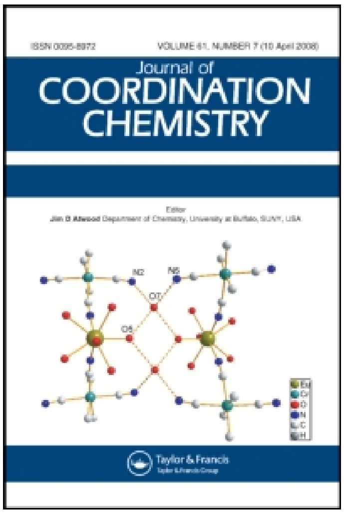

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Structural studies of mono(pentamethylcyclopentadienyl)-lanthanide complexes

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The mono(pentamethylcyclopentadienyl) lanthanide complexes $[(C_5Me_5)Yb(\mu\text{-}I)(\mu\text{-}\eta^5{:}\eta^5\text{-}C_5Me_5)Yb(C_5Me_5)]_n$ (**1**), $\{[(C_5Me_5)Sm]_3(\mu\text{-}Cl)_4(\mu_3\text{-}Cl)(\mu_3\text{-}OH)(THF)\}_2$ (**2**), $\{[(C_5Me_5)Sm]_2(\mu\text{-}OH)(\mu\text{-}Cl)_4(\mu_3\text{-}Cl)Mg(THF)_2\}_2$ (**3**), $[(C_5Me_5)_2Sm](\mu\text{-}Cl)_6(\mu_3\text{-}Cl)_2(\mu_4\text{-}Cl)[(C_5Me_5)Sm]_4$ (**4**), $\{[(C_5Me_5)Nd]_3(\mu_3\text{-}Cl)_4(\mu_4\text{-}Cl)_2(\mu_3\text{-}O_2CPh)_2K_2(\eta^6\text{-}C_7H_8)\}_2$ (**5**), $[(C_5Me_5)Nd(C_8H_8)]_2(\mu\text{-}dioxane)$ (**6**), $[(C_5Me_5)Yb(MeO^tBu)]_2(\mu\text{-}\eta^8{:}\eta^8\text{-}C_8H_8)$ (**7**), $[(C_5Me_5)Dy(\mu\text{-}I)_2]_3$ (**8**), and $[(C_5Me_5)Tm(MeCN)_6]I_2$ (**9**), have been identified by X-ray crystallography. **1** is unusual in that it has a $\mu\text{-}\eta^5{:}\eta^5\text{-}C_5Me_5$ ring that generates a local bent metallocene environment around ytterbium. Complexes **2**–**5** demonstrate the versatility of bridging chlorides in generating a variety of structures for mono(pentamethylcyclopentadienyl) lanthanide halides. Complex **6** shows how dioxane can generate a crystallographically-analyzable complex by bridging two mixed-ligand metallocene units that do not readily crystallize with THF. The structure of **7** shows how methyl tert-butyl ether (MTBE) ligates a lanthanide. Complex **8** is a trimeric cyclopentadienyl lanthanide halide unusual in that it has six bridging halides that roughly define a trigonal prism. Complex **9** constitutes an organometallic example of a lanthanide in which acetonitrile completely displaces iodide counterions.

Keywords: Lanthanide; Pentamethylcyclopentadienyl; Bridging halides; MTBE; Dioxane

1. Introduction

The $(C_5Me_5)^{1-}$ ligand is prevalent in organometallic f element chemistry and is found predominantly in bis(pentamethylcyclopentadienyl) complexes [1]. Hence, mono(pentamethylcyclopentadienyl) complexes remain relatively rare [2], as do tris species [3]. In the course of our studies of $(C_5Me_5)^{1-}$ lanthanide systems, several complexes have been inadvertently obtained and identified by X-ray crystallography that contain a single $(C_5Me_5)^{1-}$ ligand per lanthanide metal. Since these complexes were neither the main nor the intended products of the studies that produced them, we have not pursued their chemistry in detail. However, the structural data reveal that a wider range of

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mono(pentamethylcyclopentadienyl) lanthanide complexes do exist. We report here the structures of eight examples which broaden the diversity of structural possibilities known for this class. In addition, we report the structure of a ninth complex of this type, namely, $[(C_5Me_5)Yb(MeO^tBu)]_2(\mu\text{-}\eta^8:\eta^8\text{-}C_8H_8)$, that was prepared specifically in high yield to evaluate the coordination chemistry of methyl tert-butyl ether (MTBE) with the lanthanides.

2. Results and discussion

2.1. $[(C_5Me_5)Yb(\mu\text{-}I)(\mu\text{-}\eta^5:\eta^5\text{-}C_5Me_5)Yb(C_5Me_5)]_n$ (1)

Complex **1** crystallizes as a chain structure, figure 1, generated by alternating divalent $(C_5Me_5)YbI$ and $(C_5Me_5)_2Yb$ sub-units. Each Yb is ligated by one terminal $(C_5Me_5)^{1-}$ ring, one bridging $(C_5Me_5)^{1-}$ ring, and a bridging iodide to give a formal coordination number of seven. The $M(\mu-\eta^5:\eta^5-C_5Me_5)M'$ arrangement is known for lanthanides and alkali metals, but generally involves an alkali metal on one side and a lanthanide on the other [4–9]. The formation of a lanthanide based $Ln(\mu\text{-}\eta^5:\eta^5\text{-}C_5Me_5)Ln$ inverse sandwich is rare. However, this type of structure was observed in the first structurally characterized divalent ytterbium cyclopentadienyl complex, $[(MeC_5H_4)(THF)Yb(\mu\text{-}\eta^5:\eta^5\text{-}MeC_5H_4)]_n$ [10].

Crystallographic details on **1** are given in table 1 and bond lengths and angles in table 2. Complex **1** has a kinked chain structure since the Yb(1)–(C_5Me_5 ring centroid)–Yb(1A) linkage is linear and the Yb(1)–I(1)–Yb(1A) angle is 119.41(1)°. The 141.8° (C_5Me_5)–Yb(1)–(C_5Me_5) ring centroid angle is slightly smaller than the 145–146° analogs found in $(C_5Me_5)_2Yb$ [1112] which is reasonable considering the additional presence of iodide in the coordination sphere of **1**. The 2.468 Å Yb-(bridging C_5Me_5 ring centroid) distance is larger than the 2.383 Å Yb-(terminal C_5Me_5 ring centroid)

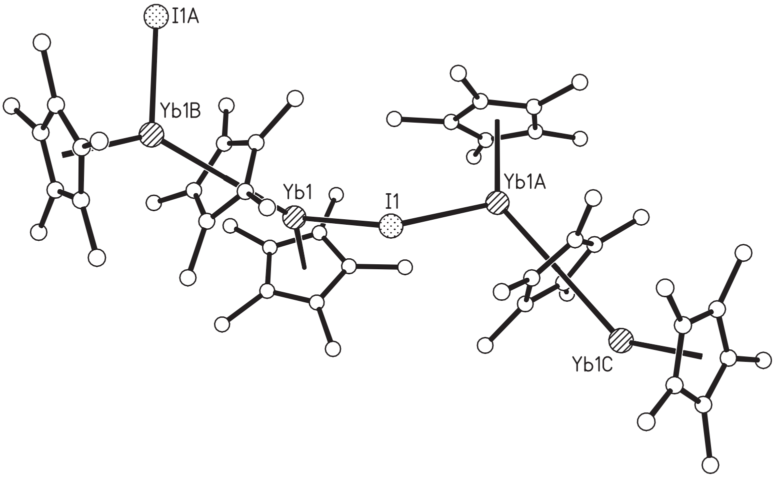

Figure 1. Ball-and-stick plot of $[(C_5Me_5)Yb(\mu\text{-}I)(\mu\text{-}\eta^5:\eta^5\text{-}C_5Me_5)Yb(C_5Me_5)]_n$ (**1**). Hydrogen atoms and carbon labels have been omitted for clarity.

