\}$, **7.**

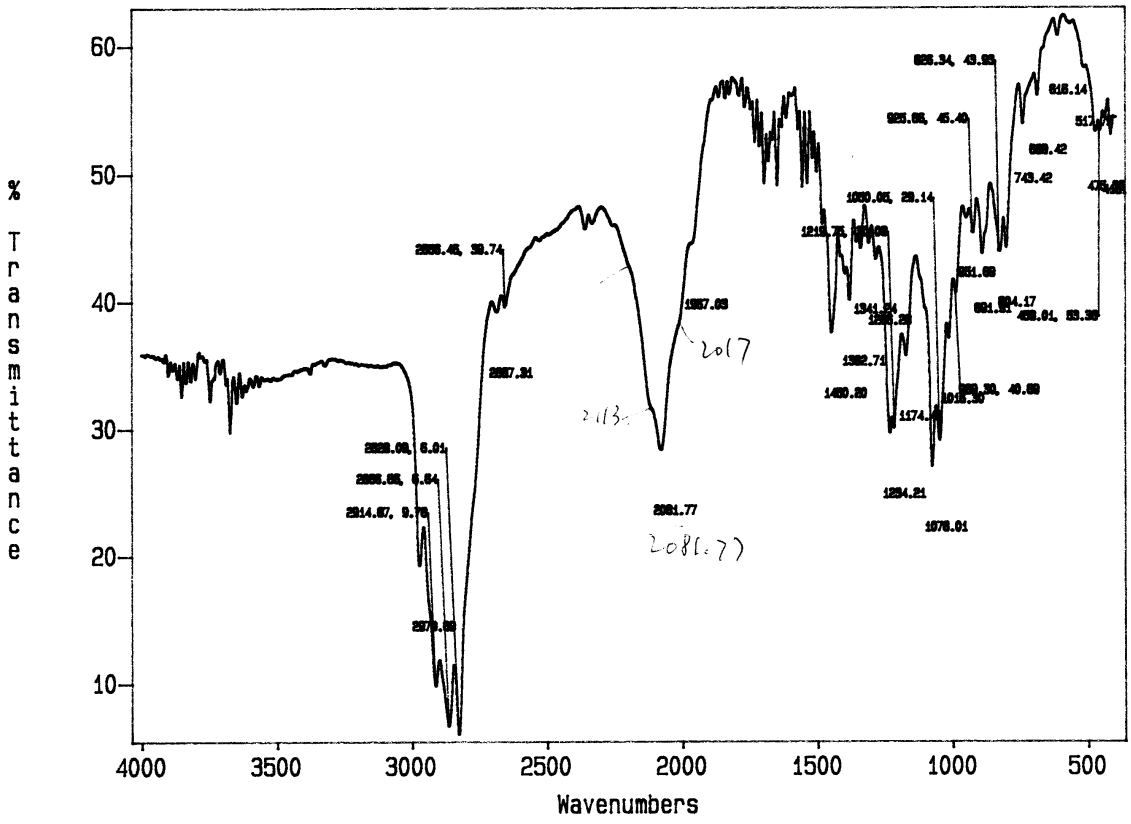


Figure 18. Solid-state (KBr) IR spectra of $\{K(MeTHF)_3\}_2\{Yb\{(\mu\text{-}H)_2BC_8H_{14}\}_4\}$, **8.**