Table 1. X-ray data collection parameters for $[(C_5Me_5)Yb(\mu\text{-}I)(\mu\text{-}\eta^5:\eta^5\text{-}C_5Me_5)Yb(C_5Me_5)]_n$ (**1**), $\{[(C_5Me_5)Sm]_3(\mu\text{-}Cl)_4(\mu_3\text{-}Cl)(\mu_3\text{-}OH)(THF)\}_2$ (**2**), $\{[(C_5Me_5)Sm]_2(\mu\text{-}OH)(\mu\text{-}Cl)_4(\mu_3\text{-}Cl)Mg(THF)_2\}_2$ (**3**), $[(C_5Me_5)_2Sm](\mu\text{-}Cl)_6(\mu_3\text{-}Cl)_2(\mu_4\text{-}Cl)[(C_5Me_5)Sm]_4$ (**4**), $\{[(C_5Me_5)Nd]_3(\mu_3\text{-}Cl)_4(\mu_4\text{-}Cl)_2(\mu_3\text{-}O_2CPh)_2K_2(\eta^6\text{-}C_7H_8)\}_2$ (**5**), $[(C_5Me_5)Nd(C_8H_8)]_2(\mu\text{-dioxane})$ (**6**), $[(C_5Me_5)Yb(MeO^tBu)]_2(\mu\text{-}\eta^8:\eta^8\text{-}C_8H_8)$ (**7**), $[(C_5Me_5)Dy(\mu\text{-}I)_2]_3$ (**8**), and $[(C_5Me_5)Tm(MeCN)_6]I_2$ (**9**).

Empirical formula	$[C_{30}H_{45}IYb_2]_\infty$ (**1**)	$C_{68}H_{108}Cl_{10}O_4Sm_6 \cdot 2(C_6H_6)$ **2** $\cdot 2(C_6H_6)$	$C_{56}H_{94}Cl_{10}Mg_2O_6Sm_4$ (**3**)
Formula weight	878.64	2402.36	1867.83
Temperature (K)	163(2)	163(2)	203(2)
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	*Fddd*	$P2_1/n$	$P\bar{1}$
a (Å)	15.5411(17)	17.2947(7)	12.4802(6)
b (Å)	26.007(3)	14.5116(6)	13.1166(6)
c (Å)	29.444(3)	18.0597(7)	13.4595(6)
α (°)	90	90	74.4430(10)
β (°)	90	91.5630(10)	72.7530(10)
γ (°)	90	90	74.3860(10)
Volume (Å^3)	11900(2)	4530.8(3)	1983.60(16)
Z	16	2	1
ρ_{calcd} (Mg m^{-3})	1.962	1.761	1.564
μ (mm^{-1})	7.301	4.163	3.307
R_1[a] ($I > 2.0\sigma(I)$)	0.0167	0.0233	0.0439
wR_2[b] (all data)	0.0409	0.0601	0.1529

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]]^{1/2}$.

Empirical formula	$C_{60}H_{90}Cl_9Sm_5 \cdot C_6H_{14}$ **4** $\cdot C_6H_{14}$	$C_{102}H_{126}Cl_{12}K_4Nd_6O_8 \cdot 6(C_7H_8)$ **5** $\cdot 6(C_7H_8)$	$C_{40}H_{54}Nd_2O_2$ (**6**)
Formula weight	1968.29	3480.07	855.31
Temperature (K)	183(2)	163(2)	163(2)
Crystal system	Orthorhombic	Triclinic	Tetragonal
Space group	*Pbcn*	$P\bar{1}$	$I4_1/a$
a (Å)	15.4831(5)	15.869(4)	20.263(3)
b (Å)	20.3874(7)	16.557(4)	20.263(3)
c (Å)	49.5500(17)	17.424(5)	17.477(4)
α (°)	90	111.339(4)	90
β (°)	90	104.197(4)	90
γ (°)	90	108.921(4)	90
Volume (Å^3)	15641.0(9)	3675.0(17)	7176(2)
Z	8	1	8
ρ_{calcd} (Mg m^{-3})	1.672	1.572	1.583
μ (mm^{-1})	4.037	2.464	2.894
R_1 ($I > 2.0\sigma(I)$)	0.0440	0.0767	0.0983
wR_2 (all data)	0.1083	0.2546	0.2245

(*continued*)

distance as is typical of bridging versus terminal ligands. The latter is equivalent to the 2.38 Å distance in $(C_5Me_5)_2Yb$ [11] and is in the divalent range [12]. For example, $[(C_5Me_5)Yb)]_2(\mu\text{-}\eta^8:\eta^8\text{-}C_8H_8)$ has 2.338 and 2.346 Å Yb-(terminal C_5Me_5 ring centroid) distances [13].

The iodide ligand is located symmetrically between the Yb centers with 3.0536(3) Å distances to both Yb(1) and Yb(1A). However, two different (C_5Me_5 ring centroid)–Yb–I angles are present: 103.2 and 111.5°. In contrast, the Yb–I–Yb angles in $[(C_5Me_5)(THF)_2Yb(\mu\text{-}I)]_2$ and $[(C_5Me_5)(DME)Yb(\mu\text{-}I)]_2$ are 95.8 and 91.7°, respectively [14]. The pairs of

Table 1. Continued.

Empirical formula	$C_{38}H_{62}O_2Yb_2$ (**7**)	$C_{30}H_{45}Dy_3I_6$ (**8**)	$C_{22}H_{33}I_2N_6Tm$ (**9**)
Formula weight	896.96	1654.56	804.27
Temperature (K)	158(2)	163(2)	158(2)
Crystal system	Rhombohedral	Cubic	Monoclinic
Space group	$R\bar{3}$	$I\bar{4}3d$	Cc
a (Å)	35.7104(13)	28.3716(10)	19.6977(18)
b (Å)	35.7104(13)	28.3716(10)	11.3372(11)
c (Å)	16.3104(8)	28.3716(10)	26.842(3)
α (°)	90	90	90
β (°)	90	90	91.219(2)
γ (°)	120	90	90
Volume (Å^3)	18012.9(13)	22837.7(14)	5992.9(10)
Z	18	16	8
ρ_{calcd} (Mg m^{-3})	1.488	1.925	1.783
μ (mm^{-1})	4.671	7.143	5.039
R_1 ($I > 2.0\sigma$(I))	0.0413	0.0528	0.0287
wR_2 (all data)	0.1132	0.1720	0.0550

Table 2. Selected bond distances (Å) and angles (°) in $[(C_5Me_5)Yb(\mu\text{-}I)(\mu\text{-}\eta^5:\eta^5\text{-}C_5Me_5)(C_5Me_5)YbI]_n$ (**1**).

Bond distances/angles	**1**
Yb–Cnt1[a]	2.383
Yb–Cnt2[b]	2.468
Yb(1)–I(1)	3.0536(3)
Yb(1A)–I(1)	3.0536(2)
Yb–C(C_5Me_5)[a] avg	2.671(3)
Yb–C(C_5Me_5)[b] avg	2.750(3)
Cnt1–Yb–Cnt2	141.8
Cnt1–Yb–I(1)	111.5
Cnt2–Yb–I(1)	103.2
Yb(1)–I(1)–Yb(1A)	119.410(11)

[a] Cnt1 is terminal C_5Me_5.
[b] Cnt2 is bridging C_5Me_5.

Yb–I distances in these compounds are 3.134(1) and 3.175(1) Å for the former and 3.102(2) and 3.120(2) Å in the latter.

2.2. $\{[(C_5Me_5)Sm]_3(\mu\text{-}Cl)_4(\mu_3\text{-}Cl)(\mu_3\text{-}OH)(THF)\}_2$(2), $\{[(C_5Me_5)Sm]_2(\mu\text{-}OH)(\mu\text{-}Cl)_4(\mu_3\text{-}Cl)Mg(THF)_2\}_2$(3), $[(C_5Me_5)_2Sm](\mu\text{-}Cl)_6(\mu_3\text{-}Cl)_2(\mu_4\text{-}Cl)[Sm(C_5Me_5)]_4$(4), and $\{[(C_5Me_5)Nd]_3(\mu_3\text{-}Cl)_4(\mu_4\text{-}Cl)_2(\mu_3\text{-}O_2CPh)_2K_2(\eta^6\text{-}C_7H_8)\}_2$(5)

In complexes **2**–**5**, all of the lanthanide ions are trivalent. The structures are comprised of variations of the common bridged trimetallic unit, $Ln_3(\mu_3\text{-}X)_2(\mu\text{-}X)_3$ (X = anion) that has been observed in many types of lanthanide complexes [15–20]. The polymetallic complexes **2**, **3**, and **5** have two of these trimetallic units. In **2** and **5**, all of the metals are lanthanides; in **3** each trimetallic unit contains two samarium ions and one magnesium. In pentametallic **4**, two trimetallic units share an edge to make a butterfly arrangement of four samarium atoms to which a trivalent bis(cyclopentadienyl) metallocene unit,

$[(C_5Me_5)_2Sm]^{1+}$, is attached by two bridging chlorides. Each metal in the trimetallic units in **2**–**5** has one terminal $(C_5Me_5)^{1-}$ ligand attached except for the magnesium ions in **3**, which are ligated by two THF molecules, and Sm(1) in **4**, which is part of a conventional metallocene moiety.

The simplest of these four structures is **2**, figure 2 and table 3. Each metal in the $Ln_3(\mu_3\text{-X})_2(\mu\text{-X})_3$ unit is samarium, each (μ-X) is chloride, Cl(2)–Cl(4), one (μ_3-X) is chloride, Cl(1), and the other is hydroxide. Each metal has one terminal monodentate ligand in addition to the terminal $(C_5Me_5)^{1-}$ group. One metal in each triangle, Sm(3), has a terminal THF as the additional ligand. The other two metals in each triangle have chloride ligands, Cl(5), which are shared between and connect the two $M_3(\mu_3\text{-X})_2(\mu\text{-X})_3$ units. Overall, each metal has a total formal coordination number of eight. Despite the smaller size of the hydroxide ligand, it is able to substitute for a chloride in the $Ln_3(\mu_3\text{-X})_2(\mu\text{-X})_3$ framework without leading to large distortions.

Complex **3**, figure 3 and table 4, is similar to **2** in that each (μ-X) is chloride, Cl(1) and Cl(3)–Cl(5), one (μ_3-X) is chloride, Cl(2), and the other is hydroxide. Again the two triangles are connected by two chloride bridges: Cl(3) in this case. As in **2**, incorporation of a smaller component in the $Ln_3(\mu_3\text{-X})_2(\mu\text{-X})_3$ framework, in this case magnesium, does not significantly alter the overall structure. The 2.442(4) and 2.465(4) Å Sm-O(μ_3-OH) distances in **3** are similar to the analogous 2.474(2) Å length in **2**.

The edge shared triangle structure found in **4**, figure 4 and table 5, has been observed before [16] and is identical to that of $[(C_5Me_5)_2Yb](\mu\text{-F})_6(\mu_3\text{-F})_2(\mu_4\text{-F})[Yb(C_5Me_5)]_4$ [18]. Hence, the larger metal/larger halide Sm/Cl combination in **4** can generate the

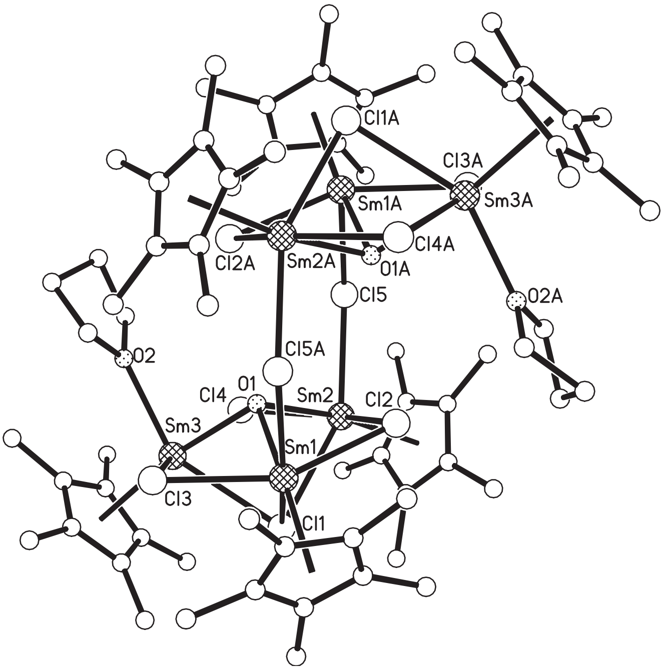

Figure 2. Ball-and-stick plot of $\{[(C_5Me_5)Sm]_3(\mu\text{-Cl})_4(\mu_3\text{-Cl})(\mu_3\text{-OH})(THF)\}_2$ (**2**). Hydrogen atoms and carbon labels have been omitted for clarity.

Table 3. Selected bond distances (Å) and angles (°) in $\{[(C_5Me_5)Sm]_3(\mu\text{-}Cl)_4(\mu_3\text{-}Cl)(\mu_3\text{-}OH)(THF)\}_2$ (**2**).

Bond distances/angles	**2**
Sm(1)–Cnt1/Sm(1A)–Cnt4	2.413
Sm(2)–Cnt2/Sm(2A)–Cnt5	2.412
Sm(3)–Cnt3/Sm(3A)–Cnt6	2.411
Sm(1)–C(C_5Me_5) avg	2.696(3)
Sm(2)–C(C_5Me_5) avg	2.691(3)
Sm(3)–C(C_5Me_5) avg	2.698(3)
Sm(1)–Cl(1)*	2.8691(7)
Sm(1)–Cl(2)	2.7815(7)
Sm(1)–Cl(3)	2.7452(8)
Sm(1)–Cl(5A)	2.7418(8)
Sm(1)–O(1)	2.474(2)
Sm(2)–Cl(1)	2.8828(7)
Sm(2)–Cl(2)	2.7730(8)
Sm(2)–Cl(4)	2.7851(8)
Sm(2)–Cl(5)	2.7311(7)
Sm(2)–O(1)	2.446(2)
Sm(3)–Cl(1)	2.8920(7)
Sm(3)–Cl(3)	2.7495(8)
Sm(3)–Cl(4)	2.7710(8)
Sm(3)–O(1)	2.443(2)
Sm(3)–O(2)	2.409(2)
Sm(1)–Cl(5A)–Sm(2A)	144.50(3)

*μ-Cl: Cl(2,3,4,5) μ_3-Cl: Cl(1).

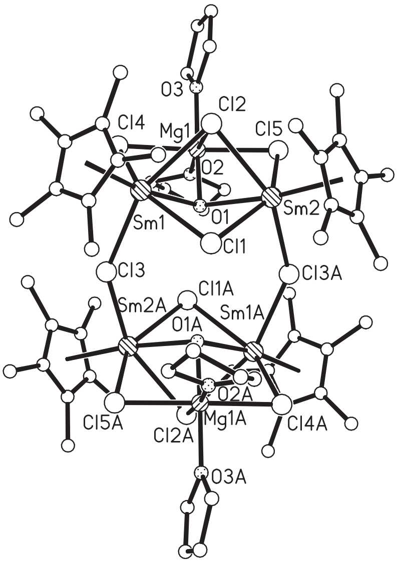

Figure 3. Ball-and-stick plot of$\{[(C_5Me_5)Sm]_2(\mu\text{-}OH)(\mu\text{-}Cl)_4(\mu_3\text{-}Cl)Mg(THF)_2\}_2$ (**3**). Hydrogen atoms and carbon labels have been omitted for clarity.

same structure as that formed in an Yb/F complex. The most unusual part of this structure is the Cl(3) ligand which bridges two wing tip samarium positions. This gives a nearly linear Sm(2)–Cl(3)–Sm(2) angle of 178.37(7)°. In comparison the analogous Yb(1)–F(1)–Yb(2) angle in $(C_5Me_5)_6Yb_5F_9$ is 170.5(2)°. The $[(C_5Me_5)_2Sm(\mu\text{-}Cl)_2]^{1-}$

Table 4. Selected bond distances (Å) and angles (°) in $\{[(C_5Me_5)Sm]_2(\mu\text{-}OH)(\mu\text{-}Cl)_4(\mu_3\text{-}Cl)Mg(THF)_2\}_2$ (**3**).

Bond distances/angles	**3**
Sm(1)–Cnt1/Sm(1A)–Cnt3	2.404/2.406
Sm(2)–Cnt2/Sm(2A)–Cnt4	2.414/2.416
Sm(1)–C(C_5Me_5) avg	2.686(6)
Sm(2)–C(C_5Me_5) avg	2.692(8)
Sm(1)–Cl(1)*	2.8160(16)
Sm(1)–Cl(2)	2.8170(17)
Sm(1)–Cl(3)	2.7274(18)
Sm(1)–Cl(4)	2.7398(18)
Sm(1)–O(1)	2.465(4)
Sm(2)–O(1)	2.442(4)
Mg(1)–Cl(2)	2.871(3)
Mg(1)–Cl(4)	2.465(3)
Mg(1)–Cl(5)	2.482(3)
Mg(1)–O(1)	2.023(5)
Mg(1)–O(2)	2.043(5)
Mg(1)–O(3)	2.027(6)
Sm(1)–Cl(3)–Sm(2A)	143.04(8)
Sm(1)–Cl(2)–Sm(2)	86.55(4)
Sm(1)–Cl(1)–Sm(2)	86.77(4)
Sm(1)–Cl(4)–Mg(1)	83.60(7)
Sm(2)–Cl(5)–Mg(1)	83.46(7)
Sm(1)–O(1)–Sm(2)	103.47(14)

*μ-Cl: Cl(1,3,4,5) μ_3-Cl: Cl(2).

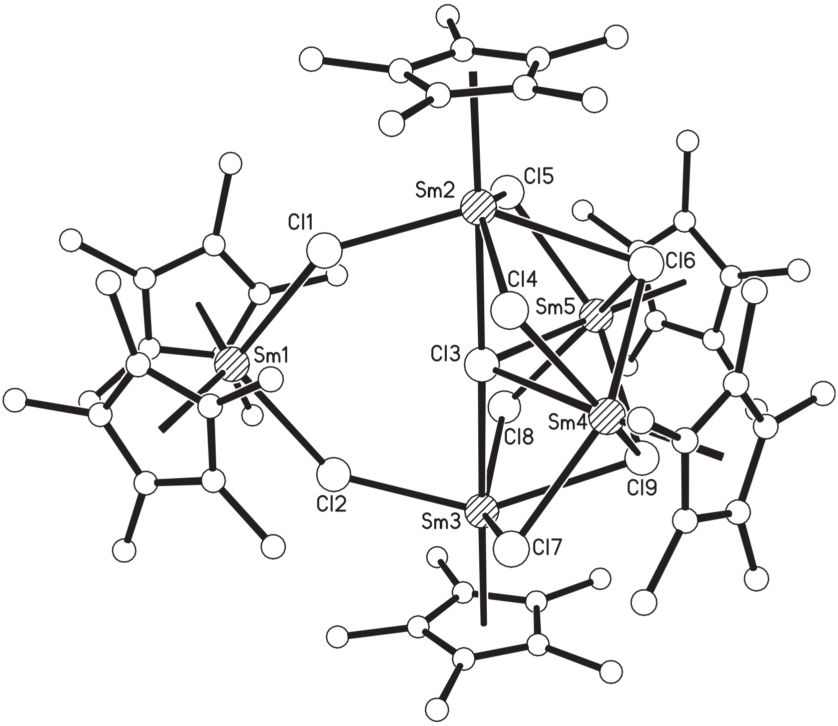

Figure 4. Ball-and-stick plot of $[(C_5Me_5)_2Sm](\mu\text{-}Cl)_6(\mu_3\text{-}Cl)_2(\mu_4\text{-}Cl)[Sm(C_5Me_5)]_4$ (**4**). Hydrogen atoms and carbon labels have been omitted for clarity.

Table 5. Selected bond distances (Å) and angles (°) in $[(C_5Me_5)_2Sm](\mu\text{-}Cl)_6(\mu_3\text{-}Cl)_2(\mu_4\text{-}Cl)[(C_5Me_5)Sm]_4$ (**4**).

Bond distances/angles	**4**
Sm(1)–Cnt1	2.431
Sm(1)–Cnt2	2.433
Sm(2)–Cnt3	2.376
Sm(3)–Cnt4	2.373
Sm(4)–Cnt5	2.371
Sm(5)–Cnt6	2.369
Sm(1)–C(C_5Me_5) avg	2.702(9)
Sm(1)–Cl(1)*	2.764(2)
Sm(1)–Cl(2)	2.754(2)
Sm(2)–Cl(1)	2.713(2)
Sm(2)–Cl(3)	2.897(2)
Sm(2)–Cl(4)	2.771(2)
Sm(2)–Cl(5)	2.770(2)
Sm(2)–Cl(6)	3.009(2)
Sm(3)–Cl(2)	2.700(2)
Sm(3)–Cl(3)	2.878(2)
Sm(3)–Cl(7)	2.794(2)
Sm(3)–Cl(8)	2.760(2)
Sm(3)–Cl(9)	2.995(2)
Sm(4)–Cl(3)	2.914(2)
Sm(4)–Cl(4)	2.733(2)
Sm(4)–Cl(6)	2.873(2)
Sm(4)–Cl(7)	2.746(2)
Sm(4)–Cl(9)	2.876(2)
Sm(5)–Cl(3)	2.928(2)
Sm(5)–Cl(5)	2.743(2)
Sm(5)–Cl(6)	2.869(2)
Sm(5)–Cl(8)	2.721(2)
Sm(5)–Cl(9)	2.850(2)
Cnt1–Sm(1)–Cnt2	136.7
Cnt1–Sm(1)–Cl(1)	102.5
Cnt1–Sm(1)–Cl(2)	104.1
Cnt2–Sm(1)–Cl(1)	104.1
Cnt2–Sm(1)–Cl(2)	101.5
Cnt3–Sm(2)–Cl(1,4,5,6) avg	107.1
Cnt3–Sm(2)–Cl(3)	178.6
Cnt4–Sm(3)–Cl(2,7,8,9) avg	106.4
Cnt4–Sm(3)–Cl(3)	178.6
Cnt5–Sm(4)–Cl(4,6,7,9) avg	107.3
Cnt5–Sm(4)–Cl(3)	177.1
Cnt6–Sm(5)–Cl avg	107.6
Cnt6–Sm(5)–Cl(3)	178.3
Sm(1)–Cl(1)–Sm(2)	143.67(8)
Sm(1)–Cl(2)–Sm(3)	142.12(8)
Sm(2)–Cl(3)–Sm(3)	178.37(7)
Sm(2)–Cl(3)–Sm(4)	90.54(5)
Sm(3)–Cl(3)–Sm(4)	91.09(5)
Sm(2)–Cl(3)–Sm(5)	90.55(5)
Sm(3)–Cl(3)–Sm(5)	89.44(5)
Sm(2)–Cl(4)–Sm(4)	97.17(6)
Sm(2)–Cl(5)–Sm(5)	97.33(6)
Sm(2)–Cl(6)–Sm(4)	89.12(5)
Sm(2)–Cl(6)–Sm(5)	89.51(5)
Sm(4)–Cl(6)–Sm(5)	92.79(6)
Sm(3)–Cl(7)–Sm(4)	96.53(6)
Sm(3)–Cl(8)–Sm(5)	96.40(6)
Sm(3)–Cl(9)–Sm(4)	89.50(5)
Sm(3)–Cl(9)–Sm(5)	88.67(5)
Sm(4)–Cl(9)–Sm(5)	93.12(6)

*μ-Cl: Cl(1,2,4,5,7,8) μ_3-Cl: Cl(6,9), μ_4-Cl: Cl(3).

metallocene moiety connected to the Sm(4) butterfly unit has conventional bond distances and angles [12, 21].

The most complicated of the triangulated polymetallics is **5**. As shown in figures 5 and 6, this complex has the two Nd_3 sub-units connected by a planar K–Cl–K–Cl ring as well as four additional KO_2CPh moieties. Each carboxylate has both oxygen atoms

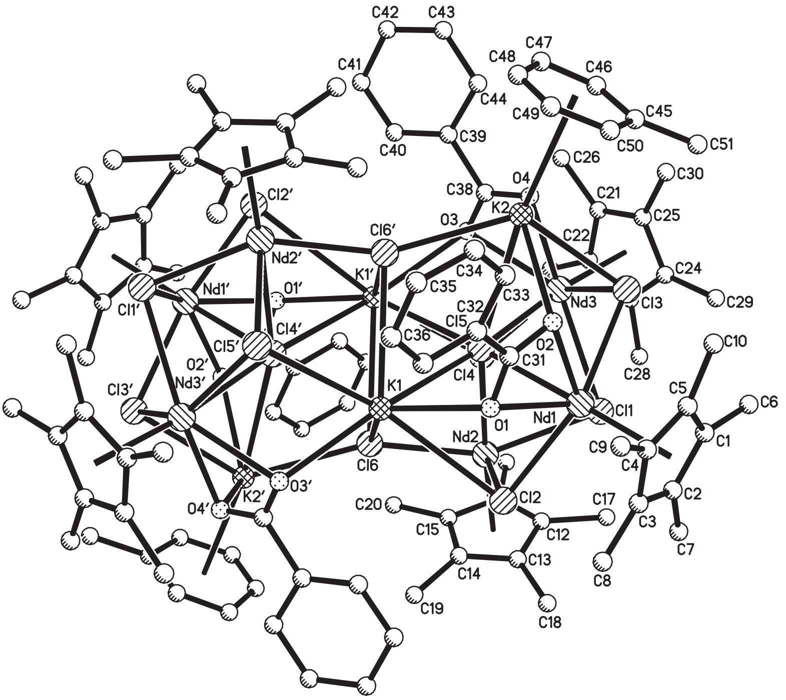

Figure 5. Ball-and-stick plot of $\{[(C_5Me_5)Nd]_3(\mu_3\text{-}Cl)_4(\mu_4\text{-}Cl)_2(\mu_3\text{-}O_2CPh)_2K_2(\eta^6\text{-}C_7H_8)\}_2$ (**5**).

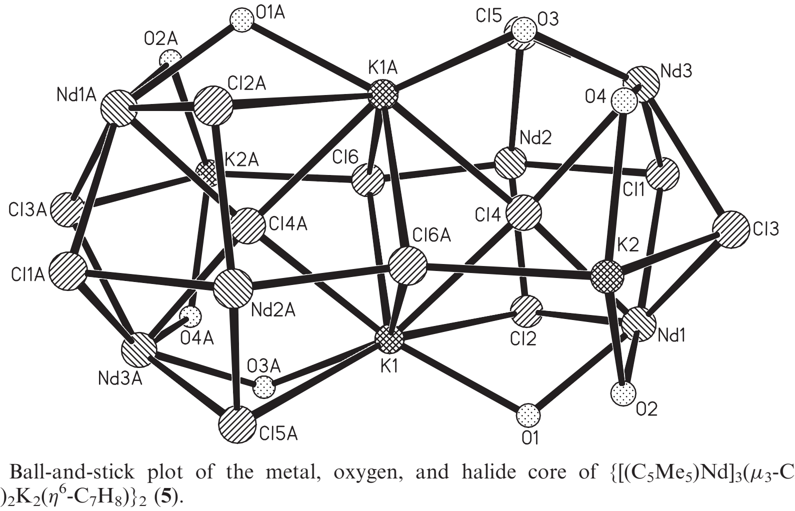

Figure 6. Ball-and-stick plot of the metal, oxygen, and halide core of $\{[(C_5Me_5)Nd]_3(\mu_3\text{-}Cl)_4(\mu_4\text{-}Cl)_2(\mu_3\text{-}O_2CPh)_2K_2(\eta^6\text{-}C_7H_8)\}_2$ (**5**).

coordinated to a neodymium, i.e. the carboxylate is bidentate to the lanthanide. Each carboxylate oxygen is also attached to a potassium ion such that each carboxylate bridges three different metals with a total of four connections. Two of the potassium ions in the structure are additionally ligated with toluene molecules, which have normal K–C(η^6-arene) distances, table 6 [4, 22].

As shown in table 7, the average metal ligand bond distances for the bridging chloride ligands in the samarium complexes **2**–**4** are quite similar. Since **5** has no doubly bridging chlorides, no comparison can be made. Table 7 also shows that triply-bridging chloride ligands have longer average Ln–Cl distances as is typical. However, the ranges that yield these averages can be quite large and indicate that there is quite a bit of flexibility in the bond lengths that lead to the $Ln_3(\mu_3\text{-}X)_2(\mu\text{-}X)_3$ units. The one bridging chloride distance in table 7 that is inconsistent with the others is the 2.718(5) Å Nd-(μ_4-Cl) length which is smaller than the 2.852(5) Nd-(μ_3-Cl) average. This chloride bridges three potassium sites as well as Nd and is evidently more closely associated with the Nd.

Table 6. Selected bond distances (Å) and angles (°) in $\{[(C_5Me_5)Nd]_3(\mu_3\text{-}Cl)_4(\mu_4\text{-}Cl)_2(\mu_3\text{-}O_2CPh)_2K_2(\eta^6\text{-}C_7H_8)\}_2$ (**5**).

Bond distances/angles	**5**
Nd–Cnt avg	2.429
Nd–C(C_5Me_5) avg	2.708(19)
Nd(1)–Cl(1–4) avg*	2.892(5)
Nd(1)–O(1–2) avg	2.527(11)
Nd(2)–Cl(1,2,5,6) avg	2.780(5)
Nd(3)–Cl(1,3,4,5) avg	2.899(5)
Nd(3)–O(3–4) avg	2.524(12)
K(1)–O(1,3A) avg	2.694(14)
K(1)–Cl(4,4A) avg	3.163(6)
K(1)–Cl(6,6A) avg	3.382(7)
K(1)–Cl(2,5A) avg	3.481(6)
K(2)–C(C_7H_8) avg	3.33(3)
K(2)–Cl(3) avg	3.136(6)
K(2)–Cl(6A) avg	3.066(7)
K(2)–O(2) avg	2.693(14)
K(2)–Cl(6A)–Nd(2A)	93.48(16)
K(1A)–Cl(6A)–K(1)	78.60(15)
Cl(6A)–K(1)–Cl(6)	101.41(15)
K(1)–O(1)–Nd(1)	111.1(5)

*μ_3-Cl: Cl(1,2,3,5), μ_4-Cl: Cl(4,6).

Table 7. Ln–Cl and Ln–Cnt bond distances (Å) in **2**–**5**.

Bond distances	**2**	**3**	**4**	**5**
Ln–Cnt	2.411–2.413	2.404–2.414	2.371–2.433	2.403–2.451
avg	2.412	2.409	2.392	2.429
Ln–(μ-Cl)	2.7311(7)–2.7851(8)	2.7125(17)–2.8160(16)	2.700(2)–2.794(2)	
avg	2.7598(5)	2.758(2)	2.748(2)	
Ln–(μ_3-Cl)	2.8813(7)	2.810(2)	2.769(2)–2.912(2)	2.769(5)–2.971(5)
avg			2.850(2)	2.852(5)
Ln–(μ_4-Cl)			2.904(2)	2.718(5)*

*Nd(2)–Cl(6) distance; Cl(6) bridges Nd(2) and K(1), K(1A), and K(2A).

2.3. *[(C_5Me_5)Nd(C_8H_8)]$_2$(μ-dioxane)(6)*

The structure of complex **6**, figure 7, is a rare example of a *solvated* trivalent mixed ligand cyclopentadienyl, cyclooctatetraenyl compound. Although the crystal structures of many unsolvated (C_5Me_5)Ln(C_8H_8) complexes have been reported (specifically with Ln = Lu, Sm, Dy, Er, Yb [23, 24]), the known THF adducts, (C_5Me_5)Ln(C_8H_8)(THF), have not been crystallographically characterized to our knowledge. The closest complex in the literature is (C_5Me_5)Nd(C_8H_8)(HMPA) (**10**) (HMPA = hexamethylphosphoramide) [25]. Complexes **6** and **10** are structurally similar but the quality of the crystal data does not allow detailed comparisons. Although the structure around the metals in bimetallic **6** is similar to monometallic **10**, it does show that dioxane can be used to obtain crystallographic data on an ether solvated (C_5Me_5)Ln(C_8H_8) complex when apparently the analogous THF complexes, (C_5Me_5)Ln(C_8H_8)(THF), are reluctant to crystallize.

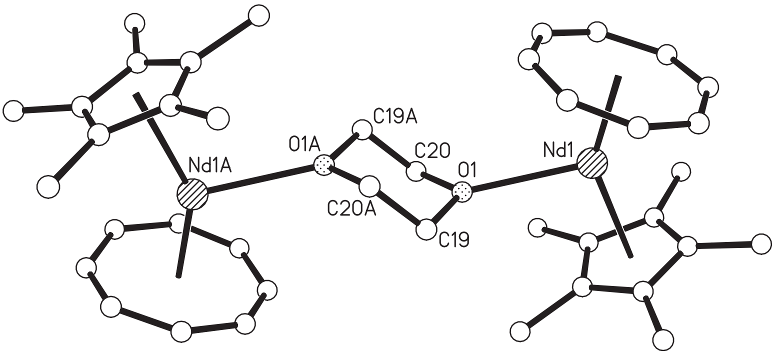

Figure 7. Ball-and-stick plot of [(C_5Me_5)Nd(C_8H_8)]$_2$(μ-dioxane) (**6**).

2.4. *[(C_5Me_5)Yb(MeO^tBu)]$_2$(μ-η^8 : η^8-C_8H_8)(7)*

Complex **7**, figure 8 and table 8, was prepared in high yield to determine if, and how, methyl tert-butyl ether (MTBE) would coordinate to a lanthanide [26]. The unsolvated triple decked bent metallocene, [(C_5Me_5)Yb]$_2$(C_8H_8) [13], was used as the precursor since the complex is a readily prepared diamagnetic lanthanide that is known to make solvates. The divalent [(C_5Me_5)Ln]$_2$(C_8H_8) series [13, 27], like the trivalent (C_5Me_5)Ln(C_8H_8) complexes discussed above are unusual in that there are several X-ray crystal structures of the unsolvated complexes, but no crystallographically determined structures of the known THF adducts, [(C_5Me_5)Ln(THF)$_x$]$_2$(C_8H_8) ($x = 1, 2$). The closest complexes in the literature are the diglyme ligated complex [(C_5Me_5)Sm(diglyme)]$_2$(C_8H_8) [27] and the partially solvated compound [(C_5Me_5)Yb(THF)](μ-η^8 : η^8-C_8H_8)Yb(C_5Me_5) (**11**) [24].

In contrast to the THF ligated complexes, the MTBE derivative of [(C_5Me_5)Yb]$_2$(C_8H_8) crystallizes readily. As in [(C_5Me_5)Ln]$_2$(C_8H_8) [13, 27], the Yb-(C_8H_8 ring centroid)-Yb angle is near linear, 175.8°. The 142.5 and 142.8° (C_5Me_5 ring centroid)-Ln-(C_8H_8 ring centroid) angles in **6** are similar to the 145.5° angle in **11**. The more acute 137.6° angle in [(C_5Me_5)Sm(diglyme)]$_2$(C_8H_8) is a result

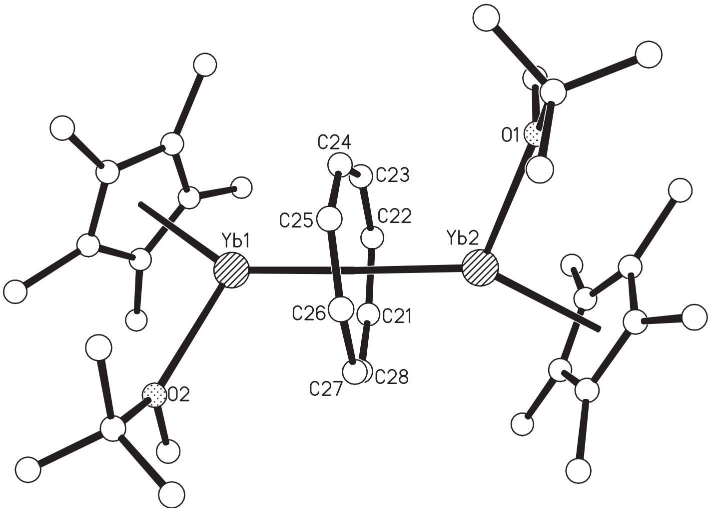

Figure 8. Ball-and-stick plot of $[(C_5Me_5)Yb(MeO^tBu)]_2(\mu\text{-}\eta^8:\eta^8\text{-}C_8H_8)$ (**7**). Hydrogen atoms have been omitted for clarity. Disorder in the $(C_5Me_5)^{1-}$ ligand attached to Yb(1) is not shown.

Table 8. Selected bond distances (Å) and angles (°) in $[(C_5Me_5)Yb(MeO^tBu)]_2(\mu\text{-}\eta^8:\eta^8\text{-}C_8H_8)$ (**7**).

Bond distances/angles	**7**
Yb(1)–Cnt1(C_5Me_5)	2.481
Yb(1)–Cnt2(C_8H_8)	2.096
Yb(2)–Cnt2(C_8H_8)	2.109
Yb(2)–Cnt3(C_5Me_5)	2.438
Yb(1)–C(C_5Me_5) avg	2.741(5)
Yb(1)–C(C_8H_8) avg	2.779(8)
Yb(2)–C(C_8H_8) avg	2.789(8)
Yb(2)–C(C_5Me_5) avg	2.721(6)
Yb(1)–O(1)	2.542(5)
Yb(2)–O(2)	2.533(4)
Yb(1) . . . C(31)	3.370
Yb(2) . . . C(36)	3.666
Cnt1–Yb(1)–Cnt2	142.8
Cnt1–Yb(1)–O(1)	102.8
O(1)–Yb(1)–Cnt2	113.4
Cnt3–Yb(2)–Cnt2	142.5
Cnt3–Yb(2)–O(1)	113.1
O(2)-Yb(2)–Cnt2	103.8
Yb(1)–Cnt2–Yb(2)	175.8
Yb(1)–O(1)–C(29)	105.6(4)
Yb(1)–O(1)–C(30)	138.3(4)
Yb(2)–O(2)–C(34)	107.3(4)
Yb(2)–O(2)–C(35)	135.5(4)

of the presence of the tridentate diglyme and the correspondingly higher coordination number.

The 2.533(4) and 2.542(5) Å Yb-O(MTBE) distances in **7** are significantly longer than the 2.437(4) Yb-O(THF) distance in **11** reflecting the greater steric bulk of MTBE

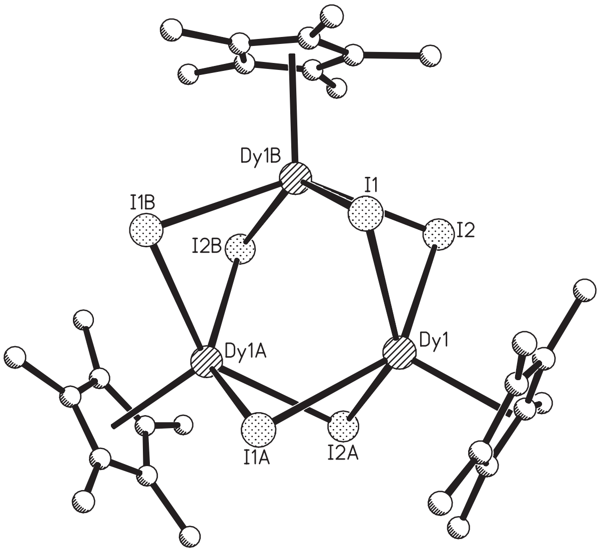

Figure 9. Ball-and-stick plot of $[(C_5Me_5)Dy(\mu\text{-}I)_2]_3$ (**8**). Hydrogen atoms and carbon labels have been omitted for clarity.

as a ligand. The 2.438 and 2.481 Å Yb-(C_5Me_5 ring centroid) distances are longer than the 2.391 Å analog in **11** also reflecting the larger ether. The Yb-(C_8H_8 ring centroid) distances are less affected: 2.096 and 2.109 Å in **7** and 2.087 Å in **11**. Hence, the structural data suggest that when a larger ether is needed, MTBE could be an excellent choice since it provided crystals of **7**, whereas the $[(C_5Me_5)Ln(THF)_x]_2(C_8H_8)$ series remains crystallographically uncharacterized.

2.5. *$[(C_5Me_5)Dy(\mu\text{-}I)_2]_3$(8)*

To our knowledge, the only previously reported mono(pentamethylcyclopentadienyl) lanthanide diiodides that were structurally characterized were the solvates $(C_5Me_5)CeI_2(THF)_3$ [28] and $(C_5Me_5)NdI_2(py)_3$ [29]. The structure of unsolvated **8**, figure 9, has a classic four legged piano stool structure around each Dy with a formal coordination number of seven for each metal. The high symmetry of the structure, with just two crystallographically unique iodide ligands, leads to a trigonal prismatic arrangement of the six iodides. This is best seen from the top view in figure 10. This figure also shows how all three $(C_5Me_5)^{1-}$ rings are similarly aligned. The poor quality of the data did not allow a detailed metrical analysis.

2.6. *$[(C_5Me_5)Tm(MeCN)_6]I_2$(9)*

Although there are numerous structures in the literature in which several acetonitrile ligands are coordinated to a lanthanide metal including homoleptic $[Ln(MeCN)_x]^{n+}$ ions [30–33], complex **9**, figure 11 and table 9, is the first example of an acetonitrile polysolvate containing a $(C_5Me_5)^{1-}$ ligand to our knowledge. The thulium center has a formal coordination number of nine. The two iodide ligands are not located

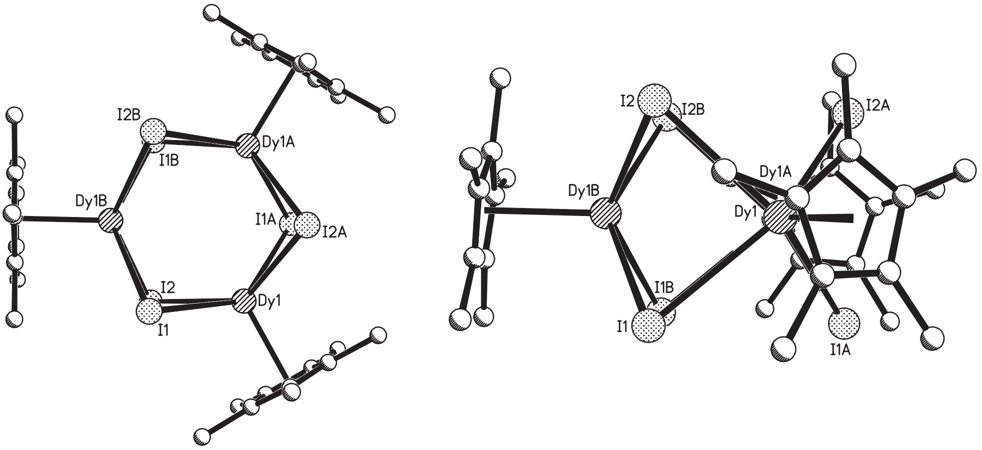

Figure 10. Top (left) and side (right) views of ball-and-stick plot of $[(C_5Me_5)Dy(\mu\text{-}I)_2]_3$ (**8**). Hydrogen atoms and carbon labels have been omitted for clarity.

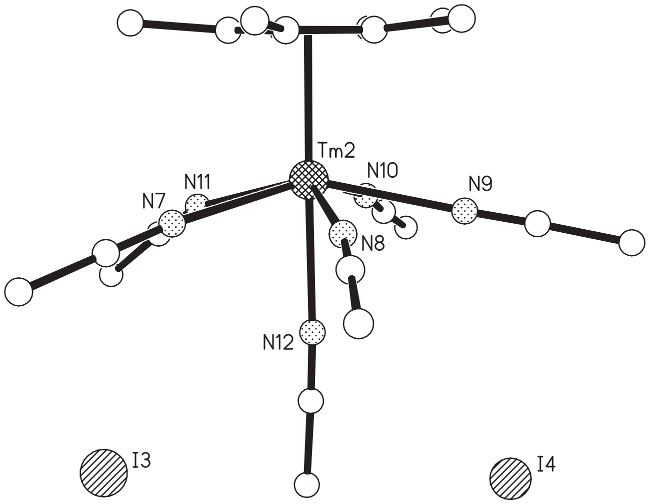

Figure 11. Side view of $[(C_5Me_5)Tm(MeCN)_6]I_2$ (**9**), with the probability ellipsoids drawn at the 50% level. Hydrogen atoms and carbon labels have been omitted for clarity.

near thulium. The composition of this complex and the high coordination number of the metal makes this a ‘‘super piano stool’’ complex with five legs and an additional ligand, the N(6) acetonitrile, coming directly down from the ‘‘seat.’’ The (C_5Me_5 ring centroid)-Tm-N(6) angle is nearly linear at 176.5°.

The Tm-N(MeCN) distances are all similar, 2.442(7)–2.466(6) Å. The acetonitrile *trans* to the $(C_5Me_5)^{1-}$ ligand did not have an unusual Tm–N distance. Subtraction of the 1.052 Å Shannon ionic radius [34] for Tm^{3+} from these distances gives a 1.39–1.414 Å difference that is equivalent to the 1.37–1.41 Å range of analogous differences previously found in lanthanide acetonitrile complexes [30, 33].

Table 9. Selected bond distances (Å) and angles (°) in $[(C_5Me_5)Tm(MeCN)_6]I_2$ (**9**).

Bond distances/angles	**9**
Tm(1)–Cnt1	2.306
Tm(1)–C(C_5Me_5) avg	2.605(8)
Tm(1)–N(1)	2.451(7)
Tm(1)–N(2)	2.462(7)
Tm(1)–N(3)	2.444(6)
Tm(1)–N(4)	2.442(7)
Tm(1)–N(5)	2.466(6)
Tm(1)–N(6)	2.442(7)
Cnt1–Tm(1)–N(1)	101.3
Cnt1–Tm(1)–N(2)	102.4
Cnt1–Tm(1)–N(3)	102.8
Cnt1–Tm(1)–N(4)	104.1
Cnt1–Tm(1)–N(5)	101.9
Cnt1–Tm(1)–N(6)	176.5
N(1)–Tm(1)–N(2)	70.70(19)
N(1)–Tm(1)–N(3)	136.4(2)
N(1)–Tm(1)–N(4)	136.6(2)
N(1)–Tm(1)–N(5)	71.5(2)
N(1)–Tm(1)–N(6)	77.6(2)
N(2)–Tm(1)–N(3)	68.9(2)
N(2)–Tm(1)–N(4)	134.8(2)
N(2)–Tm(1)–N(5)	138.2(2)
N(2)–Tm(1)–N(6)	80.4(2)
N(3)–Tm(1)–N(4)	69.9(2)
N(3)–Tm(1)–N(5)	136.1(2)
N(3)–Tm(1)–N(6)	80.0(2)
N(4)–Tm(1)–N(5)	69.23(19)
N(4)–Tm(1)–N(6)	74.9(2)
N(5)–Tm(1)–N(6)	74.6(2)

3. Conclusion

This study shows that a wide range of mono(pentamethylcyclopentadienyl) lanthanide complexes can be isolated and crystallographically characterized. This structurally diverse group of complexes demonstrates that when the kinetics of ligand exchange allow formation of mono-ring compounds, crystallographic characterization is as viable as it is with the more common bis(pentamethylcyclopentadienyl) derivatives. These studies have also shown that dioxane and methyl tert-butyl ether can be valuable alternatives to the more commonly used THF and diethyl ether to obtain crystallographic data when the latter two solvents fail.

4. Experimental

4.1. *X-ray data collection, structure determination, and refinement*

4.1.1. $[(C_5Me_5)Yb(\mu\text{-}I)(\mu\text{-}\eta^5:\eta^5\text{-}C_5Me_5)Yb(C_5Me_5)]_n$ (1). Green cubes of **1** were isolated as a minor product from a green toluene solution for a reaction in which $[Et_3NH][BPh_4]$ was added to $(C_5Me_5)_2Yb$ [11] prepared from $YbI_2(THF)_2$ [35]

and KC_5Me_5 [36]. A small amount of iodide evidently was retained throughout the synthesis and subsequent desolvation procedures. Given the halophilicity of the electropositive lanthanides, this retention is not unusual. A green crystal of approximate dimensions $0.12 \times 0.17 \times 0.27$ mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART [37] program package was used to determine the unit-cell parameters and for data collection (25 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT [38] and SADABS [39] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL [40] program. The diffraction symmetry was *mmm* and the systematic absences were consistent with the orthorhombic space group *Fddd* which was later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors [41] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. At convergence, $wR_2 = 0.0409$ and GOF = 1.111 for 159 variables refined against 3672 data. As a comparison for refinement on F, $R_1 = 0.0167$ for those 3305 data with $I > 2.0\sigma(I)$.

4.1.2. $\{[(C_5Me_5)Sm]_3(\mu\text{-Cl})_4(\mu_3\text{-Cl})(\mu_3\text{-OH})(THF)\}_2$ (2).

Orange plates of **2** were isolated as a minor product from a red THF solution from a reaction in which *t*-BuCl was added to $(C_5Me_5)_2Sm(THF)_2$ [42]. A red/orange crystal of approximate dimensions $0.15 \times 0.27 \times 0.31$ mm had diffraction symmetry $2/m$ and systematic absences consistent with the centrosymmetric monoclinic space group $P2_1/n$ which was later determined to be correct. The molecule was located about an inversion center. There were two molecules of benzene solvent present per dimeric formula unit. The benzene and coordinated THF molecules were disordered. Disordered atoms were included using multiple components with partial site-occupancy factors (0.50). There was one significant residual peak ($2.64\,e^-\,\text{Å}^{-3}$) in the final difference-Fourier map that could not be assigned. The peak was located between the μ_3-OH ligand and Cl(2)′ at distances of 1.807 Å and 1.895 Å respectively. The O(1)-peak-Cl(2)′ angle was 174.3°. The identity of the peak could not be determined from the X-ray diffraction experiment.

4.1.3. $\{[(C_5Me_5)Sm]_2(\mu\text{-OH})(\mu\text{-Cl})_4(\mu_3\text{-Cl})Mg(THF)_2\}_2$ (3).

Orange crystals of **3** were isolated from a red solution of a reaction mixture of $SmCl_3$ and $(C_5Me_5)_2Mg$ in THF. An orange crystal of approximate dimensions $0.17 \times 0.31 \times 0.42$ mm showed no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. The molecule was located about an inversion center. Carbon atoms C(25) and C(28) of one THF ligand were disordered and included using multiple components with partial site-occupancy-factors. Due to the limitations of this disorder, the hydrogen atoms associated with the disordered THF were not included. The bridging OH hydrogen was not observed or included in the refinement. A molecule of toluene solvent appeared to be present, but could not be modeled to yield a suitable geometry and was omitted from the final refinement.

4.1.4. $[(C_5Me_5)_2Sm](\mu\text{-}Cl)_6(\mu_3\text{-}Cl)_2(\mu_4\text{-}Cl)[Sm(C_5Me_5)]_4$ (4). Red crystals of **4** were isolated from a toluene solution of a multi-step synthesis of $[(C_5Me_5)_2Sm(\mu\text{-}Me)_2AlMe_2]_n$ [43] ($n = 1,2$) in which Me_3Al was added to $[(C_5Me_5)_2Sm(\mu\text{-}O_2CPh)]_2$ [44] prepared from $(C_5Me_5)_2SmCl(THF)$ [45] and KO_2CPh. As in the isolation of **1**, a small amount of halide was evidently retained throughout the synthesis. A red crystal of approximate dimensions 0.08 × 0.18 × 0.29 mm had diffraction symmetry *mmm* and systematic absences consistent with the orthorhombic space group *Pbcn* which was later determined to be correct. There was one molecule of hexane solvent present per formula unit.

4.1.5. $\{[(C_5Me_5)Nd]_3(\mu_3\text{-}Cl)_4(\mu_4\text{-}Cl)_2(\mu_3\text{-}O_2CPh)_2K_2(\eta^6\text{-}C_7H_8)\}_2$ (5). Blue crystals of **5** were isolated from a toluene solution of a reaction mixture of $(C_5Me_5)_2Nd(\mu\text{-}Cl)_2K(THF)_2$ [46] with KO_2CPh in which some contamination of a chloride source may have been present. A pale blue crystal of approximate dimensions 0.13 × 0.14 × 0.23 mm showed no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. The molecule was located about an inversion center. There were six molecules of toluene solvent present per formula unit.

4.1.6. $[(C_5Me_5)Nd(C_8H_8)]_2(\mu\text{-dioxane})$ (6). Green needles were isolated from a reaction mixture of $[(C_5Me_5)_2Nd][(\mu\text{-}Ph)_2BPh_2]$ [47] and $K_2C_8H_8$ [48] in benzene and crystallized from dioxane. Evidently some ligand redistribution occurred to form the mono(pentamethylcyclopentadienyl) complex as opposed to a bridging $(C_8H_8)^{2-}$ complex of the type $(C_5Me_5)_2Nd(C_8H_8)Nd(C_5Me_5)_2$. A pale green crystal of approximate dimensions 0.04 × 0.06 × 0.22 mm had diffraction symmetry $4/m$ and systematic absences consistent with the tetragonal space group $I4_1/a$ which was later determined to be correct. The molecule was located about an inversion center. Carbon and oxygen atoms were refined using isotropic temperature parameters due to the poor quality of the data from the weak crystal.

4.1.7. $[(C_5Me_5)Yb(MeO^tBu)]_2(\mu\text{-}\eta^8:\eta^8\text{-}C_8H_8)$ (7). Orange needles of **7** were isolated from a solution of $[(C_5Me_5)Yb]_2(C_8H_8)$ [13] in methyl *t*-butyl ether (MTBE). **7** was isolated in 93% yield. An orange crystal of approximate dimensions 0.09 × 0.11 × 0.27 mm had systematic absences consistent with the rhombohedral space groups $R3$ and $R\bar{3}$. It was later determined that the centrosymmetric space group $R\bar{3}$ was correct. The pentamethylcyclopentadienyl ligand defined by carbon atoms C(1)–C(10) was disordered and included using multiple components with partial site-occupancy-factors. It was necessary to constrain this ligand to a rigid group with equal U_{iso} values.

4.1.8. $[(C_5Me_5)Dy(\mu\text{-}I)_2]_3$ (8). Red needles of **8** were isolated as a minor product from an ether solution of DyI_2 [49] and LiC_5Me_5. A dark red crystal of approximate dimensions 0.10 × 0.22 × 0.23 mm had systematic absences consistent with the cubic space group $I\bar{4}3d$ which was later determined to be correct. Due to the poor quality of the data, it was necessary to restrain the pentamethylcyclopentadienyl ligand as a rigid group and to set all carbon U_{iso} values equal.

4.1.9. [$(C_5Me_5)Tm(MeCN)_6$]I_2 (9). Yellow crystals of **9** were isolated from a yellow solution of a reaction mixture of TmI_2 [50] and KC_5Me_5 in acetonitrile. TmI_3, a common by-product in the synthesis of TmI_2, may have been present to provide this result. A yellow crystal of approximate dimensions $0.21 \times 0.22 \times 0.33$ mm had diffraction symmetry $2/m$ and systematic absences consistent with the monoclinic space groups Cc and $C2/c$. It was later determined that the non-centrosymmetric space group Cc was correct. There were two molecules of the formula unit present ($Z = 8$). Attempts to solve and refine the structure using the centrosymmetric space group $C2/c$ were not successful.

Supplementary material

Figures and tables of crystal data, atomic coordinates, bond distances and angles, anisotropic displacement parameters, and structure factors are available from W.J.E.

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